

Petrogenesis of oxide minerals in kimberlite, Elliott County, Kentucky

JEFFREY J. AGEE, JAMES R. GARRISON, JR. AND LAWRENCE A. TAYLOR

*Department of Geological Sciences
The University of Tennessee
Knoxville, Tennessee 37916*

Abstract

Two kimberlite pipes in Elliott County, Kentucky contain inclusions of altered crustal rocks, ultramafic xenoliths, and a diverse megacryst suite in a groundmass of olivine, Mg-rich orthopyroxene, Mg-rich clinopyroxene, ilmenite, Cr-spinel, pleonaste, titanomagnetite, perovskite, calcite, phlogopite, vermiculite, pectolite, and septechlorite. The megacryst assemblage consists of olivine, garnet, ilmenite, clinopyroxene, orthopyroxene, and phlogopite. Although rare, intergrowths of clinopyroxene + ilmenite and rutile + ilmenite also occur.

Ilmenite megacrysts have reverse-zoned, Mg-rich rims at least 75–100 μm wide. Ilmenite megacryst cores show a correlation of increasing Fe_2O_3 with decreasing MgO and $\text{Mg}/(\text{Mg} + \text{Fe})$, which is interpreted as a fractionation trend. Ilmenites from clinopyroxene-ilmenite intergrowths are similar in composition to the more magnesian of the megacryst core compositions. Clinopyroxenes from the intergrowths have compositions similar to clinopyroxene megacrysts; these clinopyroxenes from the intergrowths have estimated equilibration temperatures of 1295°–1335° C. Groundmass ilmenites are more magnesian than the ilmenite megacryst cores. Groundmass ilmenites can be grouped into two compositionally distinct populations: (1) a high-MgO, low- Cr_2O_3 population (<0.73 wt.% Cr_2O_3) which is compositionally similar to the Mg-rich megacryst rims, and (2) a high-MgO, high- Cr_2O_3 population (1.43–3.76 wt.% Cr_2O_3) which is compositionally similar to small ilmenite inclusions in groundmass olivines. The former group of groundmass ilmenites is interpreted to be MgO-enriched fragments of disaggregated, recrystallized megacrysts; the latter group is interpreted to be primary ilmenites that crystallized in equilibrium with the groundmass assemblage from an MgO-enriched kimberlitic liquid. Estimated equilibration temperatures for the groundmass assemblage are from 965° to 1085° C; at these temperatures, the position of the kimberlite solidus restricts the depth at which this crystallization event occurred to be less than 100 km.

Both megacryst and groundmass ilmenites have well-developed reaction rims of perovskite + titanomagnetite + Mn-ilmenite. The Mn-ilmenite (17.9 mol% MnTiO_3) is quite distinct from either megacryst or groundmass ilmenites and is clearly of secondary origin. Discrete perovskites and titanomagnetites within the groundmass are similar in composition to the phases within the reaction assemblage. Cr-spinel (63.6–68.1 mol% $(\text{Fe}, \text{Mg})\text{Cr}_2\text{O}_4$) also occurs in the groundmass; these Cr-spinels commonly contain overgrowths of pleonaste.

Ilmenite megacrysts and clinopyroxene-ilmenite intergrowths are interpreted to have formed, along with the other members of the silicate megacryst assemblage, from a fractionating, mantle-derived liquid at about 150 km depth within the temperature interval of 1165°–1390° C (Stage I of kimberlite development). Subsequently, the minerals experienced a sudden increase of the MgO/FeO ratio in the kimberlitic liquid (Stage II of kimberlite evolution). This may have been due to upward movement of the megacrysts and xenocrysts into a different melt regime, possibly associated with assimilation of mantle wall-rock such as a carbonated peridotite. From this MgO-enriched liquid, a compositionally distinct suite of Mg-rich groundmass minerals precipitated and earlier formed olivine and ilmenite megacrysts reacted with this liquid and formed high-MgO rims (Stage III). The final recorded stage of kimberlite evolution (Stage IV) at Elliott County is the “autometasomatic” reaction of ilmenite with a CaO-enriched fluid to form the reaction assemblage perovskite + titanomagnetite + Mn-ilmenite.

