Canadian Mineralogist
Vol. 18, pp. 205-214 (1980)

LOW-TEMPERATURE RETROGRADE MINERALS IN METAMORPHOSED ARCHEAN BANDED IRON-FORMATIONS, WESTERN AUSTRALIA

M. J. GOLE*
Department of Geology, University of Western Australia, Nedlands, 6009 Australia

ABSTRACT

Low-temperature (< 450°C) retrograde minerals are a widespread but minor feature in medium and high metamorphic-grade Archean banded iron-formations in the Yilgarn Block, Western Australia. Stilpnomelane is the most common retrograde mineral. Others include greenalite [(Fe+Mn)/(Fe+Mn+Mg) = 0.98–0.49], calcite, siderite, magnetite, ferroactinolite, chlorite, talc, serpentine [(Fe+Mn)/(Fe+Mn+Mg) = 0.37–0.02], pyrite and possibly cronstedtite. Several unidentified silicates with compositions part way between stilpnomelane and greenalite, stilpnomelane and chlorite, and chlorite and greenalite occur in retrograde assemblages. These may be metastable transition phases. The Al_2O_3 contents and the "FeO"/("FeO"+MgO) and MnO/(MnO+"FeO") ratios of stilpnomelane and greenalite are generally related to the bulk composition of the host rock, although some metasomatism occurred during retrogression. Fluid compositions are an important parameter in the formation of the retrograde minerals; however, metamorphic conditions during retrogression are, in general, difficult to assess. Evidence from low-grade banded iron-formations and experimental data, together with textural evidence in retrograde assemblages, indicate that the stability fields of greenalite and ferroactinolite may overlap under very reducing conditions between ~ 300 and ~ 350°C.

Keywords: Low-temperature retrograde minerals, iron formation, Yilgarn Block, Western Australia, stilpnomelane, greenalite.

SOMMAIRE

Les minéraux rétrogrades de basse température (< 450°C) sont très répandus comme minéraux accessoires dans les formations de fer rubannées archéennes à métamorphisme modéré ou élevé du bloc Yilgarn, en Australie occidentale. C'est la stilpnomélane qui se rencontre le plus souvent, mais on trouve aussi: greenalite [(Fe+Mn)/(Fe+Mn+Mg) = 0.98–0.49], calcite, sidérite, magnétite, ferroactinote, chlorite, talc, serpentine [(Fe+Mn)/(Fe+Mn+Mg) = 0.37–0.02], pyrite et cronstedtite(?). Dans ces assemblages rétrogrades, plusieurs silicates restent nonidentifiés; en composition, ils se situent entre stilpnomélane et greenalite ou chlorite, et entre chlorite et greenalite; ce sont peut-être des phases de transition métastables. La teneur en Al_2O_3 et les rapports "FeO"/("FeO"+MgO) et MnO/(MnO+"FeO") dans la stilpnomélane et la greenalite dépendent, en général, de la composition globale de la roche, quoique la rétrogression ait été accompagnée d'un certain métasomatisme. La composition des fluides est un facteur important dans la formation des minéraux rétrogrades, mais les conditions de métamorphisme, en cours de rétrogression, sont généralement difficiles à évaluer. D'après le caractère des formations de fer rubannées faiblement métamorphiques et les résultats expérimentaux d'une part, et la texture des assemblages rétrogrades d'autre part, les domaines de stabilité de la greenalite et de la ferroactinote pourraient, en mieu très réducteur, empiéter l'un sur l'autre entre ~ 300 et ~ 350°C.

(Traduit par la Rédaction)

Mots-clés: minéraux rétrogrades de basse température, formation de fer, bloc Yilgarn, Australie occidentale, stilpnomélane, greenalite.

INTRODUCTION

Banded iron-formations (~ 2.6–2.7 *Ga*) of medium to high metamorphic grade in the Archean Yilgarn Block, Western Australia, contain a large variety of retrograde minerals that seem to have formed under a wide range of metamorphic conditions. This study has concentrated on the lower temperature retrograde assemblages, as these provide some insight into the stability of the low-temperature Fe silicates under metamorphic conditions.

ANALYTICAL METHODS

Electron-microprobe analyses were performed using an automated, 3-spectrometer ARL–SEMQ electron-probe microanalyzer. For silicates and carbonates, natural minerals were used for primary and secondary standards and the data were reduced by the method of Bence & Albee (1968) using the alpha factors of A. A.

---

*Present address: Department of Geology, Indiana University, Bloomington, Indiana 47405, U.S.A.

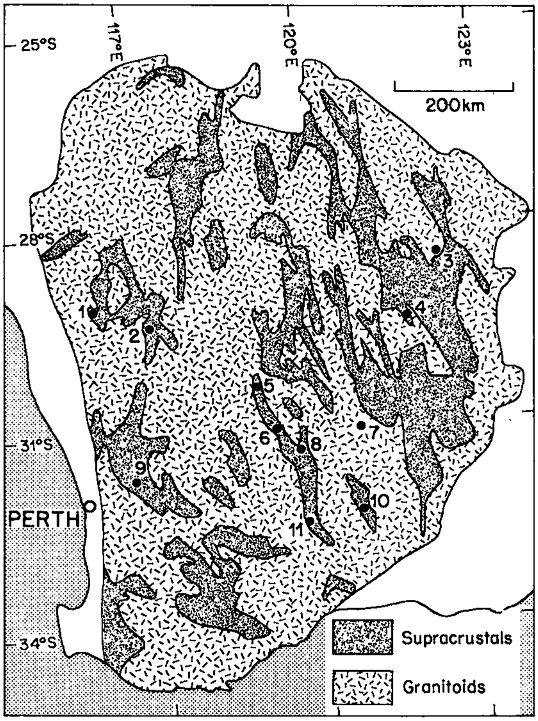

FIG. 1. Sample localities shown on a simplified geology map of the Yilgarn Block. 1 Koolanooka, 2 Atlas gold mine, 3 Windarra nickel mine, 4 Tassey Well, 5 Trough Well, 6 Corinthian gold mine, 7 Queen Victoria Rocks, 8 Nevoria gold mine, 9 Mt. Joy, 10 Lake Johnston, 11 Forrestania.

Chodos (unpublished). Estimates of H_2O for silicates and CO_2 for carbonates were made for the purposes of the reduction procedure.

Samples referred to are housed in the Department of Geology, University of Western Australia. Sample locations are shown in Figure 1.

