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MANGANOAN ILMENITE FORMED DURING REGIONAL METAMORPHISM OF ARCHEAN MAFIC AND ULTRAMAFIC ROCKS FROM WESTERN AUSTRALIA

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ABSTRACT

Ilmenite, or its alteration products, is a widespread accessory phase in regionally metamorphosed mafic and ultramafic rocks from Archean greenstone belts of Western Australia. The grain shapes of ilmenite and its interstitial nature suggest that it is a relict igneous, late-crystallized or intercumulus phase. However, its high Mn and very low Mg contents are unlike those of any igneous ilmenite from tholeiitic or komatiitic rocks, and its composition is grossly independent of bulk-rock composition or parent-magma type. Collectively, these data suggest that the ilmenite is metamorphically modified, having lost Mg and gained Mn by diffusion from its host rocks. Values of D_{Mn}^{bulk} are generally greater for ultramafic than mafic rocks, suggesting that Mn diffusion is enhanced at lower $f(O_2)$ during alteration of the former. In very-low- and low-grade metamorphic rocks, ilmenite is largely or completely altered to titanite or "leucoxene", probably as a result of high CO_2 activity. At medium to high metamorphic grades, there seems to be a progressive narrowing in the compositional range of ilmenite, suggesting enhanced equilibrium with silicate assemblages. The behavior of ilmenite is analogous to that of chromite in metamorphosed ultramafic rocks from the same domains, in that both minerals seem to be mainly relict igneous phases modified by diffusion during metamorphism, although chromite does not show pronounced Mn enrichment.

Keywords: ilmenite, manganese partition, regional metamorphism, Archean greenstones, Western Australia.

SOMMAIRE

L'ilménite (ou le produit de son altération) est un minéral accessoire répandu dans les assemblages métamorphiques développés aux dépens des roches mafiques et ultramafiques des ceintures de roches vertes de l'Australie occidentale. La morphologie de l'ilménite et sa distribution interstitielle font penser qu'il s'agit d'un reliquat magmatique intercumulus, ou d'une phase cristallisée tardivement. Toutefois, ses teneurs en Mn (élevée) et en Mg (très basse) diffèrent sensiblement de celles qui caractérisent l'ilménite ignée des roches tholéiitiques et komatiitiques: de plus, sa composition est largement indépendante de la composition globale des roches ou de l'affiliation magmatique. Dans l'ensemble, ces données indiquent que l'ilménite a été modifiée au cours du métamorphisme, ayant perdu du magnésium et s'enrichissant en manganèse par diffusion à partir des roches encaissantes. Les valeurs de D_{Mn}^{global} sont plus élevées pour les roches ultramafiques, en général, que pour les roches mafiques, ce qui fait penser que la diffusion du Mn était plus importante aux valeurs inférieures de $f(O_2)$ pendant leur altération. Dans les roches très faiblement à faiblement métamorphosées, l'ilménite est largement ou complètement transformée en titanite ou "leucoxène", tout probablement comme résultat d'une activité élevée du CO_2. Dans le cas du métamorphisme aux facies intermédiaire et élevé, l'étendue du champs de composition de l'ilménite semble se retrécir, ce qui concorde avec une équilibration plus complète avec les assemblages de silicates. Le comportement de l'ilménite est analogue à celui de la chromite dans les unités ultramafiques des mêmes domaines: les deux semblent être en grande partie des phases ignées reliques dont la composition a été modifiée par diffusion au cours du métamorphisme: toutefois, la chromite ne montre aucun enrichissement important en Mn.

(Traduit par la Rédaction)

Mots-clés: ilménite, répartition du manganèse, métamorphisme régional, roches vertes archéennes, Australie occidentale.

INTRODUCTION

Ilmenite is a widespread accessory mineral in terrestrial igneous and metamorphic rocks and some lunar basalts. Its compositions are potentially important indicators of the physicochemical conditions [*e.g.*, T, $f(O_2)$] under which host rocks have crystallized (*e.g.*, Buddington & Lindsley 1964, Andersen & Lindsley 1979, 1981, Bishop 1980), and may also be sensitive to variations in magma composition, important examples being kimberlites (*e.g.*, Mitchell 1973) and high-Mg basaltic magmas (*e.g.*, Cawthorn *et al.* 1985, Groves *et al.* 1986). Both features depend upon ilmenite forming solid-solution series with several end-members. There is substantial replacement of Fe by Mg and Mn, restricted replacement by Zn, Al, Cr, V, Ni, and minor replacement by some trace elements and rare-earth elements (*e.g.*, Carmichael *et al.* 1974, Garanin *et al.* 1980). Ilmenite associated with tholeiitic magmas is normal-

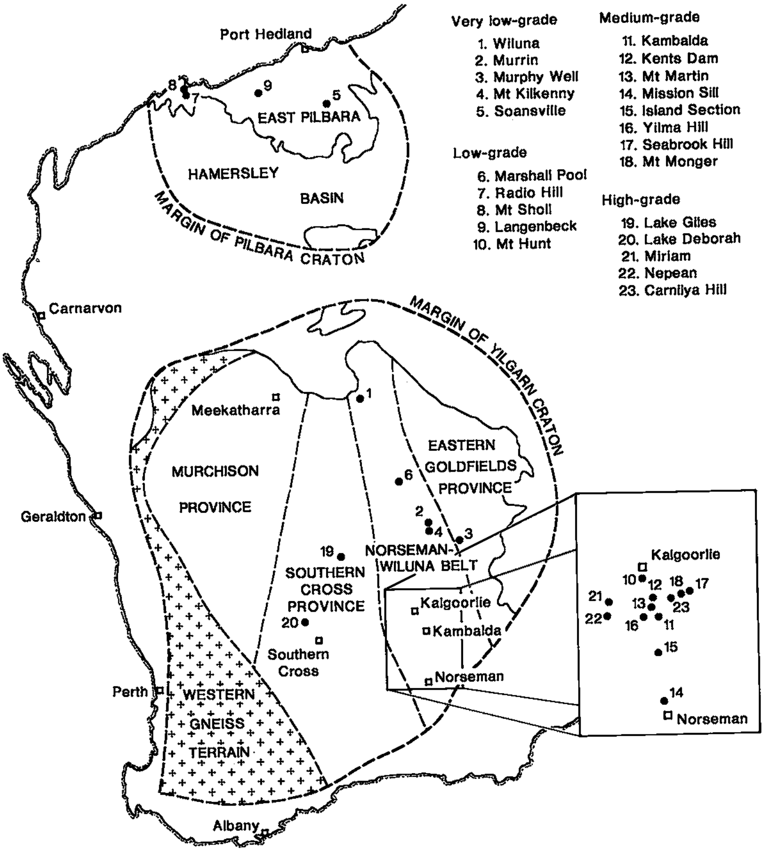

FIG. 1. Regional map of the Western Australian Shield showing major tectonic units and localities from which ilmenite-bearing mafic and ultramafic rocks were examined. Adapted from Groves *et al.* (1985).

ly a late-crystallizing mineral containing less than 3% MgO and less than 1% MnO (Haggerty 1976, Thompson 1976, Reynolds 1983), whereas high-Mg basaltic magmas may have early-crystallized ilmenite, with 4 to 10% MgO, but less than 1% MnO (Cawthorn *et al.* 1985). Ilmenite associated with acid igneous rocks is usually a late-crystallizing phase, with significant replacement of Fe by Mn and minor substitution by Mg, commonly amounting to less than 1% MgO (Lipman 1971, Haggerty 1976, Neumann 1974).

During a study designed to distinguish between ilmenite from tholeiitic and high-Mg basaltic suites (Cassidy 1985), an extension of the research of Cawthorn *et al.* (1985), a suite of metamorphosed Archean mafic and ultramafic rocks, both intrusive and extrusive, from the Western Australian Shield (Fig. 1) was investigated. The ilmenite from these rocks of variable metamorphic grade is anomalously enriched in Mn (1.1–11.1% MnO, 3–25% $MnTiO_3$) and contains negligible Mg (commonly <0.10% MgO, <0.5% $MgTiO_3$).

