Coexisting Garnets and Ilmenites Synthesized at High Pressures from Pyrolite and Olivine Basanite and Their Significance for Kimberlitic Assemblages

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Abstract. Coexisting garnets and ilmenites have been synthesized at high pressure (21–40 kb) within the temperature range between 900 and 1100° C from pyrolite-less-40% olivine and olivine basanite with various water contents. The two compositions yield phases with a range in the 100 Mg/Mg+Fe ratio for both garnet (41–76) and ilmenite (15–47). The distribution coefficient for iron and magnesiaum ($K_{D(Fe, Mg)}^{ilm-ga} = 4.0 \pm 0.5$) for coexisting phases does not appear to vary with change in the bulk composition or temperature of synthesis. The synthesized ilmenites are of similar composition to those of kimberlites in 100 Mg/Mg+Fe ratio and Al_2O_3 and Cr_2O_3 solid solution. Cr_2O_3 content in ilmenite is dependent on Cr_2O_3 in the bulk composition and also on Fe_2O_3 content of ilmenite. Fe_2O_3 content of ilmenite is very sensitive to f_{O_2} and natural ilmenites from peridotites have formed under low f_{O_2}. Al_2O_3 solid solution in ilmenite as well as TiO_2 in coexisting garnet tend to be higher with higher temperature. All the variety of compositions of ilmenites from kimberlites may be obtained from rocks rather close in composition to those used in experiments, within the same range of pressure and temperature but at variable oxygen fugacities.

Introduction

Pyrope—almandine garnets and magnesian ilmenites are among the most common minerals found in a majority of kimberlitic pipes. Garnets occur in xenoliths of various peridotites and eclogites and as discrete nodules and isolated grains in the heavy mineral concentrates from kimberlites. In most cases, garnets do not have a paragenetic relation to ilmenites. Ilmenite is mainly found as nodules of varied size and as isolated grains in concentrates, and more rarely as regular intergrowths with pyroxenes (both diopside and enstatite), (Williams, 1932; Sobolev, 1959, 1964; Frantsesson, 1970; Mitchell, 1973; Milashev *et al.*, 1963). It also occurs rarely within ilmenite-bearing peridotites. The rare occurences of ilmenite coexisting with other phases such as olivine, pyroxenes and garnet attract special attention in attempts to clarify possible systematic relationships of its formation in kimberlite. (Ringwood and Lovering, 1970; Dawson and Reid, 1970; Boyd and Nixon, 1973; Ponomarenko *et al.*, 1971, 1972).

In experimental studies of several basaltic and peridotitic compositions, mineral assemblages containing co-existing garnet and ilmenite, had been syn-

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thesized in studies aimed at determining solidus, liquidus and phase relationships as functions of pressure, temperature and water content. The known variations in composition of natural ilmenite and garnet, particularly in Ti-content of garnet, Al-content of ilmenite etc., suggested that useful constraints on P, T conditions of crystallization of the natural minerals might be obtained by analysis of the coexisting mineral pairs synthesized under known P, T conditions. The study was of reconnaissance character seeking to isolate P, T dependent substitutions or partition relationships which would then repay further detailed study in compositions chosen specifically to calibrate the potential P,T indicator (cf. the study by Raheim and Green (1974) of the $K_D^{\text{ga-cpx}}$ partition coefficient for Fe, Mg in garnet and clinopyroxene).

Experimental Methods

Selection of Compositions

For the present study the composition of pyrolite-less-40% olivine (Green and Ringwood, 1970; Green, 1973b) and also olivine basanite (Green, 1973a) were used. These compositions contain garnet and ilmenite in both subsolidus and above-solidus mineral assemblages and phase relationships have been investigated for a wide range of pressure and temperature conditions and for various water contents (Green 1972, 1973a, b, c).

The comparatively low TiO_2 content of the bulk compositions and the appreciable solubility of TiO_2 in pyroxenes, amphibole and garnet, meant that ilmenite was a minor phase and though identifiable in many runs, could only be analyzed with sufficient accuracy when crystals were >3 microns diameter. In several runs (Tables 1 and 2) garnet was analyzable but ilmenite was absent or not confirmed by electron probe (pyrolite composition). These data give information on minimum TiO_2 solubility in garnet at the varous temperatures and pressures.

Microprobe Analyses

The analyses of synthesized phases were carried out using the TPD electron probe microanalyzer with energy-dispersive detection and analysis system (Reed and Ware, 1973; Green, 1973a). This instrument is uniquely suited for complete analyses of very small grains (>3 μ) present in experimental high pressure runs. Some minerals from the kimberlites of Yakutia were analyzed using the MS46 electron probe using the procedure described by Sobolev, Lavrent'iev et al. (1969).

The ten to twenty individual analyses of garnet and ilmenite were carried out on each experimental run and the analyses listed in Tables 1 and 2 were selected as having totals between 98% and 102%, acceptable structural formulae and (for ilmenites only) $SiO_2 < 1\%$.