STILPNOMELANE

Stilpnomelane is the most common retrograde mineral in the medium- and high-grade banded iron-formations in the Yilgarn Block. It occurs in discrete veinlets 0.2–3.0 mm wide either alone or with calcite or siderite. Retrograde stilpnomelane is rarely associated with retrograde ferroactinolite or other retrograde minerals. In one sample (85080) it is itself altered to greenalite, quartz and an unknown mineral (see below). Most retrograde stilpnomelane is green and has submicron grain-size. Partial alteration to a brown-colored variant is common and is probably due to weathering.

TABLE 1. ELECTRON-MICROPROBE ANALYSES OF RETROGRADE STILPNOMELANE

Sample No.	1 12962	2 33403	3 84919	4 84928	5 85015	6 85080	7 85083
SiO_2	46.7	44.7	43.5	43.7	45.6	47.0	45.0
TiO_2	0.02	0.04	0.03	0.07	0.02	0.01	0.01
Al_2O_3	4.87	2.96	3.33	6.00	3.93	1.15	2.95
FeO^1	24.9	38.8	39.3	35.5	32.2	41.4	37.4
MnO	5.35	0.22	1.50	1.11	2.11	0.07	0.02
MgO	6.88	2.16	1.36	1.80	3.54	2.71	2.77
CaO	0.04	0.20	0.07	0.06	0.02	0.04	0.04
Na_2O	0.30	0.35	0.32	0.35	0.18	0.20	1.76
K_2O	3.77	0.90	1.64	2.32	2.52	1.14	1.60
Total	92.83	90.33	91.05	90.91	90.12	93.72	91.55
Ions on the basis of 11 oxygens							
Si	3.66	3.73	3.67	3.61	3.74	3.81	3.71
Al	0.34	0.27	0.33	0.39	0.26	0.11	0.29
	4.00	4.00	4.00	4.00	4.00	3.92	4.00
Al	0.11	0.03	0.00	0.19	0.12	0.00	0.00
Fe	1.63	2.71	2.77	2.45	2.21	2.81	2.58
Mn	0.36	0.02	0.12	0.08	0.15	0.01	0.00
Mg	0.80	0.27	0.17	0.22	0.43	0.33	0.34
Ca	0.00	0.02	0.01	0.01	0.00	0.00	0.00
Na	0.05	0.06	0.05	0.06	0.03	0.03	0.28
K	0.38	0.10	0.18	0.24	0.26	0.12	0.17
	3.33	3.21	3.30	3.25	3.20	3.30	3.37

[1] All Fe as FeO.

1. Green stilp with cal in vein in grun-act-qtz-mag assemblage. Atlas Gold Mine, D.D.H. 1/112.8 m; 2. Green stilp with cal in vein in grun-mag-qtz assemblage. Nevoria Gold Mine, D.D.H. 5/237.4 m; 3. Brown stilp with ferroact in kink band in grun-act-qtz-mag assemblage. Corinthian Gold Mine, KS 14/122 m; 4. Brown stilp associated with unidentified mineral (Table 5, no. 9) in hbld-alm assemblage. Trough Well, D.D.H. 12/73.5 m; 5. Brown stilp with sid ($Fe_{1.82}Mn_{0.21}Mg_{0.01}Ca_{0.07}$) and minor pyrite in grun-mag-pyrite assemblage. Tassey Well, D.D.H. 1/102 m; 6. Cryptocrystalline green stilp in vein in grun-mag assemblage. Stilp retrogressed to greenal (Table 2, no. 6), qtz and an unidentified mineral (Table 5, no. 8). Bunyip, Forrestania, D.D.H. 1/61.5 m; 7. Cryptocrystalline green stilp with cal ($Fe_{0.01}Ca_{2.01}$) in grun-act-chlorite-mag assemblage. Bunyip, Forrestania, D.D.H. 1/61.7 m. Abbreviations used in Tables 1-6: act = actinolite, alm = almandine, cal = calcite, ferroact = ferroactinolite, greenal = greenalite, grun = grunerite, hbld = hornblende, mag = magnetite, ol = olivine, qtz = quartz, serp = serpentine, sid = siderite, stilp = stilpnomelane.

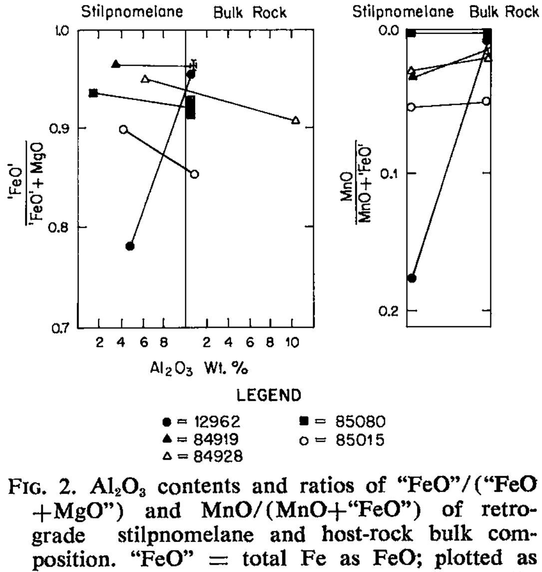

FIG. 2. Al_2O_3 contents and ratios of "FeO"/("FeO+MgO") and MnO/(MnO+"FeO") of retrograde stilpnomelane and host-rock bulk composition. "FeO" = total Fe as FeO; plotted as wt. %. Ratios for bulk rocks are from bulk-rock analyses except for samples 84919 and 85080, which are estimated from mineral compositions and modes of the primary metamorphic assemblage.