Such Mn-rich ilmenite is not normally found in unmetamorphosed mafic or ultramafic rocks (Lipman 1971, Haggerty 1976). An extensive search of the literature revealed that only Geissman *et al.* (1983) reported Mn-rich ilmenite (5.65–6.34% MnO) in tholeiitic metabasalts from the Archean Kinojevis Group in northeastern Ontario, and that Purvis (1984) and Perriam (1985) mentioned Mn-rich (1.5–3.1% MnO) ilmenite from metamorphosed komatiites and tholeiites from the Mt. Martin – Carnilya Hill region of the Yilgarn block. There are few studies of metamorphic ilmenite in general, and no systematic data on ilmenite in metamorphosed mafic rocks in particular. Some data are given by Hollander (1970), who found apparent equilibrium partition of Mn between ilmenite and hornblende in two high-grade metamorphic terranes, but disequilibrium in a third.

TABLE 1. METAMORPHIC SETTING, LITHOLOGY AND ACCESSORY ASSEMBLAGES OF LOCALITIES IN THE WESTERN AUSTRALIAN SHIELD FROM WHICH ILMENITE IN MAFIC AND ULTRAMAFIC ROCKS HAS BEEN EXAMINED

METAMORPHIC DOMAIN	LITHOLOGY	LOCALITY	METAMORPHIC FACIES	ACCESSORY ASSEMBLAGE	MAIN REFERENCES
VERY LOW GRADE	THOLEIITIC BASALT	Wiluna	prehnite–pumpellyite	Leuc–Ttn–Hem	Binns et al. (1976)
		Murrin	prehnite–pumpellyite	" " "	Miles (1950), Hallberg (1985)
		Murphy Well	prehnite–pumpellyite	" " "	Lewis & Williams (1973), Hallberg (1985)
	HIGH–Mg BASALT	Murrin	prehnite–pumpellyite	Chr–Mag–Ttn±Hem	Miles (1950), Hallberg (1985)
		Murphy Well	prehnite–pumpellyite	" " " "	Lewis & Williams (1973), Hallberg (1985)
	HIGH–Mg GABBRO	Soansville	prehnite–pumpellyite	Leuc–Hem–Mag–Ttn	McCall (1971), Jervis (1983)
LOW GRADE	(I) THOLEIITIC BASALT	Marshall Pool	low– to mid–greenschist	Leuc–Ttn	Leishman (1969), Donaldson (1983)
	THOLEIITIC GABBRO	Mt Kilkenny	lower greenschist	Mag–Ilm–Ttn–Leuc–Hem	Jaques (1971, 1976), Hallberg (1985)
	HIGH–Mg BASALT	Marshall Pool	low– to mid–greenschist	Chr–Ttn	Leishman (1969), Donaldson (1983)
	(II) THOLEIITIC GABBRO	Radio Hill	mid–greenschist	Ilm–Mag–Leuc	Richardson (1976)
		Mt Scholl	mid–greenschist	" " "	Mathison & Marshall (1981)
	HIGH–Mg GABBRO	Mt Langenbeck	mid–greenschist	Ilm–Mag–Chr–Ttn	Jones (1971)
		Mt Hunt	high–greenschist	" " " "	Hallberg (1970), Williams & Hallberg (1973)
MEDIUM GRADE	THOLEIITIC BASALT	Kents Dam	low amphibolite	Ilm–Mag	Perriam (1985)
		Kambalda	low amphibolite	" "	Lesher (1984)
		Mt Martin	mid–amphibolite	Ilm–Chr–Rt–Leuc	Purvis (1984), Perriam (1985)
	HIGH–Mg BASALT	Kambalda	low amphibolite	Ilm–Mag–Chr	Lesher (1984)
	HIGH–Mg GABBRO	Mission Sill	low amphibolite		Hallberg (1970), Williams & Hallberg (1973)
		Island Section	low amphibolite	Mafic units: Ilm–Chr–Ttn±Leuc	" , " "
		Yilmia Hill	low amphibolite	Ultramafic units: Ilm–Chr–Mag–Ttn	" , " "
		Seabrook Hill	low amphibolite		Williams (1971), Williams & Hallberg (1973)
		Mt Monger	low amphibolite		" , " "
HIGH GRADE	THOLEIITIC BASALT	Lake Giles	high amphibolite	Ilm–Ttn–Rt	Porter (1971)
		Lake Deborah	high amphibolite	" " "	"
		Nepean	high amphibolite	Ilm–Ttn–Mag–Rt	Hudson (1973)
		Miriam	high amphibolite	" " " "	Hallberg et al. (1973)
	THOLEIITIC GABBRO	Carnilya Hill	mid– to high–amphibolite	Ilm–Ttn	Arndt (1980), Perriam (1985)
	HIGH–Mg BASALT	Carnilya Hill	mid– to high–amphibolite	" "	" , "
		Lake Giles	high amphibolite	Ilm–Ttn	Porter (1971)
		Lake Deborah	high amphibolite	Ilm–Mag–Chr–Ttn	"
		Nepean	high amphibolite	" " " "	Hudson (1973), Barrett et al. (1976)
		Miriam	high amphibolite	" " " "	Hallberg et al. (1973)

The following abbreviations have been used: Chr chromite, Hem hematite, Ilm ilmenite, Leuc "leucoxene", Mag magnetite, Rt rutile, Ttn titanite.

PETROGRAPHY

Introduction

Binns *et al.* (1976) defined four types of metamorphic domain for the Eastern Goldfields Province of the Yilgarn block, and these can be extended to the Pilbara block. Samples used in this study are grouped according to a modified version of this classification (Table 1), *i.e.,* into a) very low grade: prehnite-pumpellyite facies, b) low grade: (i) low-greenschist facies, (ii) mid-greenschist facies to greenschist–amphibolite-facies transition, c) medium grade: low- to mid-amphibolite facies, and d) high grade: mid- to high-amphibolite facies, locally to amphibolite–granulite facies transition.

Polished thin sections of rocks of variable Mg content (5.1–31.9% MgO) were examined; the samples are subdivided in Table 1 on the basis of metamorphic domain, of tholeiitic or high-Mg affinity, and of intrusive or extrusive origin. All samples are catalogued in the museum collection of the Department of Geology, University of Western Australia. Where textures of the precursor rocks are well preserved, the igneous terminology is used, and the prefix "meta" is omitted. Typical textures of ilmenite grains or of its pseudomorphs are shown in Figure 2.

Very low-grade domains

All samples from very low-grade metamorphic terranes preserve relict igneous textures, and some contain relict igneous plagioclase and clinopyroxene. Carbonate metasomatism, however, is responsible for the majority of alteration products present. Distinct mineral assemblages, including alteration products of ilmenite, can be identified (Table 1) from rocks that have undergone prehnite–pumpellyite-facies metamorphism. The accessory phases comprise mainly titanite - hematite - "leucoxene" + magnetite in mafic rocks and magnetite - chromite - titanite + "leucoxene" in ultramafic rocks. No ilmenite is present. Titanite - "leucoxene" + hematite are pseudomorphs of: (i) skeletal ilmenite in Soansville Sill samples; (ii) anhedral to subhedral ilmenite laths and small blades in most rocks, and (iii) more rarely, subhedral "hopper"-shaped grains of ilmenite.

Low-grade domains: low-greenschist assemblages

Accessory assemblages from low-greenschist rocks in low-grade domains are summarized in Table 1. Most rocks preserve igneous textures, and many contain relict igneous phases.