Analytical Data (Tables 1 and 2)

(a) *Garnet.* At 35 kb, 1500° C in pyrolite composition garnet containing 1.4% TiO_2 may not coexist with ilmenite so that the TiO_2 content of 1.4% is a minimum value for TiO_2 solubility in garnet. Similarly, in the olivine basanite runs at 30 kb, 1280° C and at 25 kb, 1160° C, 1140° C and 1120° C, garnet coexists with liquid and clinopyroxene but not with ilmenite and the TiO_2 contents of these garnets are also minimal values. The increase in TiO_2 at 25 kb from the 1160° C run (1.2% TiO_2), through the 1140° C run (1.6% TiO_2) to the 1120° C run (1.8% TiO_2) is considered to reflect increasing TiO_2 content of the coexisting liquid and possibly changing partition coefficient between liquid and garnet [Mg_{68} to Mg_{55}] as the degree of crystallization increases at lower temperatures. At the same

pressure, garnet coexisting with ilmenite at $1040°$ C contains 1.4% TiO_2 but this decreases through runs at $1020°$ C, $1000°$ C to 0.8% TiO_2 at $900°$ C.

In the pyrolite (less-40%-olivine) composition, garnet coexisting with ilmenite contains $0.9–1.6\%$ TiO_2 at $1100°$ C, $0.7–1.1\%$ TiO_2 at $1000°$ C and 0.4% TiO_2 at $950°$ C (Table 1). The data suggest a decrease in TiO_2 content at lower temperatures but are not sufficient to evaluate possible systematic pressure or compositional effects as opposed to analytical uncertainty in giving rise to the rather large spread in TiO_2 at any one temperature.

We have evidence for compositional control on the amount of TiO_2 soluble in the pyrope-almandine solid solution in that garnet from pyrolite ($\sim Mg_{75}$) has lower TiO_2 content than that from basanite (Mg_{50-60}), crystallized at similar P, T conditions (Tables 1, 2 and 5).

(b) *Ilmenite*. The ilmenites analyzed from both pyrolite and basanite composition are characterized by high (Fe, Mg) TiO_2 contents and low degrees of solid solution of Cr_2O_3. Fe_2O_3 and Al_2O_3. This feature is very well illustrated in the TiO_2 vs MgO diagram utilized by Sobolev (1974) to illustrate variation in natural ilmenites from kimberlite pipes. This diagram can be contoured for Fe_2O_3 content of ilmenite and such contours are approximately correct for $(Cr_2O_3+Fe_2O_3)$ solid solutions because of similar molecular weights of Cr_2O_3 and Fe_2O_3. The analyzed magnesian ilmenites (Mg_{42}—Mg_{48}) from the experimental runs on pyrolite-less-40% olivine composition have $<5\%$ $Fe_2O_3+Cr_2O_3$ and the major substitution is Cr_2O_3 ($1.4–2.3\%$ Cr_2O_3) with minor Al_2O_3 and possibly very minor Fe_2O_3. In the basanite composition, Cr_2O_3 is not detectable in ilmenite and the more iron-rich ilmenites (Mg_{15}—Mg_{28}) require low Fe_2O_3 contents to satisfy structural formulae constraints.

In Fig. 1, the experimentally synthesized ilmenites are compared with natural ilmenites of various paragenetic associations occurring within kimberlite pipes. The synthetic magnesian ilmenites most closely resemble these ilmenites occurring in intergrowth with diamond and those occurring in intergrowth with garnet or within garnet peridotite. Most discrete ilmenite crystals within kimberlite have higher Fe_2O_3 contents, implying higher oxygen fugacity at crystallization than the conditions pertaining within the piston-cylinder apparatus. The ilmenite megacrysts occurring in basanite magmas in N.S.W. (Binns, 1969; Wass, 1971) are similar to but have slightly higher Fe_2O_3 contents than those crystallized experimentally from the basanite. One ilmenite megacryst occurring within a mantle-derived nepheline benmoreite magma (Green et al., 1974) from S.E. Queensland has low MgO content and low Fe_2O_3 content, closely resembling the ilmenite crystallized from basanite at $900°$ C (i.e. after a moderately high degree of crystallization of the basanite liquid).

The data on ilmenite compositions synthesized in the presence of a water-rich fluid phase or with water dissolved in the silicate melt phase, demonstrate that the experimental techniques used maintain oxygen fugacity at low values, consistent with equilibrium with carbon (graphite or diamond) in the C—H—O system. Experiments in a basalt-H_2O—CO_2 system (Brey and Green, 1975) at 30 kb using the oxygen buffering technique have shown that at 30 kb, 1100 to $1200°$ C with f_{O_2} buffered by the magnetite—haematite buffer, titanomagnetite rather than ilmenite coexists with garnet, and the garnet contains andradite solid

Table 1. Compositions of coexisting garnets and ilmenites in the pyrolite less 40% olivine
Ag$_{75}$Pd$_{25}$ capsules except