Introduction

Important constituents of kimberlite are oxide minerals. Since compositions of oxide phases are very susceptible to changes in temperature, bulk composition, and f_{O_2} , they provide a record of a large portion of the crystallization history and the evolution of kimberlite.

Ilmenite is the most abundant oxide phase found in kimberlite; it is present both as a megacryst (*i.e.*, a >1 cm subrounded grain) and as a groundmass mineral. A diagnostic feature of kimberlitic ilmenites is their distinctive, high-MgO composition (Mitchell, 1973; 1977). In addition to their distinctive chemical systematics, they exhibit diverse textural relationships. Megacrysts occur as large single crystals or may be totally recrystallized to mosaic polycrystalline aggregates. Ilmenite also commonly occurs in lamellar or graphic intergrowths with clinopyroxene and/or orthopyroxene (*e.g.*, Gurney *et al.*, 1973; Dawson and Reid, 1970; Frick, 1973; Garrison and Taylor, 1981). Ilmenite can also occur as small spherical inclusions in silicate phases such as olivine or garnet (*e.g.*, Boyd and Nixon, 1973).

Spinel is restricted to the kimberlite groundmass, although they may occur as exsolution lamellae in ilmenite (Danchin and D'Orey, 1972) or in late-stage reaction zones around ilmenite. Groundmass spinels show a wide variety of chemical compositions, ranging from Cr-spinel to pleonaste to titanomagnetite (Haggerty, 1976).

Perovskite is most commonly found in reaction zones associated with titanomagnetite, around both megacryst and groundmass ilmenites. Perovskite may also occur as discrete grains in the kimberlite groundmass (Boctor and Meyer, 1979; Boctor and Boyd, 1980).

The two kimberlite pipes examined in this study are located in Elliott County in eastern Kentucky along the eastern edge of the Appalachian Plateau. These kimberlites contain a variety of mantle-derived megacrysts and xenoliths, as well as fragments of highly metasomatized lower crustal and supracrustal materials. Bolivar (1972) documented the kimberlitic nature of these bodies and described their mineralogy. Zartman *et al.* (1972) reported a Rb–Sr age of 257 ± 22 m.y. for these bodies, indicating an early Permian emplacement age.

The Elliott County kimberlites are unique in several aspects. The kimberlite is extremely fresh, providing an excellent opportunity to examine both the megacrysts and the fine-grained groundmass

material. One pipe (Pipe 1), located 0.5 km south of Ison Creek, has abundant megacrysts and xenoliths, both mantle and crustal, while the other (Pipe 2), located along Ison Creek, is almost devoid of xenolithic material. Mantle xenoliths are quite small, rarely exceeding 1 cm in diameter and form volumetrically the smallest fraction of included material (Garrison and Taylor, 1980). In Pipe 1, the abundance of highly metasomatized fragments of supracrustal limestones, siltstones, and shales (up to 20 cm in diameter) approaches 20% of the rock. This metasomatism of the sedimentary and crystalline crustal materials suggests that the kimberlite must have been hot at the time of xenolith incorporation during the final emplacement (Garrison and Taylor, 1980; Garrison *et al.*, 1980).

This report summarizes petrographic and electron microprobe data for a wide variety of oxide minerals in the kimberlite pipes. Detailed chemical and textural studies of these kimberlites have allowed us to reconstruct a large portion of their crystallization history, from the early megacryst stage through the groundmass crystallization stage and the autometamorphic event associated with final emplacement.