Tholeiitic intrusions. Only rocks from the tholeiitic

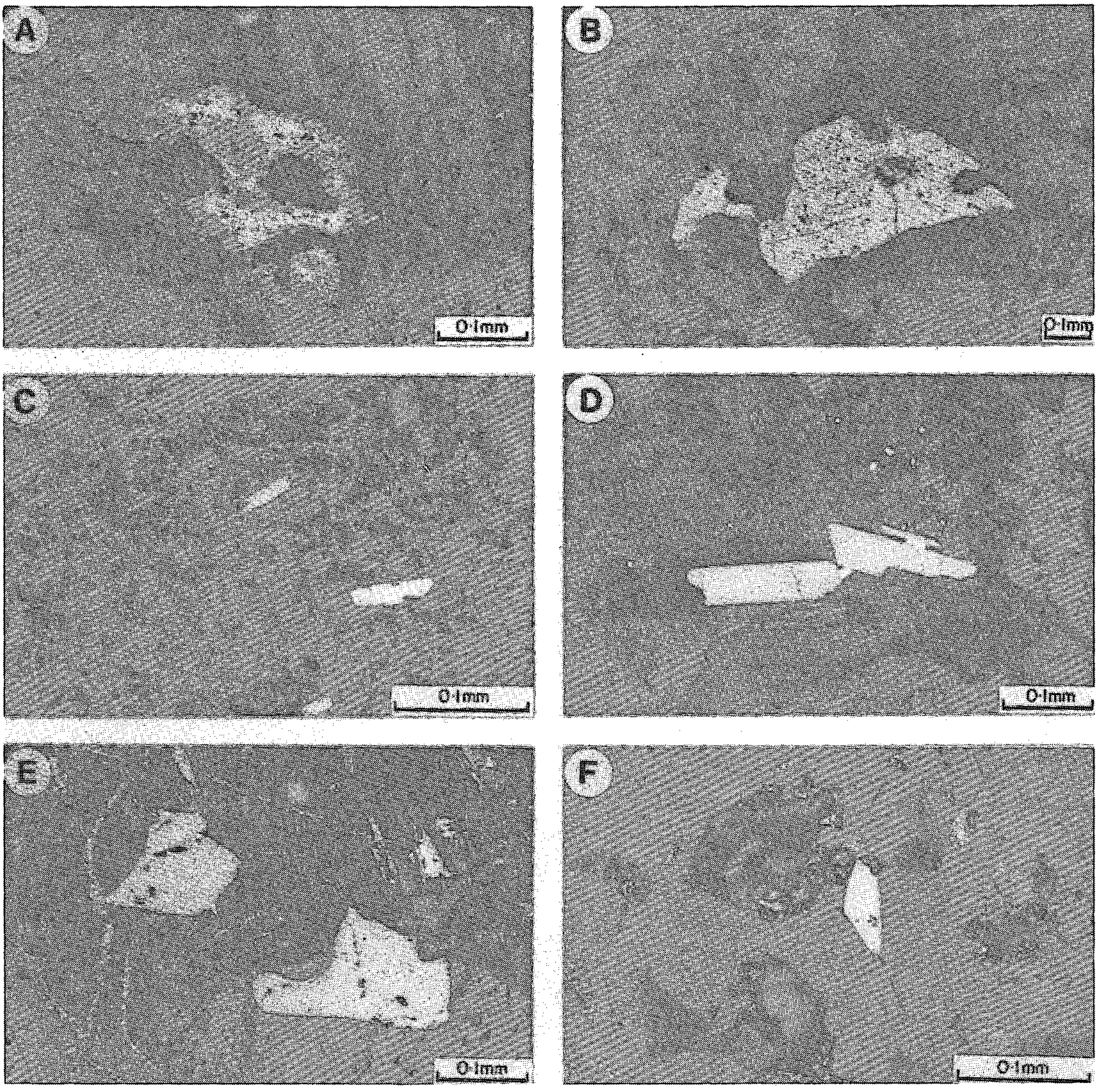

FIG. 2. Photomicrographs of (A) ilmenite completely altered to titanite + "leucoxene" ± rutile, Border zone, Seabrook Hill (65892), medium grade; (B) ilmenite partly altered to titanite + "leucoxene", orthopyroxene gabbro, Mt. Langenbeck (67156), low grade; (C) ilmenite grain showing swallow-tail termination, orthopyroxenite, Mt. Monger (65844), medium grade; (D) ilmenite grain showing igneous textures, pyroxenite, Mt. Sholl (100875), low grade; (E) ilmenite grain showing igneous textures, peridotite, Radio Hill (83259), low grade; (F) ilmenite grain (high grade) showing textures that indicate a metamorphic origin, amphibolite, Lake Giles (66711), high grade. Reflected light.

Mt. Kilkenny layered intrusion contain ilmenite. It is present as: (i) discrete, small, subhedral to anhedral elongate blades (0.04 × 0.10 mm to 0.20 × 0.50 mm), interstitial to plagioclase and pyroxene, and, (ii) irregular, anhedral (0.08 × 0.20 mm to 0.20 × 0.50 mm) grains poikilitically enclosing or interstitial to relict olivine and pyroxene or enclosed within hornblende, biotite and chlorite. The ilmenite cores are, however, surrounded by alteration rims of titanite - "leucoxene" + hematite + rutile.

Tholeiitic and high-Mg basalts. Throughout the Marshall Pool tholeiitic and high-Mg basalts, ilmenite is completely altered to "leucoxene" and rutile. Titanite - "leucoxene" and rutile form pseudomorphs after ilmenite and are present as (i) anhedral to subhedral laths and small blades, and

(ii) irregular, anhedral grains interstitial to igneous relict phases and secondary amphibole and chlorite.

Low-grade domains: mid- to upper-greenschist assemblages

Accessory minerals present in mid- to upper-greenschist metamorphic rocks are summarized in Table 1. Ilmenite is present in all rock types from this metamorphic domain.

Tholeiitic intrusions. Ilmenite is present as an accessory phase in all rock types, occurring as intercumulus grains between plagioclase, olivine and pyroxene. In the upper zones of the Mt. Sholl and Radio Hill layered intrusions, ilmenite is partly to completely altered to "leucoxene" and rutile. Ilmenite occurs in three forms: (i) small (0.03 × 0.08 mm to 0.10 × 0.25 mm), subhedral to anhedral, elongate blades interstitial to pyroxene, plagioclase and secondary biotite; these ilmenite grains have swallow-tail terminations where associated with plagioclase and pyroxene, but are roundish where associated with secondary hornblende and biotite, (ii) anhedral grains of variable size (0.03 × 0.12 mm to 0.40 × 1.00 mm), and (iii) large skeletal grains (up to 1.0 × 4.0 mm), showing grid-like textures.

High-Mg intrusions. Ilmenite is present as an accessory phase in all rock types, although there is normally partial alteration to "leucoxene", titanite and rutile. This alteration is chiefly restricted to the borders of, and fractures and cleavages, in the ilmenite grains. The latter occur as small (0.03 × 0.08 mm to 0.10 × 0.20 mm), subhedral to anhedral blades interstitial to pyroxene, plagioclase and secondary biotite. These grains develop: (i) swallow-tail terminations and less commonly hopper textures, and (ii) rounded embayments where enclosed in plagioclase and pyroxene.

Medium-grade domains

Ilmenite is present as an accessory phase in the majority of rock types. Hallberg (1970) and Williams (1971) reported only exsolved lamellae of ilmenite in titaniferous magnetite in rocks of high-Mg parentage, but careful study has shown the existence of coarser grains (primary ?) of ilmenite as well. Many samples from the high-Mg layered intrusions show preserved igneous textures, but they rarely contain relict igneous phases (Table 1). Most metamorphosed tholeiitic basalts have undergone some degree of metamorphic retexturing (Perriam 1985).

Basaltic rocks. Ilmenite is a minor phase in all tholeiitic basalts examined. It occurs as: (i) acicular to skeletal rodlets (10 × 50 μm to 40 × 100 μm) interstitial to amphibole and plagioclase; some rodlets have swallow-tail terminations and hopper textures; (ii) anhedral grains (0.04 × 0.10 mm to 0.10 × 0.40 mm), partly altered to "leucoxene" and titanite on grain margins, occurring predominantly as a late-crystallized igneous phase.

Ilmenite is an anhedral accessory phase (0.03 × 0.10 mm to 0.09 × 0.35 mm) in some Kambalda high-Mg basalt and komatiite samples. Many grains, especially along their margin, are partly altered to "leucoxene", titanite and rutile.