Run conditions	35 kb 1500° C "Dry"	40 kb 1100° C 0.3% H_2O		29 kb 1100° C 0.3% H_2O	28 kb 1100° C 0.3% H_2O		21 kb 1100° C 0.3% H_2O	
Phase	Ga[a]	Ga	Ilm	Ilm	Ga	Ilm	Ga	Ilm
SiO_2	41.3	41.3	0.6	0.6	41.9	0.6	41.3	0.9
TiO_2	1.4	0.9	57.1	56.8	1.6	57.2	1.3	55.9
Al_2O_3	20.9	21.7	0.6	0.9	20.7	0.9	21.1	1.0
Cr_2O_3	2.1	1.7	1.6	2.0	1.9	2.1	1.9	2.3
FeO	7.2	10.2	27.4	26.5	9.7	27.0	10.3	27.2
MnO	—	0.3	0.2	0.3	0.2	0.2	0.3	0.3
MgO	20.7	19.0	12.9	13.6	18.5	13.7	17.9	13.0
CaO	5.0	5.2	0.4	0.4	7.1	0.3	7.2	0.4
Na_2O	—	0.2	—	0.3	—	0.3	—	0.2
Mol. proportions								
100 Mg/Mg + Fe	83.5	76.8	45.8	47.9	77.2	47.4	75.8	45.8
Ca	12.7	13.2	—	—	17.5	—	17.9	—
Mg	72.9	66.7	45.8	47.9	63.7	47.4	62.2	45.8
Fe	14.4	20.1	54.2	52.1	18.8	52.6	19.9	54.2
$K_{D(Fe, Mg)}^{ilm-ga}$		3.91			3.76		3.70	

[a] Presence of ilmenite not confirmed by electron probe, garnet coexists with olivine, enstatite,

Table 2. Compositions of coexisting garnets and ilmenites in olivine basanite at various
except column 1

Run conditions	30 kb 1280° C 4.5% H_2O	25 kb 1160° C 4.5% H_2O	25 kb 1140° C 4.5% H_2O	25 kb 1120° C 4.5% H_2O	30 kb 1050° C 4.5% H_2O		27 kb 1050° C 4.5% H_2O	
Phase	Ga[a]	Ga[a]	Ga[a]	Ga[a]	Ga	Ilm	Ga	Ilm
SiO_2	40.9	40.5	39.9	39.2	39.2	0.8	40.2	0.7
TiO_2	1.1	1.2	1.6	1.8	1.8	53.4	1.4	53.7
Al_2O_3	22.4	22.3	21.4	20.6	20.0	0.7	21.7	0.7
FeO	8.5	12.9	15.9	17.8	17.8	38.3	19.0	39.2
MnO	0.2	0.3	0.4	0.5	0.4	0.3	0.6	0.3
MgO	18.7	15.4	13.8	12.4	11.5	6.7	12.4	6.0
CaO	5.8	7.1	6.9	6.5	7.1	0.5	6.4	0.5
Na_2O	0.1	—	0.1	0.2	0.3	0.3	0.3	0.2
K_2O	0.1	—	—	—	—	—	0.1	0.1
Mol. proportions								
100 Mg/Mg + Fe	80.0	68.0	60.4	55.3	53.5	23.9	53.8	21.2
Ca	15.0	18.5	18.0	17.3	19.1	—	16.5	—
Mg	68.0	55.4	49.7	45.8	43.3	23.9	44.9	21.2
Fe	17.0	26.1	32.3	36.9	37.6	76.1	38.6	78.8
$K_{D(Fe,Mg)}^{ilm-ga}$					3.68		4.31	

[a] No ilmenite present, garnet coexisting with liquid and clinopyroxene.

composition at various pressures, temperatures and water contents. All experiments in column 1 (Pt capsule)

31 kb 1000° C 0.3% H_2O	24 kb 1000° C 0.3% H_2O		22 kb 1000° C 0.3% H_2O		21 kb 1000° C 0.3% H_2O		30 kb 950° C 10% H_2O	
Ilm	Ga	Ilm	Ga	Ilm	Ga	Ilm	Ga	Ilm
0.9	41.2	0.7	42.1	0.7	39.6	0.7	41.0	0.1
56.3	0.7	54.4	0.9	54.6	1.1	54.8	0.4	56.4
0.6	21.7	0.5	20.5	0.7	19.3	0.7	20.9	0.5
1.4	2.2	1.6	2.0	1.8	1.8	2.0	2.0	2.1
29.4	10.7	28.4	11.0	29.0	10.7	28.0	10.4	27.2
0.2	0.3	0.3	0.3	0.2	0.3	0.3	—	0.3
12.7	16.8	12.1	17.8	11.7	17.8	12.1	17.9	13.1
0.4	7.7	0.3	7.3	0.5	7.0	0.3	6.5	0.2
0.3	—	0.2	—	0.2	—	0.2	—	—
43.9	73.8	43.3	74.2	41.7	74.8	43.8	75.6	46.4
—	19.7	—	17.9	—	17.4	—	16.5	—
43.9	59.2	43.3	60.9	41.7	61.8	43.8	63.1	46.4
56.1	21.1	56.7	21.2	58.3	20.8	56.2	20.4	53.6
	3.69		4.03		3.84		3.60	

clinopyroxene.