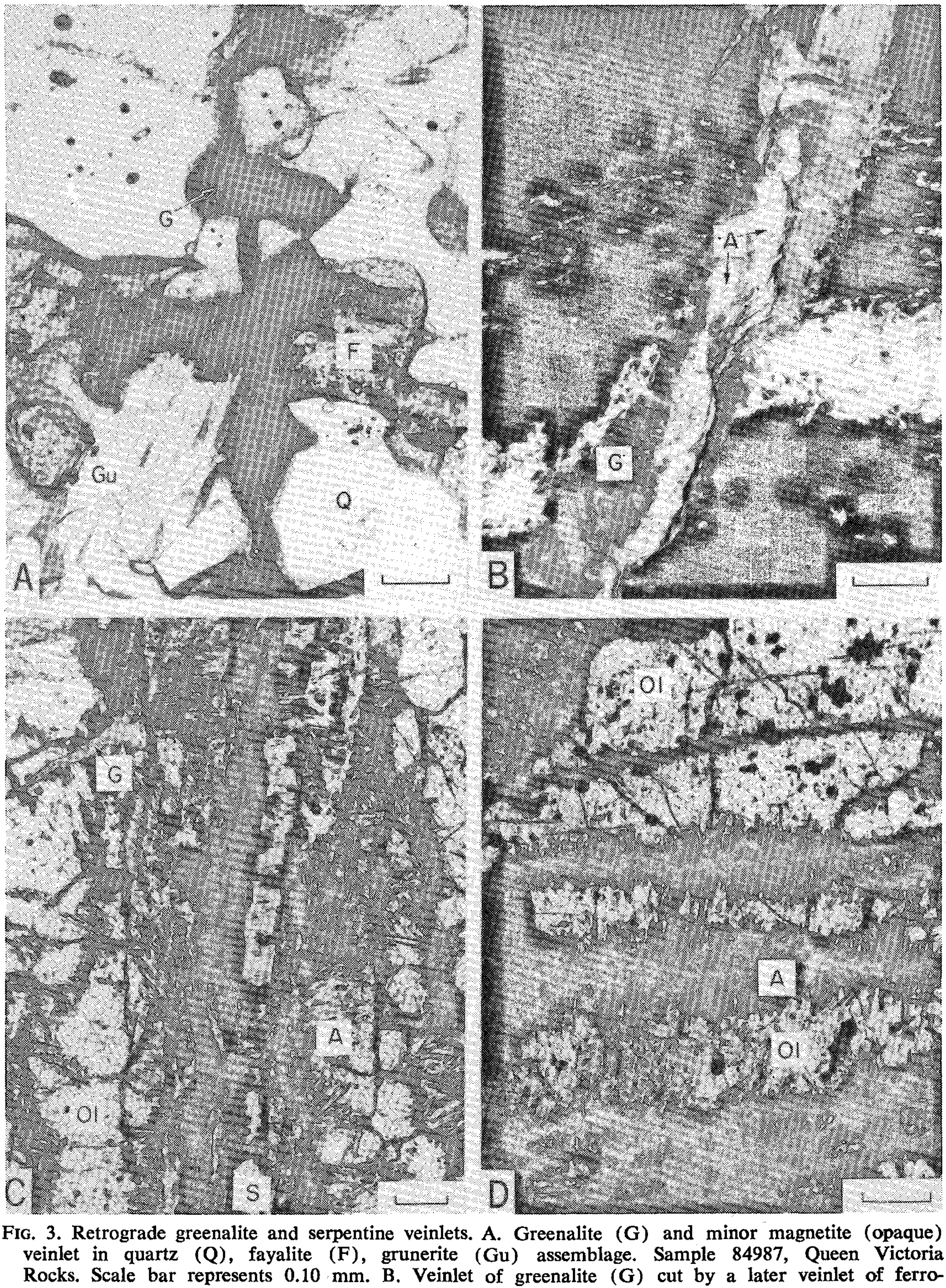

FIG. 3. Retrograde greenalite and serpentine veinlets. A. Greenalite (G) and minor magnetite (opaque) veinlet in quartz (Q), fayalite (F), grunerite (Gu) assemblage. Sample 84987, Queen Victoria Rocks. Scale bar represents 0.10 mm. B. Veinlet of greenalite (G) cut by a later veinlet of ferroactinolite (A). Primary assemblage is magnetite–grunerite–minor quartz. Sample 85001, Lake Johnston. Scale bar represents 0.3 mm. C. Composite veinlet in olivine (Ol), containing greenalite (G), pale green serpentine showing alignment of fibrous grains (S) and magnetite (opaque). Blades of antigorite (A) cut the veinlet–olivine contacts. Sample 55410, Koolanooka. Scale bar represents 0.2 mm. D. Bladed antigorite (A) projecting into olivine (Ol) from fractures. Sample 55410, Koolanooka. Scale bar represents 0.1 mm.

The compositions of retrograde stilpnomelane (Table 1) are broadly similar to those from very low metamorphic grade iron-formations (Klein 1974, Floran & Papike 1975, Lesher 1978, Gole 1980). The "FeO"/("FeO"+MgO) and the MnO/(MnO+"FeO") ratios, and to a lesser extent the Al_2O_3 contents of stilpnomelanes, are generally related to those of the host rock (Fig. 2), despite the inhomogeneity of most banded iron-formations. Some stilpnomelanes, however, show no compositional relationship to bulk composition (*e.g.*, sample 12962, Fig. 2); in such samples retrogression involved considerable metasomatic transfer of components. In most samples, with the exception of sample 84928, which contains K-bearing hornblende and almandine as primary phases, K and Al must have been introduced from outside the host assemblage, as the bulk samples contain negligible amounts of these elements.

It is not possible to estimate accurately the temperature of formation of the retrograde stilpnomelane-bearing assemblages. Based on assemblages in low and medium metamorphic grade iron-formations (Floran & Papike 1978, Klein 1978, Gole 1979) and on the stability of ferroactinolite (Ernst 1966), the stilpnomelane associated with ferroactinolite (sample 84919) probably formed at moderate temperatures ($\simeq$ 350–450°C). Other retrograde stilpnomelane assemblages could have formed at similar or lower temperatures.

GREENALITE AND SERPENTINE

Greenalite is a widespread though minor retrograde phase whereas serpentine, as a retrograde product in banded iron-formation, is known from only one locality (Koolanooka, Fig. 1).

Retrograde greenalite occurs in generally monomineralic veinlets (0.1–0.6 mm wide, Fig. 3A) that locally may contain calcite (Table 2, nos. 5, 7) or other minerals. Retrograde greenalite occurs rarely as a pervasive alteration (Table 2, nos. 1, 2). It is generally cryptocrystalline, but in some veinlets it shows a brown–yellow to green pleochroism owing to the optical alignment of extremely fine, fibrous grains. Greenalite-bearing retrograde assemblages in sample 85001 are somewhat more complex than other retrograde greenalite assemblages. In this sample, a veinlet (Fig. 3B) consisting of greenalite (Table 3, no. 2), minor siderite and trace amounts of an extremely fine-grained, dark green–brown mineral (Table 3, nos. 3–5), is itself cut by a later monomineralic veinlet of retrograde ferroactinolite (Table