High-Mg layered intrusions. Ilmenite has a similar form in both mafic and ultramafic units. It occurs predominantly as interstitial, anhedral to euhedral grains associated with plagioclase, orthopyroxene and clinopyroxene, and with biotite and other intercumulus phases. There is partial alteration to "leucoxene", titanite and rutile in most samples. The main occurrences are as: (i) discrete, very small, elongate blades (up to 0.05 × 0.10 mm) interstitial to plagioclase and pyroxene, and (ii) discrete, small subhedral to anhedral elongate grains (0.04 × 0.10 mm to 0.20 × 0.50 mm), either interstitial to cumulate phases or poikilitically enclosing plagioclase. Many grains have swallow-tail terminations or hopper textures. Granular intergrowths of magnetite and ilmenite occur in the upper units of mafic zones in the intrusions.

High-grade domains

Ilmenite is an accessory phase in all tholeiitic and high-Mg rocks from high-grade terranes.

Tholeiitic assemblages. Ilmenite is an accessory phase in tholeiitic basalt and gabbro, both of which are characterized by complete recrystallization of the original rocks (Porter 1971, Hudson 1973). Ilmenite occurs as: (i) acicular to skeletal ilmenite rodlets (10 × 50 μm to 40 × 100 μm) interstitial to, and commonly embayed by, amphibole and plagioclase, and (ii) anhedral ilmenite grains (20 × 50 μm to 40 × 200 μm) interstitial to amphibole and plagioclase.

High-Mg assemblages. These assemblages are characterized by completely recrystallized rocks, some with porphyroblastic metamorphic olivine. Ilmenite is an accessory phase, along with magnetite and chromite, plus rutile, titanite and "leucoxene" as alteration products. Ilmenite occurs as: (i) subhedral, acicular to elongate blades (10 × 40 μm to 30 × 80 μm) interstitial to all metamorphic silicates, and (ii) anhedral grains (0.04 × 0.10 mm to 0.1 × 0.4 mm) interstitial to tremolite and anthophyllite.

Summary and interpretation

Ilmenite generally has been completely replaced by alteration products in very low-grade metamorphic domains; ilmenite cores in the Mt. Kilkenny intrusion are the only exception. In low-, medium- and high-grade domains, ilmenite is present both in tholeiitic and high-Mg basalts and in layered intrusions; some grain margins are altered.

In all cases where igneous textures are preserved, ilmenite is present predominantly as an interstitial or intercumulus phase, suggesting late crystallization. The delicate forms of many grains in more completely altered rocks, with swallow-tail terminations, hopper crystals, *etc.*, suggest that most are igneous relics rather than new metamorphic phases. The only ilmenite grains that could be the result of metamorphic crystallization are acicular to bladed forms intergrown with, and partly embayed by, metamorphic silicate minerals.

ILMENITE CHEMISTRY

Analytical procedures and nomenclature

The chemical compositions of discrete ilmenite grains were measured by electron microprobe and standard wavelength-dispersion X-ray-spectrometry techniques. Analyses were obtained with an ARL SEMQ instrument in the Electron Microscopy Centre at the University of Western Australia. Operating conditions were: 15 kV accelerating potential, 20 nA specimen current (on benitoite), beam diameter approximately 1 µm. Data correction was by the method of Bence & Albee (1968) using the revised alpha factors of A.A. Chodos. Forty-second counts were made on peaks and 10-second counts on high and low backgrounds for Si, Al, Cr, Fe, Ca, Mn and V. For Mg and Ti there were 80-second counts on peaks and 20-second counts on both high and low backgrounds. Vanadium and Ti were determined after deconvolution of the V*Kα* and Ti*Kβ* peaks.

Generally, three to six mineral grains were analyzed per specimen, depending on their suitability for microanalysis. Each mineral analysis represented in the Tables is an average of 3–6 individual analyses. Detection limits for the oxides analyzed are about 0.02 wt.%. Accuracy of the analyses is estimated at ± 1% of the amount present for oxides more abundant than 5 wt.%, and ± 10 relative percent for oxides less abundant than 1 wt.%. In calculating ilmenite formulae, Fe^{2+} and Fe^{3+} are derived from Fe_{total} assuming stoichiometry. Over 600 analyses of ilmenite, with totals ranging from 97 to 103 percent, were used for interpretation and discussion.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF ILMENITE FROM METAMORPHOSED MAFIC AND ULTRAMAFIC ROCKS FROM LOW-GRADE DOMAINS, WESTERN AUSTRALIAN SHIELD

wt%	1	2	3	4	5	6	7	8	9	10
TiO_2	50.27	49.40	42.80	50.40	49.53	46.81	51.32	52.66	52.63	50.56
Cr_2O_3	0.05	0.01	0.09	0.13	0.01	0.15	0.21	0.03	0.11	0.02
Fe_2O_3	0.46	3.82	18.10	2.07	4.91	8.75	2.55	0.02	0.09	3.14
FeO	39.89	40.25	36.45	40.45	40.83	37.13	40.86	40.95	43.06	37.70
MgO	0.03	0.02	0.49	0.03	0.01	0.06	0.09	0.04	0.15	0.18
MnO	4.95	4.03	1.15	4.45	3.46	5.30	5.03	4.40	3.86	7.38
V_2O_3	0.43	0.15	0.10	0.13	0.15	0.10	0.03	0.06	0.06	0.01
Total*	99.27	97.73	100.23	98.09	99.04	98.74	99.76	98.09	100.03	99.23
Mole percent end member (not including hematite)										
%$MnTiO_3$	11.15	9.20	3.03	10.01	7.90	12.60	11.05	9.45	8.28	16.43
%$FeTiO_3$	88.73	90.72	94.71	89.87	92.06	87.15	88.60	90.40	91.16	82.86
%$MgTiO_3$	0.12	0.08	2.27	0.12	0.04	0.25	0.35	0.15	0.57	0.71

Specimens: **1** – metagabbro, Mt. Kilkenny 67251; **2** – metagabbro, Mt. Kilkenny 67252; **3** – metanorite, Mt. Kilkenny 67260; **4** – metagabbro, Mt. Sholl 100882; **5** – metagabbro, Radio Hill 83232; **6**– metaperidotite, Mt. Sholl 100877; **7** – metapyroxenite, Radio Hill 8325; **8** – metagabbro, Mt. Langenbeck 67078; **9** – metagabbro, Mt. Langenbeck 67082; **10** – metaperidotite, Mt. Langenbeck 67070. Compositions obtained from electron-microprobe data. Proportion of ferrous and ferric iron calculated assuming stoichiometry.

* Total includes minor components — SiO_2, Al_2O_3, CaO — which have contents typical of mafic and ultramafic rocks (Haggerty 1976).

Low-grade domains: low-greenschist assemblages

Typical ilmenite compositions from Mt. Kilkenny, the only locality to contain discrete unaltered ilmenite, are listed in Table 2. Ilmenite grains from extensively altered samples of lower units of the layered intrusion have variable contents of Mg (0.20–0.29% MgO) and Mn (2.78–5.18% MnO). Ilmenite from the upper units of the intrusion has similar values: 0.02 to 0.05% MgO and 3.62–4.95% MnO (Fig. 3A). Ilmenite containing higher Mg (0.48–1.96% MgO) and lower Mn (0.99– 1.15% MnO) is from a partly serpentinized olivine–plagioclase heteradcumulate and has both major-element and minor-element compositions typical of those in unmetamorphosed mafic and ultramafic rocks (Haggerty 1976).

Low-grade domains:
mid- to upper-greenschist assemblages

Ilmenite in rocks with mid- to upper-greenschist assemblages from low-grade domains has Mn-rich and Mg-poor compositions unlike those of ilmenite from igneous rocks of similar composition. Contents of other minor components are typical of ilmenite from basic rocks.

In ilmenite from the Mt. Sholl and Radio Hill layered intrusions, MgO ranges from <0.01% to 1.0 (commonly <0.04%) and MnO ranges from 1.57% to 11.1% (commonly >4.25%). Ilmenite from the Fe–Ni–Cu-mineralized basal gabbro of the Mt. Sholl intrusion (Mathison & Marshall 1981) is the least magnesian (<0.01% to 0.10% MgO), whereas ultramafic rocks and other mafic rocks from both layered intrusions contain ilmenite with 0.03% to 1.0% MgO and 0.02% and 0.20% MgO, respectively. The Mn content of ilmenite from the basal gabbro at Mt. Sholl ranges from 1.57 to 4.5% MnO; other ultramafic rocks and mafic rocks from both localities have 3.0% to 11.1.% MnO and 2.0% to 4.0% MnO, respectively (Fig. 3A). Ilmenite from more differentiated (mafic) units contains less Mn than that from ultramafic units, the opposite of trends for igneous rocks, where more differentiated suites typically contain more Mn-rich ilmenite (Haggerty 1976).