pressures, temperatures and for various water contents. All experiments in $Ag_{75}Pd_{25}$ capsules (Pt. capsule)

25 kb 1040° C 4.5% H_2O		25 kb 900° C 4.5% H_2O		25 kb 1020° C 30% H_2O		25 kb 1000° C 30% H_2O		25 kb 1000° C[b] 30% H_2O	
Ga	Ilm	Ga	Ilm	Ga	Ilm	Ga	Ilm	Ga	Ilm
39.3	0.9	38.6	1.0	39.9	0.3	40.7	—	39.8	—
1.4	53.6	0.8	52.2	1.1	53.4	0.9	53.5	1.2	52.9
21.3	0.9	21.4	0.7	21.2	0.5	21.2	0.5	21.0	0.7
18.8	38.6	23.0	41.2	14.4	36.7	16.9	37.9	16.1	38.1
0.5	0.4	1.0	0.5	0.4	0.3	0.3	0.2	0.8	0.6
11.9	6.3	9.0	4.2	13.0	7.9	12.1	7.4	11.5	6.9
6.4	0.6	6.2	0.8	9.6	0.5	7.8	0.3	9.0	0.3
—	0.3	0.2	0.3	—	—	—	—	0.3	—
—	—	—	0.2	—	0.1	0.1	0.1	0.1	0.1
53.2	22.4	41.2	15.3	61.5	27.6	56.0	25.7	53.5	24.2
17.0	—	16.9	—	24.5	—	20.6	—	24.2	—
44.1	22.4	34.2	15.3	46.5	27.6	44.4	25.7	42.4	24.2
38.9	77.6	48.9	84.7	29.0	72.4	35.0	74.3	33.4	75.8
	3.93		3.88		4.19		3.68		3.97

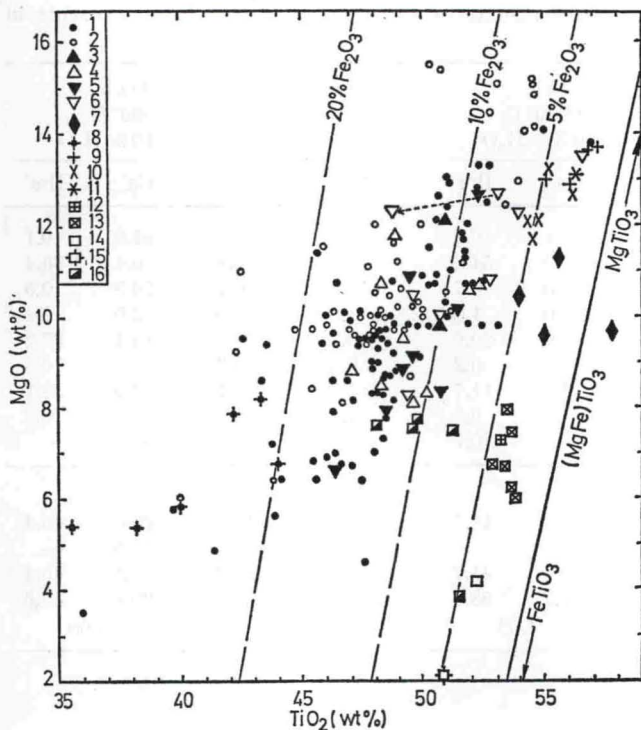[b] Nepheline mugearite bulk composition (Irving and Green, in preparation).

Fig. 1. Plot of MgO vs TiO_2 for experimentally synthesized ilmenites and ilmenites from various associations in kimberlite illustrating the divergence of ilmenites from the simple $FeTiO_3$—$MgTiO_3$ solid solution.