TABLE 2. ELECTRON-MICROPROBE ANALYSES OF RETROGRADE GREENALITE

Sample No.	1 33583	2 84934	3 84987	4 84996	5 85027	6 85080	7 85093
SiO_2	36.7	37.0	35.7	36.6	38.0	36.1	35.6
TiO_2	0.00	0.02	0.00	0.00	0.01	0.01	0.00
Al_2O_3	0.03	0.09	0.00	1.50	0.52	0.00	0.00
FeO^1	51.7	48.1	51.1	38.1	45.8	50.8	51.7
MnO	0.65	0.57	0.15	1.07	1.45	0.06	0.22
MgO	2.23	2.90	2.00	11.80	3.22	1.90	1.44
CaO	0.04	0.13	0.12	0.06	0.16	0.00	0.11
Na_2O	0.02	0.02	0.08	0.04	0.07	0.04	0.07
K_2O	0.00	0.00	0.00	0.00	0.23	0.00	0.00
Total	91.37	88.83	89.15	89.17	89.46	88.91	89.14
Ions on the basis of 14 oxygens							
Si	4.26	4.34	4.26	4.06	4.37	4.29	4.26
Al	0.00	0.01	0.00	0.20	0.07	0.00	0.00
Fe	5.02	4.72	5.09	3.53	4.41	5.06	5.18
Mn	0.06	0.06	0.02	0.10	0.14	0.01	0.02
Mg	0.39	0.51	0.36	1.95	0.55	0.34	0.26
Ca	0.01	0.02	0.02	0.01	0.02	0.00	0.01
Na	0.01	0.01	0.02	0.01	0.02	0.01	0.02
K	0.00	0.00	0.00	0.00	0.03	0.00	0.00
OCT	5.49	5.33	5.51	5.80	5.24	5.42	5.49

[1] All Fe as FeO.

1. Pleochroic yellow brown to green greenal as patches in act-mag assemblage Nevoria Gold Mine, D.D.H. 9/177.7 m; 2. Pleochroic yellow brown to green greenal as patches in grun-act. Trough Well, D.D.H. 12/112.5 m; 3. Pleochroic yellow brown to green greenal with mag in vein in ferrosalite-eulite-grun-fayalite-qtz assemblage. Queen Victoria Rocks, D.D.H. 13/125.9 m; 4. Greenal vein in act-grun-hbld-mag assemblage. Queen Victoria Rocks, D.D.H. 13/181.4 m; 5. Cryptocrystalline greenal with qtz, cal ($Fe_{0.04}Mn_{0.03}Mg_{0.01}Ca_{2.09}$) and unidentified mineral (Table 5, nos. 4-6) in vein in qtz-grun-act-mag assemblage. Windarra Nickel Mine, D.D.H. AE 558/1021.4 m; 6. Cryptocrystalline greenal with qtz and unidentified mineral (Table 5, no. 8) in center of retrograde stilp vein (Table 1, no. 6). Bunyip, Forrestania, D.D.H. 1/201.9 m; 7. Cryptocrystalline greenal with cal ($Fe_{0.07}Mg_{0.02}Ca_{2.04}$) in vein in qtz-mag-grun-act assemblage. Mt. Hope, Forrestania, D.D.H. 8/131.5 m.

TABLE 3. ELECTRON-MICROPROBE ANALYSES OF RETROGRADE MINERALS IN SAMPLE 85001[1]

	1	2	3	4	5
SiO_2	50.0	35.3	29.9	27.7	29.1
TiO_2	0.00	0.00	0.00	0.02	0.00
Al_2O_3	0.05	0.15	0.00	0.00	0.00
FeO^2	36.3	53.3	51.7	51.5	49.7
MnO	0.27	0.18	0.02	0.00	0.00
MgO	1.16	0.67	6.25	6.23	6.10
CaO	10.4	0.08	0.14	0.22	0.80
Na_2O	0.14	0.04	0.15	0.21	0.30
K_2O	0.07	0.00	0.00	0.00	0.04
Total	98.39	89.72	88.16	87.88	86.04
Fe_2O_3			9.1^3	9.6^3	9.9^3
FeO			43.5	42.9	40.8
Total			89.06	88.88	87.04
Ions on the basis of A. oxygens B. cations					
	A 23	A 14	B 10	B 10	B 10
Si	8.00	4.23	3.61	3.59	3.58
Al	0.00	0.00	0.00	0.00	0.00
Fe^{3+}	--	--	0.39	0.41	0.42
	8.00	4.23	4.00	4.00	4.00
Al	0.01	0.02	0.00	0.00	0.00
Fe^{3+}	--	--	0.44	0.46	0.50
Fe^{2+}	4.86	5.35	4.39	4.34	4.20
Mn	0.04	0.02	0.00	0.00	0.00
Mg	0.28	0.12	1.12	1.12	1.12
Ca	1.78	0.10	0.02	0.03	0.11
Na	0.04	0.01	0.03	0.05	0.07
K	0.01	0.00	0.00	0.00	0.00
	7.02	5.62	6.00	6.00	6.00

[1] Lake Johnston, D.D.H. 5/135.6 m; [2] All Fe as FeO; [3] Fe_2O_3 estimated assuming 10 cations.

1. Ferroact in vein cutting greenal vein; 2. Greenal in vein with green-brown mineral (3-5) and sid ($Fe_{1.2}Mn_{0.06}Mg_{0.45}Ca_{0.14}$); 3-5. Green-brown mineral in greenal vein adjacent to mag band.

3, no. 1). The green–brown mineral occurs only in the greenalite-rich vein adjacent to magnetite mesobands. X-ray powder patterns show the mineral to have a 001 spacing of approximately 7.14 Å. Recalculation of electron-probe analyses of this mineral on the basis of 10 cations [assuming an ideal formula of $Y_6Z_4O_{10}(OH)_8$], suggests the presence of considerable Fe^{3+} in the tetrahedral site (Table 3, nos. 3–5). The mineral may be cronstedtite, but the 001 spacing is much closer to the basal spacing of greenalite (d_{001} = 7.12 Å) than to that of cronstedtite (d_{001} = 7.09 Å).

The banded iron-formations from D.D.H. 22, Koolanooka, contain very unusual primary metamorphic as well as retrograde mineral assemblages. The primary assemblages, described by Baxter (1965), consist of olivine Fa_{67-6} and magnetite with minor magnesite, muscovite, cummingtonite and tremolite [Fe/(Fe+Mg) 0.01, 0.30, 0.25–0.45, 0.20–0.60, respectively].

The coexistence of magnetite and Mg-rich silicates and carbonates suggests that the prograde metamorphic reactions in these iron formations were similar to those proposed by Mueller (1960) and Butler (1969) to account for Mg-rich silicates in magnetite and magnetite–hematite-bearing assemblages in iron formations of the Labrador Trough. They proposed a prograde reaction: hematite + Fe–Mg silicates (or carbonates) → magnetite + Mg-silicates (or carbonates) + H_2O (or CO_2). The reactant and product assemblages have the same Fe^{3+}/Fe^{2+} ratio (*i.e.*, O_2 behaves as an inert species). In very oxidized assemblages, partition of much of the Fe into magnetite may produce very Mg-rich silicates and carbonates. Because of the Fe-rich bulk composition of iron formations, the reaction should result in the prograde assemblage having a high proportion of magnetite relative to that of Mg–Fe silicates and carbonates, as is observed in the olivine-bearing iron-formations at Koolanooka.