Ilmenite grains from the Mt. Langenbeck and Mt. Hunt localities have compositions ranging from 0.04 to 0.16% MgO and 1.55 to 7.4% MnO. Again,

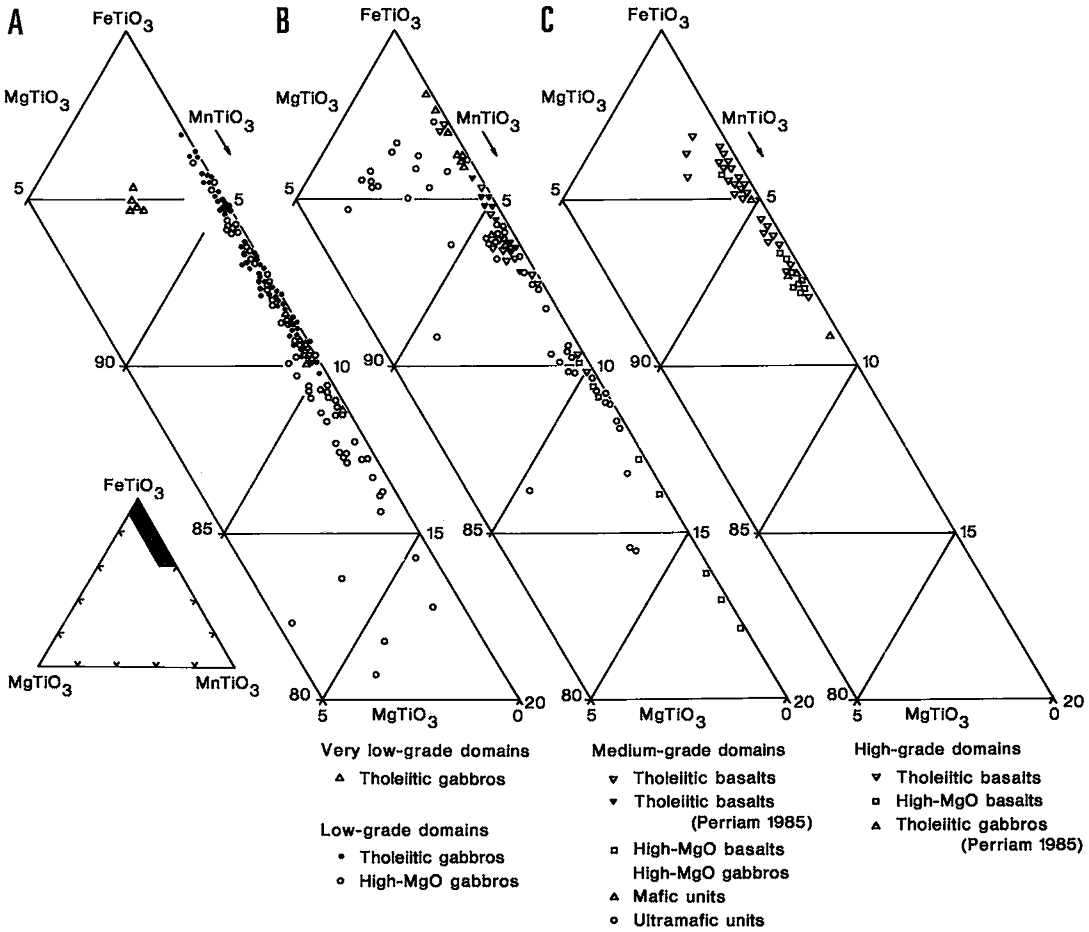

FIG. 3. Plot of the proportion of the end members $MnTiO_3$, $FeTiO_3$ and $MgTiO_3$ in analyzed ilmenite from metamorphosed mafic and ultramafic rocks. (A) Plot of ilmenite from very-low- and low-grade metamorphic domains; (B) ilmenite from medium-grade metamorphic domains; (C) ilmenite from high-grade metamorphic domains.

ilmenite from the lowermost ultramafic unit is more manganiferous (6.2 to 7.4% MnO) than that from more differentiated units (1.55 to 4.4% MnO).

Medium-grade domains

Ilmenite is present in most rocks from medium-grade metamorphic domains (Table 3). Ilmenite in high-Mg rocks from Kambalda has Mn-rich (4.5–8.46% MnO) and Mg-poor (<0.10% MgO) compositions (Fig. 3B), as has ilmenite in tholeiitic basalts, with 1.25–5.07% MnO and 0.04–0.34% MgO. As above, minor-element compositions are typical of ilmenite in igneous rocks. Perriam (1985) reported compositionally similar ilmenite in tholeiitic basalts from the Kent's Dam and Mt. Martin locali-

TABLE 3. REPRESENTATIVE COMPOSITIONS OF ILMENITE FROM METAMORPHOSED MAFIC AND ULTRAMAFIC ROCKS FROM MEDIUM–GRADE DOMAINS, WESTERN AUSTRALIAN SHIELD

wt%	1	2	3	4	5	6	7	8	9	10
TiO_2	52	52.03	52.53	52.08	52.30	52.6	52.54	51.60	51.27	52.49
Cr_2O_3	<0.2	0.02	0.02	0.09	0.10	0.05	0.11	0.04	0.05	0.04
Fe_2O_3	n.d.*	1.53	2.07	0.89	0.27	0.13	0.27	0.88	0.40	0.01
FeO	44	42.48	41.71	38.49	41.85	42.68	39.95	43.46	41.31	40.98
MgO	<0.12	0.07	0.05	0.05	0.02	0.04	0.48	0.17	0.06	0.05
MnO	3	3.08	5.07	7.96	4.81	3.79	6.36	2.60	4.59	5.40
V_2O_3	n.d.	0.03	0.02	0.05	0.03	0.01	0.02	0.04	0.02	0.00
Total **	99.5	100.04	101.57	99.75	99.60	99.23	99.73	98.80	97.73	99.04
Mole percent end member (not including hematite)										
$\%MnTiO_3$	n.d.	6.66	10.33	17.00	10.42	8.13	13.63	5.68	10.09	11.61
$\%FeTiO_3$	n.d.	93.06	89.48	82.82	89.51	91.72	84.56	93.67	89.68	88.20
$\%MgTiO_3$	n.d.	0.28	0.19	0.18	0.08	0.15	0.81	0.65	0.23	0.19

Specimens: **1** – tholeiitic metabasalt, Kent Dam, AA681622 (Perriam 1985); **2** – tholeiitic metabasalt, Kambalda 79860; **3** – tholeiitic metabasalt, Kambalda 79885; **4** – komatiitic metabasalt, Kambalda 79782; **5** – komatiitic metabasalt, Kambalda 79784; **6** – tholeiitic metabasalt (contact), Yilmia Hill 63177; **7** – harzburgite, Mission Sill 63511; **8** – orthopyroxenite, Yilmia Hill 63180; **9** – peridotite, Seabrook Hill 65874; **10** – orthopyroxenite, Mt. Monger 65844. Compositions obtained from electron-microprobe data. Proportion of ferrous and ferric iron calculated assuming stoichiometry.

* n.d. = not determined.

** Total includes minor components — SiO_2, Al_2O_3, CaO — which have contents typical of mafic and ultramafic rocks (Haggerty 1976).

ties: ilmenite from these localities typically has less than 0.12% MgO and contains 4 to 7% MnO.

Ilmenite from high-Mg layered sills (*e.g.*, Mission Sill, Seabrook Hill, Mt. Monger) has similar Mn and Mg contents to that from high-Mg basalts in low- and medium-grade domains. The range is from 0.02 to 1.14% MgO (majority <0.15% MgO), and 0.66 to 6.50% MnO. Ilmenite from the margins (Williams & Hallberg 1973) of the ultramafic–mafic layered sills contains from 0.43 to 1.14% MgO and 0.66 to 1.25% MnO. Ilmenite from ultramafic zones has 0.02 to 0.93% (av. 0.11%) MgO and 1.34 to 6.50% MnO, whereas that from mafic zones has <0.15% MgO, and 1.0 to 3.0% MnO.