Petrography

Megacrysts of olivine, ilmenite, garnet, clinopyroxene, phlogopite, and orthopyroxene occur within the fine-grained kimberlitic groundmass. These megacrysts average 0.5–1.0 cm in diameter, although discrete crystals of garnet, clinopyroxene, ilmenite, and phlogopite up to 1.5 cm in diameter are not uncommon. Pipe 1 contains megacrysts in the following relative abundance: olivine > ilmenite > garnet > phlogopite > clinopyroxene > orthopyroxene (Garrison and Taylor, 1980). Pipe 2 has the relative abundance: olivine > ilmenite > phlogopite > garnet > orthopyroxene > clinopyroxene. Olivine and phlogopite have corroded, fritted rims reflecting reaction with the kimberlitic magma. Garnet is always surrounded by a "kelyphitic" rim of dark microcrystalline material, probably spinel + phyllosilicates. Olivine megacrysts commonly exhibit fracturing and kink banding; many have been totally recrystallized to mosaic polycrystalline aggregates (dunites; Garrison and Taylor, 1980). Three graphic clinopyroxene–ilmenite intergrowths (Garrison and Taylor, 1981) and one rutile–ilmenite intergrowths were recovered from the Elliott County kimberlites.

The groundmass of the kimberlite consists of

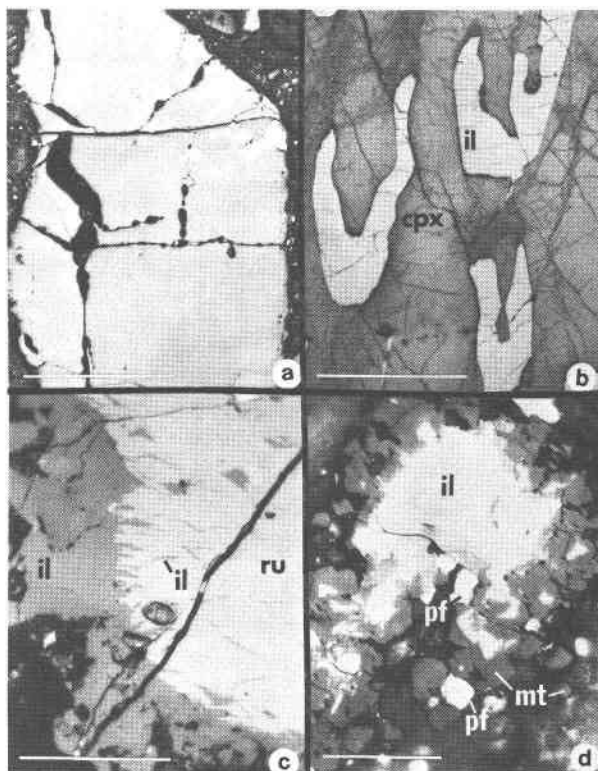


Fig. 1. Reflected light photomicrographs of ilmenite textural types. (a) *Type I* megacryst ilmenite; scale bar = 1 mm. (b) *Type II* ilmenite in clinopyroxene-ilmenite intergrowth; il = ilmenite; cpx = clinopyroxene; scale bar = 2 mm. (c) *Type III* ilmenite in rutile-ilmenite intergrowth; il = ilmenite; ru = rutile; scale bar = 100 μm . (d) *Type IV* groundmass ilmenite; il = ilmenite; mt = titanomagnetite; pf = perovskite; scale bar = 75 μm .

euhedral phenocrysts of olivine and subhedral grains of olivine, ilmenite, Cr-spinel, pleonaste, Mg-rich orthopyroxene, Mg-rich clinopyroxene, perovskite, titanomagnetite, phlogopite, vermiculite, pectolite, calcite, and septeclorite. Locally, calcite occurs in veins and fractures. Possible dewatering of sedimentary inclusions has produced extensive serpentinization of the surrounding groundmass olivines (to Al-poor lizardite).