The retrograde minerals, which replace the olivine and rarely the amphiboles, are magnetite and members of the greenalite–serpentine group. They generally occur in veinlets 0.05–1.0 mm wide or along olivine grain boundaries and replace 10–30% of the host assemblage. In a few samples, the retrograde alteration almost completely replaces the primary olivine.

In samples 55395 and 55410, several optically

TABLE 4. ELECTRON-MICROPROBE ANALYSES OF RETROGRADE GREENALITE AND SERPENTINE FROM OLIVINE-RICH BANDED IRON-FORMATIONS, KOOLANOOKA[1]

Sample No.	1 55395	2 55395	3 55395	4 55395	5 55395	6 55398	7 55399	8 55410	9 55410	10 55410	11 55414	12 55415
SiO_2	36.3	36.5	36.7	37.1	39.5	41.2	42.6	38.2	38.5	41.4	42.0	41.4
TiO_2	0.01	0.01	0.01	0.01	0.00	0.03	0.00	0.00	0.00	0.02	0.01	0.00
Al_2O_3	0.00	0.00	0.00	0.00	0.50	0.03	0.00	0.00	0.10	0.09	0.54	0.70
FeO[2]	34.9	34.7	33.5	30.9	22.8	5.87	1.71	32.3	23.9	20.1	1.77	2.00
MnO	1.87	2.14	1.66	1.16	1.67	0.20	0.15	1.18	0.50	0.25	0.17	0.03
MgO	13.33	14.56	16.40	18.68	23.4	39.6	41.7	16.7	24.2	26.6	42.1	41.7
CaO	0.10	0.06	0.04	0.03	0.05	0.01	0.01	0.02	0.02	0.01	0.02	0.01
Na_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	86.51	87.97	88.31	87.88	87.92	86.94	86.17	88.40	87.22	88.47	86.61	85.84
Ions on the basis of 14 oxygens												
Si	4.12	4.07	4.04	4.03	4.09	3.93	4.01	4.14	4.03	4.15	3.94	3.92
Al	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.08
	4.12	4.07	4.04	4.03	4.09	3.93	4.01	4.14	4.03	4.15	4.00	4.00
Al	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Fe	3.31	3.23	3.08	2.81	1.97	0.47	0.13	2.92	2.09	1.69	0.14	0.16
Mn	0.18	0.20	0.16	0.11	0.15	0.02	0.01	0.11	0.04	0.02	0.01	0.00
Mg	2.26	2.42	2.69	3.02	3.61	5.64	5.84	2.69	3.78	3.97	5.88	5.88
Ca	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	5.76	5.86	5.94	5.94	5.80	6.13	5.98	5.72	5.92	5.69	6.03	6.04
$\frac{Fe+Mn}{Fe+Mn+Mg}$	0.61	0.59	0.55	0.49	0.37	0.08	0.02	0.53	0.36	0.30	0.03	0.03

[1] All samples from D.D.H. 22. Depth in parentheses; [2] All Fe as FeO.

1. Cryptocrystalline dark-red greenal (171.25 m); 2-3. Cryptocrystalline dark-green greenal; 4. Pale-green greenal in vein cutting dark-green greenal; 5. Very-pale-green serp showing blue-grey birefringence; 6. Lizardite (179.15 m); 7. Lizardite (181.05 m); 8. Dark-green greenal (204.52 m); 9. Very-pale-green serp showing blue-grey birefringence; 10. Colorless, lath-shaped antigorite grains radiating from fractures and ol grain boundaries; 11. Thin vein of serp cutting ol-mag assemblage (210.44 m); 12. Lizardite (210.69 m)

distinct greenalites and serpentines accompanied by abundant ragged magnetite occur in veinlets (0.05–0.4 mm wide). Extremely fine-grained (< 1–2 μm) greenalite appears to be the earliest retrograde mineral based on the cross-cutting relationships of other, later retrograde silicates. In sample 55395 this early greenalite has been altered locally to a dark red product (Table 4, no. 1). In both samples 55395 and 55410, greenalite and host olivine (Fa$_{67}$ and Fa$_{64}$, respectively) have been progressively replaced by a series of minerals that have optical properties similar to those of serpentine (fibrous, pale green to colorless, first-order yellow birefringence). In samples 55395 five generations of retrograde greenalite or serpentine can be distinguished, each replacing an earlier mineral and each having sharp contacts with the other retrograde minerals. In sample 55410, three retrograde greenalite–serpentine-type minerals can be recognized, replacing either olivine or earlier retrograde silicates or both (Figs. 3C, D). Electron-microprobe analyses of the retrograde silicates in samples 55395 and 55410 (Table 4) show that the earliest retrograde mineral is Mg-rich greenalite. Retrograde silicates are progressively more Mg-rich later in the retrograde paragenetic sequence. The most Mg-rich serpentine in sample 55410 occurs as relatively coarse-bladed grains and contains a significant excess of Si (Table 4, no. 10). The presence of a strong peak at 2.53 Å on X-ray powder patterns and the excess Si show the mineral to be ferroan antigorite (Page 1968, Whittaker & Wicks 1970). Unfortunately, because the greenalite and other serpentine types in samples 55395 and 55410 are intergrown and fine-grained, they cannot be separated for X-ray determinations. However, the serpentine-like minerals in these samples optically resemble lizardite, and their Si contents (Table 4) suggest that they may be ferroan lizardites (Page 1968, Whittaker & Wicks 1970). Samples 55398, 55399, and 55415 contain only one retrograde silicate, Mg-rich serpentine (Table 4). In these samples almost all olivine (Fa$_{47}$, Fa$_{43}$ and Fa$_{6}$, respectively) has been replaced, and only small relict grains are preserved in a mesh of serpentine. X-ray powder patterns of these serpentines show them to be lizardites. In sample 55414, the serpentine is found in thin veins, and most of the primary olivine (Fa$_{42}$) and magnetite have not been affected by the retrogression.