High-grade domains

Representative compositions of ilmenite from high-grade metamorphic domains are listed in Table 4, and end-member proportions are plotted in Figure 3C. Compositions of ilmenite from metamorphosed tholeiitic and high-Mg basalts and komatiites are similar, ranging from 1.1 to 3.6% MnO and 0.02 to 0.41% MgO. Within this range, tholeiitic basalts have 1.1 to 2.7 (commonly 1.9)% MnO and 0.02 to 0.41 (usually <0.04)% MgO, high-Mg basalts have 2.3 to 2.7% MnO and 0.03 to 0.05 (usually <0.04)% MgO, and komatiites have 1.67 to 3.6 (commonly >2.3)% MnO and 0.03 to 0.15 (usually <0.07) MgO. Qualitatively, a small increase in the Mn content of ilmenite occurs as the bulk Mg content of the rocks increases. This trend is similar to the direction of compositional change for ilmenite from layered intrusions. Perriam (1985) reported similar Mn-rich ilmenite in tholeiitic intrusive rocks from the Carnilya Hill locality (typically <0.12% MgO, 2.5 to 4.5% MnO).

TABLE 4. REPRESENTATIVE COMPOSITIONS OF ILMENITE FROM METAMORPHOSED MAFIC AND ULTRAMAFIC ROCKS FROM HIGH–GRADE DOMAINS, WESTERN AUSTRALIAN SHIELD

wt%	1	2	3	4	5	6	7	8
TiO_2	51.19	52.17	50.96	52	52	52.16	51.75	51.24
Cr_2O_3	0.02	0.02	0.03	<0.02	<0.02	0.05	0.07	0.14
Fe_2O_3	1.35	0.14	1.99	n.d.*	n.d.	0.05	0.02	1.23
FeO	43.60	44.57	42.97	43	42	43.12	42.95	44.04
MgO	0.03	0.04	0.03	<0.12	<0.12	0.05	0.03	0.15
MnO	2.15	2.03	2.46	3	4	3.60	3.35	1.67
V_2O_3	0.03	0.0	0.01	n.d.	n.d.	0.05	0.02	0.01
Total**	98.53	99.15	98.69	98.5	98.5	99.12	98.30	98.54
Mole percent end member (not including hematite)								
$\%MnTiO_3$	4.75	4.40	5.47	n.d.	n.d.	7.78	7.31	3.68
$\%FeTiO_3$	95.13	95.44	94.41	n.d.	n.d.	92.03	92.57	95.74
$\%MgTiO_3$	0.12	0.15	0.12	n.d.	n.d.	0.19	0.12	0.58

Specimens: 1 – tholeiitic metabasalt, Miriam 80150; 2 – tholeiitic metabasalt, Lake Deborah 71692; 3 – tholeiitic metabasalt, Nepean 73092; 4 – tholeiitic metabasalt, Carnilya Hill, AA681629 (Perriam 1985); 5 – tholeiitic metagabbro, Carnilya Hill, AA315637 (Perriam 1985); 6 – komatiite, Lake Deborah 71691; 7 – komatiite, Lake Giles 66708; 8 – komatiite, Miriam 80145. Compositions obtained from electron-microprobe data. Proportion of ferrous and ferric iron calculated assuming stoichiometry.

* n.d. — not determined.

** Total includes minor components — SiO_2, Al_2O_3, CaO — which have contents typical of mafic and ultramafic rocks (Haggerty 1976).

Summary

It is evident that ilmenite from metamorphosed extrusive and intrusive rocks of both tholeiitic and high-Mg affinity has anomalously low Mg and high Mn contents relative to unmetamorphosed igneous rocks of similar bulk composition. The only significant trend is for ilmenite to be more Mn-rich in ultramafic units than in associated mafic units of some layered intrusions (*e.g.*, Yilmia Hill, Mt. Sholl, Mt. Kilkenny), irrespective of their affinity. Even in this case, there is substantial overlap in ilmenite compositions (Figs. 3A, B) The Mn contents of ilmenite reported here are distinctly higher than those reported by Hollander (1970) in amphibolites and gneisses from Scandinavia.

Figures 3A, B and C show that although ilmenite compositions from the domains of different metamorphic grade do overlap, there is progressively less scatter in compositions with increasing grade. This trend appears to be real despite the fewer ilmenite analyses from high-grade domains. There is a general absence of hematite exsolution bodies in ilmenite grains, and most ilmenite contains less than 5 mole % Fe_2O_3, which, in the absence of coexisting rutile (Brothers *et al.* 1987), suggest relatively reducing conditions during metamorphism, in agreement with the conclusions of Groves *et al.* (1977) and Phillips & Groves (1983).

DISCUSSION

Absence of ilmenite from very low-grade domains

Binns *et al.* (1976) concluded that the nature of relict primary phases surviving in metavolcanic rocks at various metamorphic grades in greenstone belts of the Yilgarn block implies non-progressive metamorphism, imposed relatively rapidly on previously largely unaltered sequences. The rarity of relict ilmenite in the very-low- and low-grade metamorphic domains is consistent with this interpretation. The former presence of ilmenite is indicated by various alteration products, including "leucoxene", finely crystalline rutile, titanite and hematite.

Ilmenite, with similar Mn contents to those reported here from low- to high-grade domains, has been recorded elsewhere from prehnite–pumpellyite facies domains (*e.g.*, Geissman *et al.* 1983, Merriman *et al.* 1986). Merriman *et al.* (1986) recorded Mn-rich ilmenite (up to 4.7 wt% MnO) in the central portion of an olivine dolerite sheet of Ordovician age in Wales. Titanite, with negligible Mn, replaced ilmenite in the altered marginal zones of the intrusion. However, most studies indicate that ilmenite is normally replaced by alteration products as described above (*e.g.*, Zen 1974, Itaya & Banno 1980, Offler *et al.* 1981). A similar situation exists in the low-greenschist facies, where ilmenite either may be present (Mt. Kilkenny, this study; Zen 1974, Braun & Raith 1985) or completely altered. These data suggest that ilmenite preservation depends on very low CO_2 activity (Yang 1987), which is unlikely for areas of very-low- and low-grade metamorphism (*e.g.*, Hallberg 1985) where carbonate alteration is commonly present (*e.g.*, Barley & Groves 1987).

The major products of metamorphic reactions are "leucoxene", titanite and hematite. These may form *via* reactions such as:

$$2FeTiO_3 + O_2 \rightarrow Fe_2O_3 + 2TiO_2$$

and

$$2FeTiO_3 + O_2 + CaCO_3 + 2SiO_2 \rightarrow 2CaTiSiO_5 + Fe_2O_3 + 2CO_2.$$

The formation of titanite is expected, as most mafic and ultramafic rocks have significant amounts of calcite or other carbonates as a result of premetamorphic CO_2 metasomatism (Donaldson 1983, Hallberg 1985), which may include both seafloor alteration or regional, fault-related alteration (*e.g.*, Barley & Groves 1987). Excess SiO_2 is also present in most tholeiitic rocks.

Ilmenite in rocks from greenschist- and amphibolite-facies metamorphic domains shows partial alteration to titanite – "leucoxene" + rutile. Itaya & Banno (1980) suggested that ilmenite is stable at metamorphic grades greater than the biotite isograd of the greenschist facies, whereas titanite and rutile form owing to retrograde reactions at lower temperatures. With decomposition, Fe, then Mn are removed from, and Ca added to, the former site of the ilmenite (*e.g.*, Itaya & Banno 1980, Merriman *et al.* 1986). The partial alteration of ilmenite is more pronounced in the more differentiated units of layered intrusions (*e.g.*, Mt. Kilkenny, Mt. Langenbeck, Radio Hill). This finding may be due to retrograde alteration, although the possibility of autometasomatism by reaction of ilmenite with residual magmatic fluids should not be ignored (*e.g.*, Haggerty 1976).