1. Ilmenite in kimberlites of Yakutia (Frantsesson, 1970; Milashev et al., 1963; Sobolev, ed., 1959, 1964)
2. Ilmenite in kimberlites of West Africa and South Africa (Danchin, d'Orey, 1972; Kukharenko et al., 1971; Mitchell, 1973; Vladimirov et al., 1971)
3. Ilmenite in intergrowth with clinopyroxene, Yakutia (Ponomarenko et al., 1971; Sobolev, ed., 1964)
4. Ilmenite in intergrowth with clinopyroxene, S. Africa (Boyd, Dawson, 1972; Boyd, Nixon, 1973; Dawson, Reid, 1970; Ringwood, Lovering, 1970)
5. Ilmenite from garnet peridotites or intergrown with pyrope garnets, Yakutia (Ponomarenko et al., 1971, 1972; Sobolev, ed., 1964, this paper, Table 6)
6. Ilmenite from garnet peridotites or intergrown with pyrope garnets, S. Africa (Boyd, Nixon, 1972, 1973; this paper, Tables 4, 5)
7. Ilmenite intergrown with diamond, Mir pipe, Yakutia (Sobolev, 1974; Sobolev et al., 1971; this paper, Table 6)
8. Inclusions of ilmenite in zoned garnet from Mir pipe, Yakutia (Sobolev et al., 1974)
9. Ilmenites synthesized from pyrolite-40% olivine at $T=1100°$ C (this paper, Table 2)
10. Ilmenites synthesized from pyrolite-40% olivine at $T=1000°$ C (this paper, Table 2)
11. Ilmenites synthesized from pyrolite-40% olivine at $T=950°$ C (this paper, Table 2)
12. Ilmenites synthesized from olivine basanite at $T=1100°$ C
13. Ilmenites synthesized from olivine basanite at $T=1000$–$1050°$ C
14. Ilmenite synthesized from olivine basanite at $T=900°$ C (data for 12, 13, 14 are from this paper, Table 3)
15. Ilmenite synthesized by Akella and Boyd (1972)
16. Ilmenite megacrysts from basaltic lavas (Green et al., 1974; Wass, 1971)

Table 3. Coexisting primary and secondary phases in peridoite xenolith W.S.S.l, Wesselton pipe, South Africa

	Primary					Secondary	
	Olivine	Enstatite	Diopside	Garnet	Ilmenite	Ilmenite	Chromite
SiO_2	40.5	57.1	54.0	41.2	0.1	—	—
TiO_2	—	—	1.3	0.6	53.1	48.3	8.0
Al_2O_3	—	0.6	1.3	20.8	0.7	0.8	5.2
Cr_2O_3	—	0.2	0.7	3.4	4.1	8.6	43.2
Fe_2O_3	—	—	—	—	4.1[a]	10.4[a]	9.3[a]
FeO	10.8[b]	6.5[b]	4.1[b]	9.4[b]	25.0[a]	20.9[a]	25.4[a]
MnO	—	—	—	0.3	0.2	0.5	0.5
MgO	49.0	33.9	17.4	19.9	12.7	12.2	9.3
CaO	—	0.5	20.6	4.4	—	0.1	—
Na_2O	—	—	1.1	—	—	—	—
Totals	100.3	98.8	100.5	100.0	100.0	101.8	100.9
Mol. proportions							
$100\,Mg/Mg + Fe$	89.0	90.3	88.7	79.3	47.0	51.0	39.5
Ca	—	1.0	43.0	11.0	—	—	—
Mg	89.0	89.0	51.0	70.0	47.0	51.0	39.5
Fe	11.0	10.0	6.0	19.0	53.0	49.0	60.5

[a] Calculated from the mineral formula.
[b] Total Fe as FeO.

solution. The experimental syntheses of ilmenite confirm earlier conclusions based on analyses of FeO, Fe_2O_3 in bulk charges and evaluation of buffer assemblages, that the standard experimental techniques used in the piston cylinder apparatus result in f_{O_2} conditions considerably lower than the haematite-magnetite buffer, and close to the nickel-nickel oxide or magnetite-wustite buffers (Allen et al., 1972; Green and Ringwood, 1967; Nichols and Ringwood, 1974). Comparison of the natural ilmenites from garnet peridotite parageneses with those synthesized, suggests that the natural assemblages have crystallized at f_{O_2} much lower than the magnetite-haematite buffer but within a small range of f_{O_2} close to and slightly greater than f_{O_2} for the Ni—NiO buffer. Similarly, the analyses of ilmenite megacrysts in basanitic magmas argues that the crystallization and deep seated crystal fractionation processes in which ilmenite plays a role have occurred under conditions of low f_{O_2}, close to that of the Ni—NiO buffer.

The range of higher Fe_2O_3 contents in discrete ilmenite megacrysts in kimberlite, the crystallization (Table 3) within the garnet peridotite WSS1 of a more Fe_2O_3-rich secondary ilmenite (Fig. 1, Table 3) and the rimming of ilmenite megacrysts in basanitic magmas with titanomagnetite (Green et al., 1974) are all features suggesting that in the transport or eruptive stages of extraction of xenolithic material from the upper mantle, the f_{O_2} in the host magma (fluid) increases to higher values than appropriate to the upper mantle source environment.