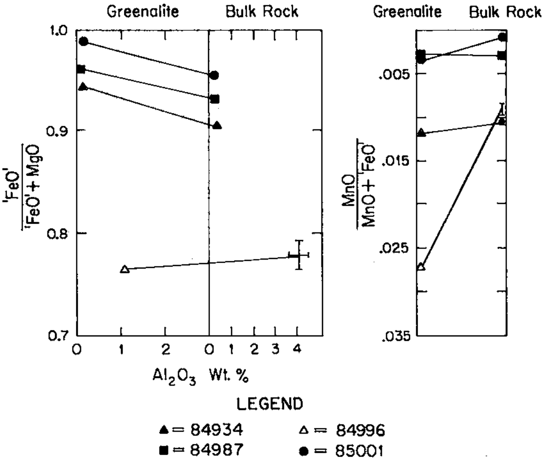

FIG. 4. Al$_2$O$_3$ contents and ratios of "FeO"/("FeO"+MgO) and MnO/(MnO+"FeO") of retrograde greenalite and host-rock bulk compositions. "FeO" = total Fe as FeO; plotted as wt. %. Ratios for bulk rocks are from bulk-rock analyses except for sample 84996, which is estimated from mineral compositions and the mode of the primary metamorphic assemblage.

Discussion

Retrograde greenalites, recalculated on a basis of 14 oxygens, show an excess of Si and an octahedral deficiency compared with the ideal formula of $Fe_6Si_4O_{10}(OH)_8$ (Tables 2–4). Similar characteristics have been found in greenalites from very low metamorphic grade iron-formations (Klein 1974, Floran & Papike 1975, Gole 1980). The greenalite-like material in sample 85027 (Table 2), which has the highest Si excess of all the retrograde greenalites, contains 0.23 wt. % K_2O and may be a mixture of layer silicates. The Al_2O_3 contents and the "FeO"/("FeO"+MgO) and MnO/(MnO+"FeO") ratios of retrograde greenalites are generally closely related to the bulk composition of the host rock (Fig. 4). Those from Koolanooka are an exception. Here greenalites and serpentines show a wide range in (Fe+Mn)/(Fe+Mn+Mg) ratios with breaks in the ratio between 0.49 and 0.37 and between 0.30 and 0.08 (Fig. 5). The gap in the (Fe+Mn)/(Fe+Mn+Mg) ratio between 0.49 and 0.37 corresponds to a change in the optical characteristics of the minerals from greenalite-like to serpentine-like in appearance. The gap in the (Fe+Mn)/(Fe+Mn+Mg) ratio between 0.30 and 0.08 is probably due to a lack of samples containing serpentine with appropriate compositions (Jasmund *et al.* 1975). Magnesian greenalites and ferroan serpentines with compositions similar to those in samples 55395 and 55410

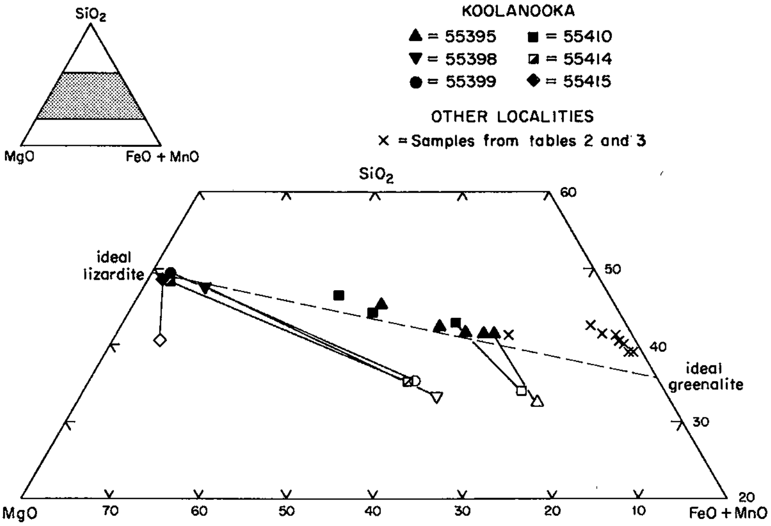

FIG. 5. Compositional variations in (a) retrograde greenalites and serpentines (filled symbols and crosses) and (b) olivines (open symbols), plotted in wt. % within the system $(FeO+MnO)-MgO-SiO_2$. Total Fe as FeO. Tie lines join host olivines and the earliest retrograde silicate in Koolanooka samples.

have been reported by Dietrich (1972) and Frondel (1962) in retrograde assemblages. At Koolanooka the retrograde silicates all have lower (Fe+Mn)/(Fe+Mn+Mg) ratios than the host olivine (Fig. 5). In samples 55395 and 55410, in which retrograde minerals have altered only a small part of the primary assemblage (10–30 vol. %), the difference in the (Fe+Mn)/(Fe+Mn+Mg) ratio between the host olivine and the earliest retrograde silicate is slight and increases with each subsequent retrograde silicate. In samples 55398 and 55399, in which retrograde minerals have replaced most of the host olivine, there is only one generation of retrograde serpentine that is much more Mg-rich than the host olivine. Most of the olivine in sample 55415 has been altered, but owing to its high forsterite content the retrograde serpentine has only a slightly lower (Fe+Mn)/(Fe+Mn+Mg) ratio. In sample 55414 there is a marked difference in the (Fe+Mn)/(Fe+Mn+Mg) ratio between olivine and serpentine despite the small degree of alteration (< 10 vol. %).

Retrograde conditions

It is not possible to estimate accurately the conditions of formation for the greenalite- or serpentine-bearing retrograde assemblages described above. The character of the metamorphic fluids clearly is an important parameter in the stability of these retrograde assemblages; unfortunately, the composition of the fluid present during formation of some of these minerals can be estimated only in general terms. The presence of a Fe^{3+}-bearing mineral (probably cronstedtite) in the greenalite-rich veinlet of sample 85001 suggests that retrograde metamorphic conditions were, locally at least, relatively oxidizing. Evidence from low-grade metamorphic assemblages (Gole 1980) suggests that greenalite is stable up to 320 ± 50°C (a) in Si-deficient assemblages and (b) in the presence of excess Si under relatively reducing conditions ($\log f(O_2) \sim -32$ bar at 327°C). Experimental data (Ernst 1966) indicate that ferroactinolite is stable under relatively reducing conditions at moderate temperatures (450°C at $\log f(O_2) = -32$ bars, extrapolated from data of Ernst 1966). The ferroactinolite veinlet in sample 85001 may therefore have formed during a reheating event after the formation of the retrograde greenalite. Evidence for such reheating in the Yilgarn Block has been found in Ni sulfide environments (Barrett *et al.* 1977). Alternatively, the ferroactinolite vein may have formed under very reducing conditions at temperatures similar to or below that at which the greenalite veinlet formed.