Metamorphosed igneous ilmenite

As discussed above, all ilmenite in mafic and ultramafic suites from low- to-medium-grade domains, and even most ilmenite from high-grade domains, retains textural characteristics indicative of late-magmatic crystallization. Despite this, the ilmenite contrasts markedly in terms of Mg and Mn contents with igneous ilmenite from unmetamorphosed tholeiitic and high-Mg suites. Most ilmenite described here contains less than 0.15% MgO and 1 to 11% MnO, whereas typical igneous ilmenite from mafic–ultramafic rocks has 0.5 to 10% MgO and less than 1% MnO. It is apparent that the majority of ilmenite represents igneous grains that have been compositionally modified by diffusion processes during metamorphism.

The high Mn and low Mg contents reported here reflect a marked contrast in partition of these components, presumably dictated by both the crystal chemistry of ilmenite and the coexisting silicate minerals. Under the ambient conditions during regional metamorphism, Mg preferentially entered coexisting silicate phases (*cf.* the olivine–ilmenite thermometer at the upper-temperature range of its applicability: Andersen & Lindsley 1979, 1981), and a surprisingly limited partition toward ilmenite led to such low contents that the relationship cannot be quantitatively assessed. Mn favors ilmenite (Rumble 1973, 1976, Neumann 1974), such that relatively high contents can be generated in this accessory phase even though bulk rock contents are low. Although there seem to be no experimental data pertinent to partitioning of Mn between ilmenite and the silicates typical of mafic and ultramafic rocks, mass-balance calculations for ilmenite in rocks from the Tal y Fan intrusion indicate that up to 90% of the whole-rock Mn budget is contained in ilmenite (Merriman *et al.* 1986). It is also known that Mn is enriched in ilmenite relative to coexisting magnetite in igneous rocks, particularly at low temperatures (Lipman 1971, Haggerty 1976, Rollinson 1979, 1980) and that except for garnet, ilmenite is the favored receptor of Mn during metamorphism of pelitic rocks (Evans & Guidotti 1966, Guidotti 1974, Woodsworth 1977, Itaya & Banno 1980, Pownceby *et al.* 1987). Braun & Raith (1985) recorded Mn-rich ilmenite in greenschist- to lower-amphibolite-facies metamorphosed basic rocks, and concluded that there had been re-equilibration, under these *P–T* conditions, of the Fe–Ti oxide assemblages. Guidotti (1974) noted that there seems to be no systematic change in Mn partition between ilmenite and bulk rock with metamorphic grade. Alternatively, Itaya & Banno (1980)

TABLE 5. DISTRIBUTION OF Mn/Fe IN CALCIC AMPHIBOLE AND IN ILMENITE FROM MAFIC AND ULTRAMAFIC ROCKS OF VARIABLE METAMORPHIC GRADE

SPECIMEN	METAMORPHIC DOMAIN	LITHOLOGY	CALCIC^1 AMPHIBOLE		ILMENITE	$K_{D\ \text{Ilm–Amph}}^{\text{Mn–Fe}}$
			wt% Al_2O_3	Mn/Fe	Mn/Fe	
79890	MEDIUM	THOLEIITIC	9.3	0.0178	0.0295	1.7
79860	MEDIUM	BASALT	5.5	0.0177	0.0734	4.1
79885	MEDIUM		7.0	0.0203	0.1231	6.1
79782	MEDIUM		6.8	0.0204	0.2095	10.3
79784	MEDIUM	HIGH–Mg	7.7	0.0228	0.1164	5.1
″	″	BASALT	3.0*	0.0317	″	3.7
79785	MEDIUM		6.5	0.0221	0.1162	5.3
66711	HIGH	THOLEIITIC	4.3	0.0190	0.0416	2.2
71692	HIGH	BASALT	7.8	0.0171	0.0461	2.7
″	″		3.8*	0.0178	″	2.6
80150	HIGH		8.7	0.0176	0.0499	2.8
80145	HIGH	HIGH–Mg	0.5*	0.0235	0.0384	1.6
66708	HIGH	BASALT	8.3	0.0168	0.0790	4.7
71691	HIGH		1.2*	0.0224	0.0846	3.8

SPECIMENS: 79890,79860,79885,79782,79784,79785: Kambalda; 66711,66708: Lake Giles; 71691, 71692: Lake Deborah; 80145,80150: Miriam.

[1] — calcic amphibole is hornblende unless indicated otherwise.

* — calcic amphibole is actinolite.

recorded that the MnO/FeO values of discrete ilmenite grains decrease with increasing metamorphic grade.

To assess whether the observed ilmenite compositions (*i.e.,* Mn contents) reflect an approach to metamorphic equilibrium, two approaches have been attempted. For some of the medium- and high-grade rocks studied, silicate minerals also have been analyzed by electron microprobe. Calcic amphibole, either hornblende (mafic compositions) or aluminum-poor actinolite (ultramafic compositions), is a common phase to most samples. The calculated distribution-coefficient

$$K_D^{\mathrm{MnFe}} = (\mathrm{Mn/Fe})_{\mathrm{ilm}} \times (\mathrm{Fe/Mn})_{\mathrm{amphibole}}$$

varies considerably between 1.6 and 10.3 (Table 5). There is slightly more diversity among medium-grade pairs (1.7–10.3) than among high-grade pairs (1.6–4.7), which does not seem to depend systematically on either the Al or Mg contents of the amphibole phase. These values suggest that the distribution of Mn in ilmenite and hornblende is irregular, probably owing to nonequilibrium conditions, a similar interpretation to that reached by Hollander (1970) for the distribution of Mn in ilmenite and hornblende in metamorphosed gabbros. Alternatively, K_D may be temperature-dependent.

For a larger number of samples where bulk-rock compositions are available, an alternative partition parameter,

$$D_{\mathrm{Mn}}^{\mathrm{bulk}} = (\text{wt.\% MnO in ilmenite}) / (\text{wt.\% MnO in bulk total silicates})$$

has been calculated (Table 6). The bulk-rock value has been adjusted for Mn in ilmenite by assuming that bulk-rock TiO_2 (corrected for the small amount of TiO_2 in coexisting silicates either from direct analyses of the latter or by using comparable values from similar rocks) is contained solely in ilmenite: where calculated, contents vary between 0.1 and 1.6% of the rocks. The values obtained for $D_{\mathrm{Mn}}^{\mathrm{bulk}}$ range from 10 to 28 and from 25 to 63 for medium-grade tholeiitic and high-Mg rocks, respectively. The $D_{\mathrm{Mn}}^{\mathrm{bulk}}$ values for high-grade equivalents are smaller and more consistent, ranging from 9 to 21.

TABLE 6. PARTITION COEFFICIENT (D_{Mn}^{bulk}) FOR ILMENITE/ROCK FROM MAFIC AND ULTRAMAFIC ROCKS AT VARIABLE METAMORPHIC GRADE

SPECIMEN	METAMORPHIC DOMAIN	LITHOLOGY	ROCK (wt%)		ILMENITE (wt%)			
			TiO2	MnO	TiO2	MnO	% Ilm*	D_{Mn}^{bulk}
79890	MEDIUM	THOLEIITIC BASALT	0.75	0.14	51.99	1.30	1.13	10
79860	MEDIUM		0.93	0.18	52.03	3.08	1.59	23
79885	MEDIUM		0.68	0.23	52.53	5.07	1.01	28
79782	MEDIUM	HIGH-Mg BASALT	0.58	0.19	52.08	7.96	0.81	63
79784	MEDIUM		0.54	0.23	52.55	4.85	0.76	25
79785	MEDIUM		0.57	0.19	52.49	4.82	0.80	32
66711	HIGH	THOLEIITIC BASALT	0.73	0.21	52.45	1.85	0.71	9
66668	HIGH		0.73	0.19	52.27	1.85	1.01	11
71692	HIGH		0.86	0.19	52.17	2.03	1.34	12
73902	HIGH		0.81	0.18	50.96	2.46	1.19	16
73711	HIGH		0.69	0.24	51.05	2.68	0.96	12
73741	HIGH		0.45	0.16	50.51	1.74	0.49	11
80150	HIGH	HIGH-Mg BASALT	0.71	0.19	51.19	2.15	0.86	12
80145	HIGH		0.25	0.17	51.24	1.67	0.41	10
66708	HIGH		0.34	0.16	51.75	3.35	0.10	21
71691	HIGH		0.49	0.20	52.16	3.60	0.82	21

SPECIMENS: 79890, 79860, 79885, 79782, 79784, 79785: Kambalda; 66711, 66668, 66708: Lake Giles; 71691, 71692: Lake Deborah; 73711, 73741, 73902: Nepean; 80145,80150: Miriam.