The synthesized ilmenites show an increase in Al_2O_3 with increasing temperature but with considerable scatter in the data. Natural ilmenites show a similar spread in Al_2O_3 contents but extending to lower values, particularly in ilmenites

Table 4. Coexisting garnets and ilmenites in Peridotite Xenoliths of Udachnaya pipe, Yakutia (UV-494, Uv-600), and ilmenites from intergrowths with individual diamond (spec. BM-10[a]), and with polycrystalline diamond aggregate (MR-331) from the Mir pipe, Yakutia

	Uv-494		Uv-600		BM-10	MR-331
	Ga	Ilm	Ga	Ilm	Ilm	Ilm
SiO_2	40.2	0.21	40.9	0.23	0.03	0.21
TiO_2	0.78	48.5	0.69	49.7	55.6	54.0
Al_2O_3	19.8	0.55	20.1	0.46	0.22	0.69
Cr_2O_3	1.91	1.94	1.32	1.41	0.23	0.76
Fe_2O_3	1.8[b]	12.4[b]	2.4	12.0[b]	1.20[b]	4.20[b]
FeO	11.0	29.7	10.4	28.5	29.6	29.9
MnO	0.44	0.24	0.35	0.20	0.28	0.20
MgO	17.1	7.79	17.7	9.05	11.3	10.5
CaO	5.34	0.02	5.28	0.01	—	—
Totals	98.37	101.35	99.14	101.56	98.46	100.46
Mol. proportions						
100 Mg/Mg + Fe	73.5	31.9	75.3	36.2	40.5	38.5
Ca	14.1	—	13.9	—	—	—
Mg	63.2	31.9	64.8	36.2	40.5	38.5
Fe	22.7	68.1	21.3	63.8	59.5	61.5

[a] Data from Sobolev *et al.* (1971).
[b] Calculated from mineral formulae.

associates with diamond. Al_2O_3 content of ilminite appears to be independent of Cr_2O_3 and Fe_2O_3 contents of ilmenite.

Element Partition between Coexisting Garnet and Ilmenite

(a) Distribution of Iron and Magnesium

The data of Tables 1 and 2 illustrate correlation between the Mg/Mg+Fe-values, and the Cr_2O_3 contents of both ilmenite and garnet. Ilmenite has much lower Mg-value $\left(\dfrac{100 \text{Mg}}{\text{Mg} + \text{Fe}}\right)$ than coexisting garnet and we may define a distribution coefficient.

$K_{D(\text{Fe}, \text{Mg})}^{\text{ilm-ga}} = \dfrac{(\text{Fe}^{++}/\text{Mg})_{\text{ilm}}}{(\text{Fe}^{++}/\text{Mg})_{\text{ga}}}$ to express the compositional relationships between the coexisting solid solutions. $K_{D(\text{Fe}, \text{Mg})}^{\text{ilm-ga}}$ will be a function of pressure, temperature and possibly of composition if either garnet or ilmenite solid solutions are non-ideal. Fig. 2 and Tables 1 and 2 show that $K_{D(\text{Fe}, \text{Mg})}^{\text{ilm-ga}} = 4.0 \pm 0.5$ for all synthesized assemblages. In pyrolite composition at 1100° C, variation in pressure from 21 kb to 40 kb shows slight increase in K_D with increasing pressure (3.70 to 3.91) but further data would be required to substantiate this trend. There is no obvious temperature effect on K_D within the temperature interval 900° C to 1050° C for the basanite composition or within the temperature 950° C to 1100° C for pyrolite composition. The wide range of Mg-values of garnet (41–77) and ilmenite (47 to 15) without systematic change in K_D suggests that K_D is dependent
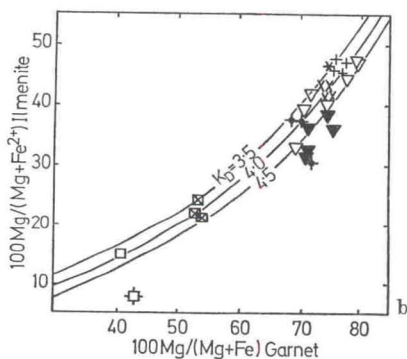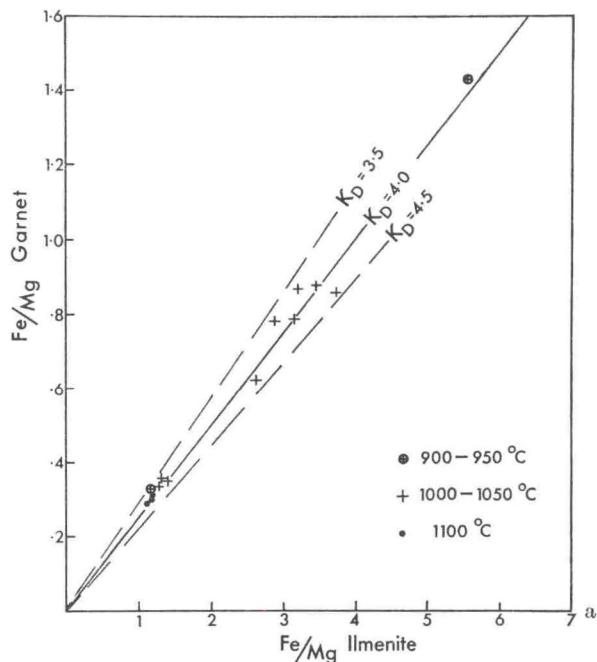
Fig. 2a and b. Partitioning of Fe and Mg between garnet and ilmenite for synthesized samples (a) and for both natural and synthesized ilmenites (b). Symbols (b) as for Fig. 1

of compositional (Mg-value only) variation over the range of compositions of interest for natural ultramafic or basic rocks.