Ultramafic xenoliths included in the kimberlite are small and usually represent incomplete peridotite assemblages (Garrison and Taylor, 1980). Pipe 1 contains the greatest abundance of ultramafic xenoliths; these include garnet peridotite, spinel peridotite, spinel-ilmenite websterite, and dunite. Only two xenoliths were recovered from Pipe 2: a dunite and a serpentinized garnet peridotite.

Ilmenite

Ilmenite is the most abundant oxide phase in the Elliott County kimberlites. Six *textural types* have

been identified: (I) subrounded megacrysts (0.5–1.5 cm in diameter) which exhibit various degrees of recrystallization (Fig. 1a); (II) graphic intergrowths of ilmenite in clinopyroxene (Fig. 1b); (III) thin lamellae of ilmenite in rutile “phenocrysts” (Fig. 1c); (IV) anhedral, single, groundmass crystals (0.05–1.0 mm) (Fig. 1d); (V) round inclusions (up to 25 μm) within euhedral to subhedral groundmass olivines (Fig. 2a); (VI) small ilmenite grains associated with titanomagnetite and perovskite in reaction rims around megacryst and groundmass ilmenites (Fig. 2b).

Ilmenite megacrysts have rounded anhedral to subhedral shapes which are attributed to abrasion during emplacement of the kimberlite (Mitchell, 1973). Textures indicate a continuous variation from single crystals with slightly undulose extinction to totally recrystallized polycrystalline mosaics with sharp extinction. The following textural features provide evidence that the mosaic aggregates of ilmenite within the Elliott County kimberlites are in fact recrystallized megacrysts: (1) twin lamellae are occasionally present near the edges of megacrysts (Fig. 3a), (2) bands of fine mosaic ilmenite cut large grains (Fig. 3b), (3) long bands or tapering wedges within grains have slightly different extinction angle from the host (Fig. 3c), and (4) foliation in some megacrysts was formed by alignment of elongate sutured grains (Fig. 3d).

Three nodular clinopyroxene-ilmenite intergrowths were collected from the Elliott County kimberlite Pipe 1 (Garrison and Taylor, 1981). These nodular intergrowths from Elliott County are texturally similar to other such intergrowths from

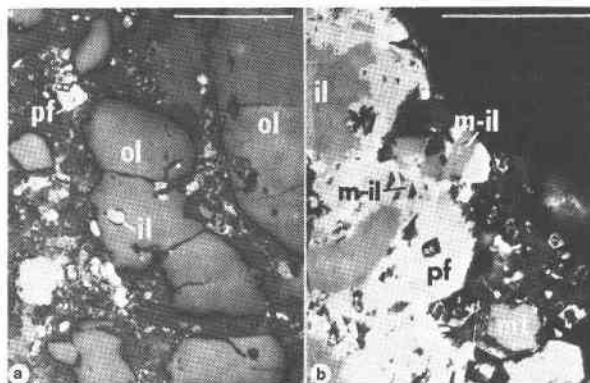


Fig. 2. Reflected light photomicrographs of ilmenite textural types. (a) *Type V* ilmenite inclusion in olivine; il = ilmenite; ol = olivine; pf = perovskite; scale bar = 250 μm . (b) *Type VI* secondary Mn-ilmenite; il = ilmenite; pf = perovskite; m-il = Mn-ilmenite; scale bar = 100 μm .

kimberlites in South Africa (e.g., Gurney *et al.*, 1973) and the United States (e.g., Eggler *et al.*, 1979). The intergrowths from Pipe 1 range in size from 0.5 cm to 2.0 cm in diameter and consist of large single crystals of pale-green clinopyroxene with graphic intergrowths of ilmenite (Fig. 1b). These graphic ilmenites (100–400 μm thick) form one optically continuous crystal (up to 30 modal % of nodule), although occasionally they exhibit minor recrystallization to polygonal mosaics or show undulose extinction. The host clinopyroxene commonly shows undulose extinction but rarely recrystallization. The grain boundaries between the graphic ilmenite and host clinopyroxene are generally free of alteration, although in some cases, traces of phlogopite can be observed. The ilmenites frequently extend out into the host kimberlite beyond the clinopyroxene; this is probably due to fragmentation and abrasion during transport through the kimberlite conduit.