At Koolanooka, the retrograde formation of magnetite, coincident with the formation of progressively more Mg-rich greenalite or serpentine, indicates that both hydration and oxidation occurred during retrogression. A general reaction for the retrograde alteration is: olivine + H_2O + O_2 → serpentine + magnetite + Si + H_2O. The H_2O released by this reaction is probably consumed by further alteration of the host olivine. Oxidation of Fe^{2+} to Fe^{3+} in early-formed greenalite during these reactions may account for the red color in the most Fe-rich greenalite in sample 55395 (Table 4, no. 1). The samples in which retrograde magnetite and serpentine have replaced most of the primary olivine may be the end products of a continuous retrogression. Alternatively, they may have been formed by a single hydration and oxidation event. The presence of ferroan antigorite suggests a minimum temperature of about 150–200°C (Evans *et al.* 1976) for the retrogression.

TALC AND CHLORITE

Retrograde talc has been found in only one sample of banded iron-formation in the Yilgarn Block. This sample (71586), from Mt. Joy in the granulite terrain in the southwest of the Yilgarn Block, contains the high-temperature metamorphic assemblage quartz–magnetite–ferrosalite–ferrohypersthene–grunerite. The talc, which is Fe-rich, replaces ferrohypersthene and has a slightly lower Fe/(Fe+Mg) ratio (0.43) than the relict orthopyroxene (0.49). Minnesotaite was not observed as a retrograde product in any banded iron-formation; its absence is somewhat surprising in view of its widespread occurrence in very low and low metamorphic grade iron-formation assemblages.

In iron formations with aluminous bulk compositions, chlorite is a common retrograde phase that rims or veins almandine.

UNIDENTIFIED MINERALS

Unidentified minerals have been found in several retrograde mineral assemblages. Based on electron-microprobe analyses, these minerals can be grouped broadly into stilpnomelane-like, chlorite-like and greenalite–chlorite-like minerals.

The stilpnomelane-like minerals are optically very similar to retrograde stilpnomelane. They are fine-grained and green, and are altered to brown along contacts with other minerals and along fractures. In sample 85080 a pale green stilpnomelane-like phase occurs between stilpnomelane (Table 1, no. 6), which forms the outside margins of a retrograde vein, and greenalite (Table 2, no. 6) and quartz, which occur in the centre of the vein. The stilpnomelane-like mineral, greenalite and quartz appear to have been formed by retrogression of the stilpnomelane. In sample 85027, a stilpnomelane-like mineral is intergrown with calcite, quartz and greenalite (Table 2, no. 5), and in sample 84999 (same locality as retrograde greenalite, sample 85001) it is intergrown with fibrous, retrograde ferroactinolite. In samples 85027 and

TABLE 5. ELECTRON-MICROPROBE ANALYSES OF UNIDENTIFIED RETROGRADE MINERALS

Sample No.	1 84999	2 84999	3 84999	4 85027	5 85027	6 85027	7 85080	8 85080	9 84928	10 84928
SiO_2	45.1	46.1	46.3	38.9	40.1	48.6	42.1	47.6	32.0	26.7
TiO_2	0.03	0.02	0.00	0.00	0.00	0.02	0.02	0.02	0.14	0.34
Al_2O_3	1.17	0.83	0.96	0.65	0.88	0.35	0.05	0.66	12.1	15.7
FeO^1	37.4	36.5	34.7	46.5	44.9	36.1	46.5	42.0	39.0	41.3
MnO	0.25	0.31	0.24	1.49	1.45	1.44	0.11	0.06	0.76	0.42
MgO	4.00	4.14	5.18	3.04	3.22	3.44	2.45	2.75	3.09	3.84
CaO	2.55	4.86	5.17	0.23	0.24	4.32	0.04	0.01	0.05	0.07
Na_2O	0.42	0.70	0.32	0.06	0.07	0.16	0.07	0.04	0.23	0.04
K_2O	0.22	0.16	0.09	0.20	0.23	0.32	0.09	0.63	1.24	1.50
Total	91.14	93.62	92.96	91.07	91.09	94.75	91.43	93.77	88.61	89.91

[1] All Fe as FeO.

1-3. Dark-brown mineral intergrown with fibrous ferroact in retrograde vein. Lake Johnston, D.D.H. 5/100.7 m; 4-6. Dark-green mineral with greenal (Table 2, no. 5), cal and qtz in retrograde vein. Windarra Nickel Mines, D.D.H. AE 558/1021.4 m; 7-8. Pale-green mineral between stilp (Table 1, no. 6) and qtz-greenal (Table 2, no. 6) in retrograde vein. Bunyip, Forrestania. D.D.H. 1/61.5 m; 9-10. Colorless, fine-grained mineral in contact with retrograde stilp (Table 1, no. 4) in hbld-alm assemblage. Trough Well, D.D.H. 12/73.5 m.

85080, the composition of the unknown mineral varies markedly over several microns (Table 5, nos. 4–6 and 7–8, respectively) and is intermediate between stilpnomelane and greenalite. The composition of a stilpnomelane-like mineral in sample 84999 also varies markedly over a few microns, and approximates that of stilpnomelane except for a deficiency in Al_2O_3 and K_2O (Table 5, nos. 1–3).

A colorless, very fine-grained mineral coexisting with stilpnomelane (Table 1, no. 4) forms a retrograde assemblage in a hornblende–almandine-bearing assemblage. It shows faint, first-order yellow birefringence and has diffuse contacts against hornblende at high magnification. It is chlorite-like in composition (Table 5, nos. 9 and 10) except for high TiO_2 and K_2O.

Greenalite–chlorite-like retrograde minerals occur in a veinlet in sample 84999. The veinlet assemblage contains (1) a slightly pleochroic, pale to dark brown mineral in parts of the vein that cuts magnetite bands and (2) a highly pleochroic, colorless to green mineral in those parts of the vein that cut across quartz–actinolite bands. Electron-microprobe analyses indicate that the vein minerals (Table 6) vary between greenalite-like and chlorite-like compositions, with Al substituting for Si. Analyses show small but significant amounts of CaO and Na_2O. The unidentified stilpnomelane-like retrograde mineral described from this sample (see above) occurs in an intergrowth that is separate from the vein assemblage. The paragenetic relationship between the two retrograde assemblages is uncertain.

Some of these unidentified minerals may be structurally disordered. For example, those with a composition intermediate between stilpnomelane and greenalite (samples 85027 and 85080) may represent mixed-layer structures of stilpnomelane and greenalite. Similarly, the chlorite-like mineral (sample 84928) may be a stacking mixture of stilpnomelane and chlorite. Such mixed-layer structures might be metastable transitional phases between stilpnomelane and chlorite, respectively. The greenalite–chlorite-like minerals from sample 84999 may also be mixed phases, although 7 Å minerals with compositions broadly similar to those in Table 6 have been reported from iron-formation assemblages of very low metamorphic grade (Klein & Fink 1976, Gole 1979).