The temperature range over which K_D variation can be examined is not large in the experiments reported and further experiments are required at lower and higher temperatures to evaluate the K_D vs T relationship. It may be noted that $K_{D(Fe, Mg)}^{ga\text{-}cpx}$ has values of 4.7 (900° C), 4.0 (950° C), 3.0 (1050° C) and 2.7 (1100° C) at 30 kb (Raheim and Green, 1974) and the data presented herein shows that $K_{D(Fe, Mg)}^{ilm\text{-}ga}$ is less sensitively dependent on temperature than $K_{D(Fe, Mg)}^{ga\text{-}cpx}$. Our data

Table 5. Compositional features of coexisting synthesized garnets and ilmenites

Run conditions		Garnet				Ilmenite						
P (kbar)	T (°C)	n^a	$\dfrac{100\,Mg}{Mg+Fe}$	TiO_2	Cr_2O_3	n^a	$\dfrac{100\,Mg}{Mg+Fe}$	Al_2O_3	Cr_2O_3	SiO_2	CaO	Na_2O
Pyrolite less 40% Olivine												
21–40	1100	9	76.2	1.3	2.0	4	46.7	0.8	2.0	0.7	0.4	0.2
21–31	1000	7	74.4	0.8	1.8	7	43.1	0.6	1.8	0.7	0.3	0.2
30	950	5	75.7	0.6	2.1	3	45.7	0.5	2.1	0.2	0.2	—
Olivine basanite												
25–30	1050	3	53.4	1.5	—	4	23.1	0.8	—	0.8	0.5	0.3
25	900	5	41.2	1.0	—	1	15.2	0.7	—	1.0	0.8	0.3

[a] $n =$ No. of analyses obeying structural formulae and S_1O_2 (in ilmenite) restrictions, see text.

suggests that Fe/Mg partition between ilmenite and clinopyroxene (or olivine, or orthopyroxene) is likely to be more useful as a petrological tool in deduction of P, T conditions of equilibration than Fe/Mg partition between ilmenite and garnet. From Fig. 2 and the data of Raheim and Green (1974) $K_{D\,(Fe,\,Mg)}^{ilm\text{-}cpx} \approx 18.8$ at 900° C, 30 kb and $K_{D\,(Fe,\,Mg)}^{ilm\text{-}cpx} \approx 10.8$ at 1100° C, 30 kb.

In Table 3, we list analyses of coexisting phases from an ilmenite-bearing garnet peridotite from the Wesselton mine, South Africa. For this assemblage $K_{D(Fe,\,Mg)}^{ilm\text{-}ga} = 4.26$ and $K_{D(Fe,\,Mg)}^{ilm\text{-}cpx} = 8.75$. Garnet and ilmenite from two Yakutian garnet peridotite xenoliths are listed in Table 4 and both ilmenites contain much higher Fe_2O_3 contents than the synthetic or Wesselton minerals. $K_{(Fe^{++},\,Mg)}^{ilm\text{-}ga} = 5.98$ and 5.34 for these two assemblages if Fe^{+++} is allocated to ilmenite and garnet to satisfy structural formulae constraints. Boyd and Dawson (1973) list analyses of coexisting ilmenite and garnet from the Excelsior Pipe in which ilmenite has intermediate (7–9%) Fe_2O_3 contents and in which $K_{D(Fe^{++},\,Mg)}^{ilm\text{-}ga} = 5.1$ and 4.86 if Fe^{+++} is allocated to garnet according to structural formulae constraints (note that garnet then has minor Fe_2O_3 content). For the Wesselton garnet peridotite (Table 4), $K_{D(Fe^{++},\,Mg)}^{ilm\text{-}cpx} = 8.75$; for ilmenite (8.6% Fe_2O_3) and diopside (sub-calcic) in lamellar intergrowth from Uintjes Berg Pipe, $K_{D(Fe^{++},\,Mg)}^{ilm\text{-}cpx} \simeq 8.02$ (Boyd and Nixon, 1973) and for ilmenite (2.61% Fe_2O_3) and diopside (sub-calcic) from Matsoku Pipe $K_{D(Fe^{++},\,Mg)}^{ilm\text{-}cpx} \simeq 7.15$ (Akella and Boyd, 1973).

We conclude, from the experimental data and the comparison with natural ilmenite/garnet and ilmenite/clinopyroxene parageneses that $K_{D(Fe^{++},\,Mg)}^{ilm\text{-}ga} = 4.0 \pm 0.5$ for a range of P, T conditions about 20–40 kb, 900–1100° C and is probably not sensitively dependent on P, T or Mg-value of the bulk composition. However, $K_{D(Fe^{++},\,Mg)}^{ilm\text{-}ga}$ is probably sensitively and positively correlated with Fe_2O_3 substitution in ilmenite. It appears probable that $K_{(Fe^{++},\,Mg)}^{ilm\text{-}cpx}$ is more sensitively dependent on temperature and it is of interest that two independent parameters (the more sub-calcic pyroxene and lower $K_{D(Fe^{++},\,Mg)}^{ilm\text{-}cpx}$ indicate that the Matsoku Ol+Cpx+Opx+Ilm assemblage (Akella and Boyd, 1973) is a higher temperature assemblage than the Wesselton example (Table 3).