* Ilmenite corrected for TiO_2 content in amphibole, chlorite and titanite.

The higher, but more variable, $D_{\mathrm{Mn}}^{\mathrm{bulk}}$ values obtained for medium-grade high-Mg rocks may reflect the metamorphic ferromagnesian silicate mineralogy as much as the crystal chemistry of ilmenite. Ferromagnesian silicates, such as talc, serpentine, tremolite – actinolite, chlorite, resulting from low- to medium-grade metamorphic processes, are less accommodating to Mn than their igneous precursors, *i.e.*, olivine, pyroxene (Deer *et al.* 1966). Enhanced Mn diffusion out of ferromagnesian silicates and into ilmenite, in low- to medium-grade ultramafic rocks, provides a good explanation for the higher Mn content of ilmenite.

These results, which are reflected in the narrowing of ilmenite compositional ranges evident at high metamorphic grade in Figure 3, are consistent with an increased tendency toward diffusional equilibrium for ilmenite and coexisting silicates at higher metamorphic grades. Even so, equilibrium has rarely, if at all, been completely achieved, as is indicated by the variability in both K_D and $D_{\mathrm{Mn}}^{\mathrm{bulk}}$ and indeed by the pronounced variation of ilmenite compositions within single samples (*e.g.*, 2.32–5.4 wt.% MnO, samples 65874). In fact, ferromagnesian silicates also show significant compositional variation within samples, particularly in medium-grade domains, but also within the more thoroughly recrystallized, high-grade mafic and ultramafic rocks. Imperfect equilibration, or short-range equilibration, may be an unique feature of possibly short-duration regional metamorphism in Archean greenstone belts. This, and the probable diffusion into and out of a pre-existing igneous relict mineral (*i.e.*, ilmenite), may explain the diversity of K_D and $D_{\mathrm{Mn}}^{\mathrm{bulk}}$ values. A further complication is that the amphiboles used to calculated K_D are likely to act as imperfect solid-solutions for Mn relative to Fe, for Mn is known to favor the Ca site (Deer *et al.* 1966).

Part of the variation in ilmenite composition within rocks of very-low- and low-grade metamorphic domains may be related to changes in oxidation state of the rock or metamorphic fluid (or both) during progressive alteration: this will be particularly important in ultramafic rocks at low metamorphic grades (*e.g.*, Eckstrand 1975). Several authors (Chinner 1960, Kramm 1973, Rumble 1974) have shown that Mg/(Mg + Fe) values of silicate minerals are dependent on $f(O_2)$ in a variety of rock compositions and that there may be complementary variations in ilmenite compositions [*e.g.*,

$Fe_2O_3/(Fe_2O_3 + FeTiO_3)$]. Although there are no data on Mn partitioning in mafic–ultramafic rocks under metamorphic conditions, such partitioning is likely to depend on $f(O_2)$ by analogy with magmatic systems (Haggerty 1976, Klobcar & Taylor 1985). Himmel *et al.* (1953) gave good experimental evidence that diffusion rates of Fe in oxides are strongly dependent on Fe^{2+}/Fe^{3+}. The diffusion rates for Mn in ilmenite are also probably dependent on this ratio. For example, Woodsworth (1977) concluded that the diffusion rate for Mn increases at lower $f(O_2)$. This finding could explain the generally higher Mn contents of ilmenite from more magnesian rocks, as unusually reduced fluids may be developed during their early hydration stage (Eckstrand 1975).

Comparison with metamorphosed chromite

There are analogies between the behavior of ilmenite during metamorphism and that of chromite (Evans & Frost 1975, Groves *et al.* 1977, Donaldson 1983). Groves *et al.* (1977) studied chromite from komatiitic rocks from the same range of metamorphic domains as the ilmenite studied here. They found that chromite is a relict magmatic phase whose composition was modified during metamorphism. Chromite in very-low- and low-grade domains is partly or completely altered to stichtite (Groves & Keays 1979, Donaldson 1983) or to chromium-rich valleriite-like minerals (Nickel & Hudson 1976). As with the ilmenite, relict chromite from these domains and from higher-grade metamorphic domains is strongly depleted in Mg relative to predicted original compositions and to that of rare relict chromite in unserpentinized ultramafic rocks from medium-grade domains. The metamorphosed chromite is, however, enriched in Fe rather than Mn, as in ilmenite.

The analogy also applies to the decreasing range of compositions shown by chromite and ilmenite at increasing metamorphic grade. Chromite at lower grades has a wide range of MgO/(MgO + FeO), but approaches iron-rich chromite (or "ferritchromite") at high metamorphic grades (Groves *et al.* 1977, Donaldson 1983). These data suggest that both chromite and ilmenite have non-equilibrium compositions at very low and low metamorphic grades, but more closely approach equilibrium compositions at medium and high metamorphic grades.

SUMMARY AND CONCLUSIONS

Ilmenite is a widely dispersed, accessory mineral in mafic and ultramafic rocks of both komatiitic and tholeiitic affinity from low- to high-grade metamorphic domains in the Archean greenstone belts of Western Australia. Textural data, particularly the occurrence of hopper crystals, swallow-tail terminations, and delicate bladed crystals, suggest that ilmenite is a relict igneous phase. Its textural position, typically interstitial to all silicate minerals, suggests that it was a late-crystallized or intercumulus phase. Some ilmenite grains from high-grade metamorphic domains, particularly those that are acicular to bladed forms intergrown with, and partly embayed by, metamorphic silicate minerals, could be newly formed metamorphic phases.

Despite the igneous appearance of the majority of ilmenite grains, their high Mn contents are anomalous. The grains are more similar in composition to ilmenite from both unmetamorphosed and metamorphosed felsic igneous rocks. This finding suggests that these ilmenite grains are metamorphosed igneous ilmenite whose composition has been severely modified by diffusional processes.

The high Mn content of ilmenite from metamorphosed, mafic to ultramafic, extrusive and intrusive rocks suggests that Mn must be partitioned strongly into ilmenite relative to silicate minerals under the inferred reducing conditions of regional metamorphism. The high Mn content of the ilmenite also relates to the low modal abundance of ilmenite in these rocks (*cf.* Tracy 1978). Very high Mn contents in ilmenite from some ultramafic rocks suggest that $f(O_2)$ was important in controlling Mn diffusion rates, low $f(O_2)$ favoring higher rates. A combination of whole-rock analyses and microprobe analyses of ilmenite allow a D_{Mn}^{bulk} to be calculated; such calculations suggest that D_{Mn}^{bulk} is greater than 10, and highly variable, although it becomes more constant with increasing metamorphic grade. For some rocks it is also possible to calculate K_D for Mn/Fe between coexisting ilmenite and amphibole: variable values, normally greater than 2, are obtained and also show a tendency to be more consistent at higher metamorphic grade. These data, combined with compositional variation of both ilmenite and amphibole in individual samples, suggest imperfect or short-range equilibration in the Archean volcanic and intrusive rocks.

The almost complete replacement of ilmenite by titanite + hematite + "leucoxene" in very-low-grade metamorphic domains, the rimming of ilmenite grains by these phases in low-grade domains, and the highly variable Mn contents in ilmenite irrespective of rock type in both domains, suggest that ilmenite may be metastable under these metamorphic *T–P* conditions. However, ilmenite seems to be a more stable phase at higher metamorphic grades, with a progressively less variable composition from medium to high metamorphic grade, reflecting a greater approach to equilibrium.

Ilmenite from mafic and ultramafic rocks shows analogous behavior to chromite from ultramafic rocks in the same metamorphic domains. Both phases are igneous relics whose compositions have been modified by diffusional processes: both become less magnesian with progressive metamorphism. Neither phase has achieved complete equilibration, perhaps reflecting unusual conditions (*e.g.*, short duration) during metamorphism of Archean greenstone belts.

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