CONCLUSIONS

The compositions of retrograde minerals are, in general, closely related to the bulk composition of the host rock, although some metasomatic transfer, particularly involving K and Al in stilpnomelane-bearing assemblages, must have occurred during retrogression.

TABLE 6. ELECTRON-MICROPROBE ANALYSES OF RETROGRADE VEIN MINERALS, SAMPLE 84999[1]

	1	2	3	4	5
SiO_2	33.0	31.3	29.8	27.8	29.9
TiO_2	0.00	0.03	0.02	0.00	0.01
Al_2O_3	2.92	5.90	8.10	9.50	14.4
FeO[2]	47.1	43.1	44.1	44.5	40.5
MnO	0.87	0.05	0.08	0.08	0.07
MgO	3.51	6.63	6.85	6.75	3.85
CaO	0.25	0.36	0.25	0.14	0.73
Na_2O	0.14	0.55	0.40	0.18	0.05
K_2O	0.00	0.00	0.00	0.00	0.00
Total	87.79	87.92	89.60	88.95	89.51
			Ions on the basis of 14 oxygens		
Si	3.95	3.65	3.43	3.24	3.33
Al	0.05	0.35	0.57	0.76	0.67
	4.00	4.00	4.00	4.00	4.00
Al	0.36	0.46	0.53	0.55	1.22
Fe^{2+}	4.72	4.21	4.24	4.34	3.77
Mn	0.09	0.01	0.01	0.01	0.00
Mg	0.63	1.15	1.17	1.17	0.64
Ca	0.03	0.05	0.03	0.02	0.09
Na	0.03	0.12	0.09	0.04	0.01
	5.86	6.00	6.07	6.13	5.73

[1] Lake Johnston, D.D.H. 5/100.7 m. [2] All Fe as FeO.

1-4. Retrograde brown minerals in contact with magnetite;.
5. Retrograde green mineral in contact with act-qtz.

The conditions of formation of the retrograde assemblages are difficult to estimate, partly owing to the simplicity of the assemblages formed and, regarding stilpnomelane-bearing assemblages, to the very wide stability field of stilpnomelane. Under very reducing conditions, the stability fields of greenalite and ferroactinolite may overlap in the region of 300 to 350°C.

ACKNOWLEDGEMENTS

This study was undertaken during tenure of an Australian Commonwealth Postgraduate Research Award at the University of Western Australia. I thank the many mining and exploration companies that kindly allowed access to their diamond-drill core. Support from NSF grant EAR–76–11740 (to Dr. C. Klein) during preparation of this paper is gratefully acknowledged.

REFERENCES

BARRETT, F.M., BINNS, R.A., GROVES, D.I., MARSTON, R.J. & MCQUEEN, K.G. (1977). Structural history and metamorphic modification of Archean volcanic-type nickel deposits, Yilgarn Block, Western Australia. *Econ. Geol.* 72, 1195-1223.

BAXTER, J.L. (1965): *Petrology of a Banded Iron-Formation, Koolanooka Hills, Western Australia.* B.Sc. Honours thesis, Univ. Western Australia, Nedlands.

BENCE, A.E. & ALBEE, A.L. (1968): Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* **76**, 382-403.

BUTLER, P. (1969): Mineral compositions and equilibria in the metamorphosed iron formation of the Gagnon region, Quebec, Canada. *J. Petrology* **10**, 56-101.

DIETRICH, V. (1972): Ilvait, Ferroantigorit und Greenalith als Begleiter oxidish-sulfidischer Vererzungen in den Oberhalbsteiner Serpentiniten. *Schweiz. Mineral. Petrog. Mitt.* **52**, 57-74.

ERNST, W.G. (1966): Synthesis and stability relations of ferrotremolite. *Amer. J. Sci.* **264**, 37-65.

EVANS, B.W., JOHANNES, W., OTERDOOM, H. & TROMMSDORFF, V. (1976): Stability of chrysotile and antigorite in the serpentinite multisystem. *Schweiz. Mineral. Petrog. Mitt.* **56**, 79-93.

FLORAN, R.J. & PAPIKE, J.J. (1975): Petrology of the low-grade rocks of the Gunflint Iron-Formation, Ontario–Minnesota. *Geol. Soc. Amer. Bull.* **86**, 1169-1190.

——— & ——— (1978): Mineralogy and petrology of the Gunflint Iron Formation, Minnesota–Ontario: correlation of compositional and assemblage variations at low to moderate grade. *J. Petrology* **19**, 215-288.

FRONDEL, C. (1962): Ferroan antigorite (jenkinsite). *Amer. Mineral.* **47**, 783-785.

GOLE, M.J. (1979): *Metamorphosed Banded Iron Formations in the Archean Yilgarn Block, Western Australia.* Ph.D. thesis, Univ. Western Australia, Nedlands.

——— (1980): Mineralogy and petrology of very low metamorphic grade Archaean banded iron-formations, Weld Range, Western Australia. *Amer. Mineral.* **65**, 8-25.

JASMUND, K., SYLLA, H.M. & FREUND, R. (1975): Solid solution in synthetic serpentine phases. *Proc. Int. Clay Conf. 1975*, 267-274.

KLEIN, C., JR. (1974): Greenalite, stilpnomelane, minnesotaite, crocidolite and carbonates in a very low-grade metamorphic Precambrian iron-formation. *Can. Mineral.* **12**, 475-498.

——— (1978): Regional metamorphism of Proterozoic iron-formation, Labrador Trough, Canada. *Amer. Mineral.* **63**, 898-912.

——— & FINK, R.P. (1976): Petrology of the Sokoman Iron Formation in the Howells River area, at the western edge of the Labrador Trough. *Econ. Geol.* **71**, 453-488.

LESHER, C.M. (1978): Mineralogy and petrology of the Sokoman Iron Formation near Ardua Lake, Quebec. *Can. J. Earth Sci.* **15**, 480-500.

MUELLER, R.F. (1960): Compositional characteristics and equilibrium relations in mineral assemblages of a metamorphosed iron-formation. *Amer. J. Sci.* **258**, 449-497.

PAGE, N.J (1968): Chemical differences among the serpentine "polymorphs". *Amer. Mineral.* **53**, 201-215.

WHITTAKER, E.J.W. & WICKS, F.J. (1970): Chemical differences among the serpentine "polymorphs": a discussion. *Amer. Mineral.* **55**, 1025-1047.

Received August 1979, revised manuscript accepted December 1979.