The rutile-ilmenite intergrowth recovered from Elliott County Pipe 2 consists of small 5 μm \times 10 μm sigmoidal lenses of ilmenite in a rutile host. The rutile is mantled by a rim of polycrystalline ilmenite (Fig. 1c). This texture is very similar to that described from South African kimberlites by Haggerty (1975, 1976) and Mitchell (1973). Haggerty (1975) described two types of rutile-ilmenite intergrowths: (1) those in which rutile and ilmenite are equally abundant, and (2) those in which ilmenite forms only a few percent of the intergrowth. The Elliott County intergrowth belongs to the latter type.

Anhedral single crystals of ilmenite, ranging from 0.05 to 1.0 mm in diameter, occur throughout the groundmass of the kimberlite and in this study are *texturally* referred to as *groundmass ilmenites* (Fig. 1d). These groundmass ilmenites are never polycrystalline and show uniform extinction. They could have two possible origins (Pasteris, 1980): (1) disaggregated recrystallized megacrysts, and/or (2) a compositionally distinct second generation of ilmenite that crystallized with the other groundmass phases.

Spinel

Four different types of spinel can be distinguished in the Elliott County kimberlites: (I) pale-blue chromite, (II) gray-blue pleonaste, (III) brown titanomagnetite, and (IV) brown spinel rodlets in ilmenite. Types I, II, and III occur in the groundmass of the kimberlites. *Type I* chromites (up to 50 μm in diameter) are commonly rimmed by *Type II* pleo-

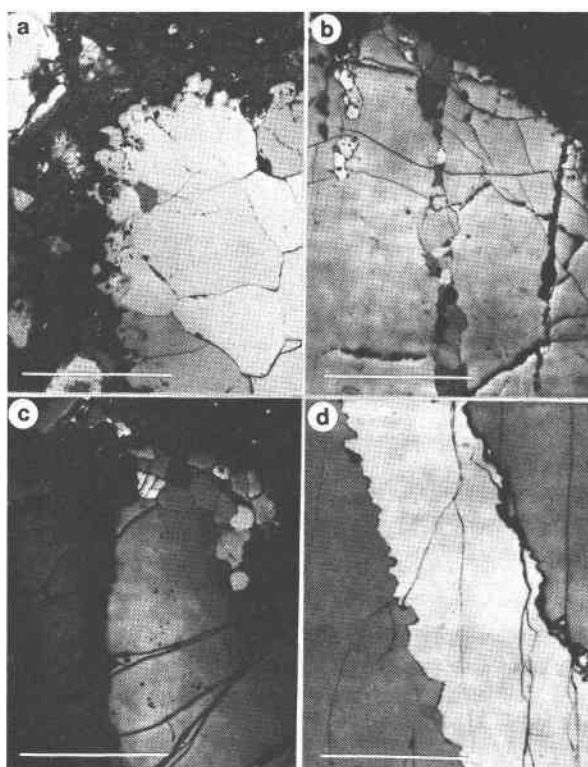


Fig. 3. Deformation and recrystallization textures in ilmenite megacrysts. (a) Twin lamellae near the edge of a megacryst; scale bar = 1 mm. (b) Bands of mosaic polycrystalline ilmenite crossing ilmenite megacryst; scale bar = 1 mm. (c) Undulose extinction in large single crystal ilmenite megacryst; scale bar = 1 mm. (d) Foliation in ilmenite megacryst outlined by elongate sutured grain boundaries; scale bar = 1 mm. All are reflected light photomicrographs.

naste (Fig. 4a). *Type II* pleonastes also occur as discrete single grains (up to 30 μm in diameter) in the groundmass. *Type III* titanomagnetites occur as discrete grains (up to 75 μm in diameter) in the groundmass and associated with perovskite in reaction rims around ilmenite (Figs. 1d and 4a). *Type IV* spinel occurs as small (<1 μm thick) rodlets in ilmenite (Fig. 4c). This texture is similar to that described from the Premier Mine, South Africa by Danchin and D'Orey (1972). These spinel rodlets are found in three of the six textural types of ilmenite in the Elliott County kimberlites; they occur in megacrysts, groundmass ilmenites, and in the ilmenite inclusions in olivines.