(b) Chromium Partition between Ilmenite and Garnet

Examination of Tables 1, 3 and 4 shows that coexisting garnet and ilmenite have similar contents of Cr_2O_3 (weight %) in both the synthesized assemblages and in those of natural garnet-ilmenite asociations. Comparison of $(100 \ Cr/R^{VI})_{garnet}$ vs $(100 \ Cr/R^{VI})_{ilmenite}$ $(R^{VI} = Ti + Al + Cr + Fe^{+++})$ reveals a wide spread of Cr content in natural garnet-ilmenite paragenesis and preference by Cr^{+++} for the six-fold co-ordination sites in garnet. The synthesized mineral pairs are similar to the more Cr-rich of the natural assemblages but the Wesselten garnet peridotite WSSl is exceptionally high in Cr-content. The coexisting ilmenite/garnet analyses from a zoned garnet from Mir pipe (Sobolev et al., 1974) are anomalous in that Cr^{+++} shows preference for ilmenite-haematite$_{ss}$ sites rather than garnet sites — this exceptional behavior may be directly linked to the very high Fe_2O_3 content ($>20\%$) of these particular ilmenites. The ilmenites with highest Cr_2O_3-contents occur within compositional zones of the garnet containing 4.7–4.0% Cr_2O_3 together with coexisting inclusions of chromite (V. S. Sobolev et al., 1972; N. V. Sobolev et al., 1974). Further evidence of the relationship between Cr_2O_3 and Fe_2O_3 content in ilmenite is provided by the secondary ilmenite within alteration zones of the Wesselton peridotite (Table 3). Ilmenite containing 10.4% Fe_2O_3 and coexisting with chromite, contains 8.6% Cr_2O_3 and is in addition a much more magnesian (12.2% MgO) ilmenite than the Fe_2O_3 and Cr_2O_3-rich ilmenites from zoned garnet in the Mir pipe.

Conclusions

In garnet+ilmenite parageneses, the TiO_2 content of garnet appears to be proportional to temperature of equilibration. The synthesized garnet/ilmenite pairs presented support this conclusion over the temperature range 950° C to 1100° C and the similarity of TiO_2 contents of natural and synthesized garnets (Tables 2 and 3) argues for similar temperatures of equilibration for most natural ilmenite-bearing peridotite assemblages. The most TiO_2-rich natural garnet (2.38% TiO_2, Ponomarenko et al., 1971) known from ilmenite-bearing peridotite of Yakutia contains high temperature, sub-calcic clinopyroxene (100 Ca/Ca+Mg = 30) and on the data presented here implies equilibration temperatures above 1150°.

The synthesized ilmenites from pyrolite and basanite compositions demonstrate that very low f_{O_2} conditions are normally present under the experimental procedures using the piston cylinder apparatus. In particular, f_{O_2} conditions are very close to these under which natural ilmenites coexisting with diamond were formed. Other natural ilmenites from peridotite xenoliths contain a small range of Fe_2O_3 contents, implying a small range of f_{O_2} conditions in the source region. Ilmenites with considerably higher Fe_2O_3 contents occur as secondary products in peridotite xenoliths and as discrete crystals within kimberlite breccias. The higher f_{O_2} conditions implied by these ilmenites probably reflect rapidly changing conditions during transport and eruption of the kimberlitic magma. We infer that mantle-derived ilmenite may be used as a sensitive indicator of f_{O_2} conditions within the mantle and furthermore that f_{O_2} conditions close to the magnetite-haematite oxygen buffer are too high, and inappropriate for experiments aimed at highly undersaturated magma genesis. In contrast, experimental conditions of equilibrium

with graphite (system C—H—O) or close to the Ni—NiO oxygen buffer are appropriate for upper mantle conditions.

The distribution of iron and magnesium between coexisting garnet and ilmenite $(K_{D(\text{Fe}^{++},\,\text{Mg})}^{\text{ilm-ga}})$ appears to be a relatively insensitive function of temperature of equilibration but may increase with increasing pressure at constant temperature. The partition coefficient $(K_{D(\text{Fe}^{++},\,\text{Mg})}^{\text{ilm-cpx}})$ offers more promise as a temperature—dependent variable of use in estimation of conditions of equilibration of natural ilmenite-bearing assemblages. However, the f_{O_2}-dependent substitution of Fe_2O_3 in ilmenite markedly affects Cr_2O_3 solubility relationships and may affect Fe^{++}/Mg partition relation relationships. Natural ilmenites show sufficient variation in major and minor element composition to warrant further study and initiation of experimental projects specifically designed to investigate ilmenite solid solutions under controlled physical conditions.

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