Perovskite

Perovskite occurs as discrete, equant, anhedral blebs (up to 30 μm across) scattered throughout the groundmass and in reaction rims around groundmass and megacryst ilmenites (Fig. 4a, b). It is most

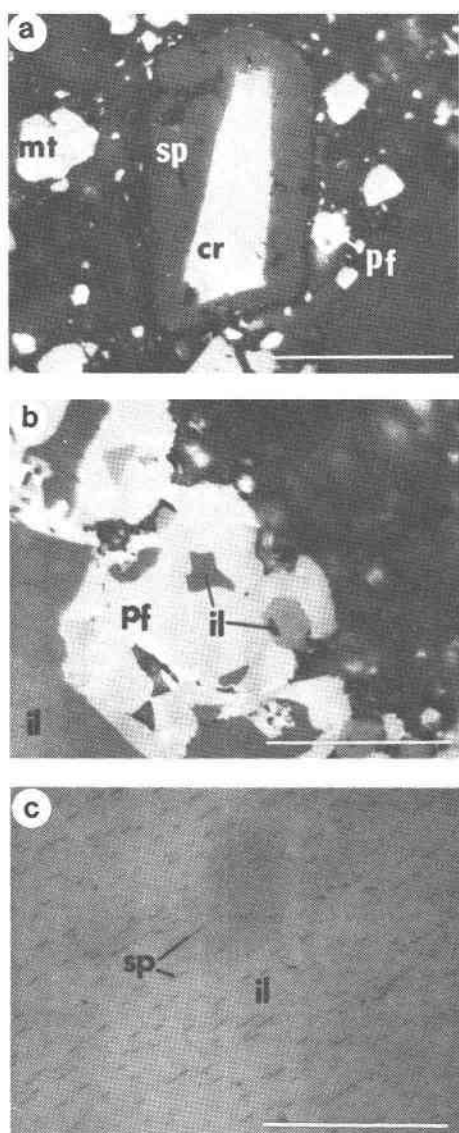


Fig. 4. Reflected light photomicrographs of spinel types and perovskite. (a) Composite spinel grain consisting of *Type I* chromite rimmed by *Type II* pleonaste; mt = titanomagnetite; sp = pleonaste; cr = chromite; scale bar = 100 μm . (b) Reaction selvage on ilmenite megacryst. Note islands of ilmenite within the zone of perovskite and titanomagnetite; il = ilmenite; pf = perovskite; scale bar = 100 μm . (c) *Type IV* spinel rodlets in ilmenite; sp = spinel; il = ilmenite; scale bar = 40 μm .

common in the reaction rims around ilmenite. This reaction rim of perovskite is developed as a 50–75 μm wide zone with a fritted, digitate boundary that projects into the ilmenite. The outer boundary of the perovskite zone (*i.e.*, nearest the host kimberlite) is in contact with a discontinuous zone of subhedral (up to 50 μm wide) *Type III* titanomagnetite (Fig. 1d). Within these zones, optically continu-

ous fragments of the host ilmenite occur; these islands of ilmenite indicate that extensive reaction must have occurred. Between the spinel and perovskite zones are rare occurrences of secondary *Type VI* ilmenite (Fig. 2b).

Mineral chemistry

Minerals were analyzed with a MAC 400 S electron microprobe utilizing the correction procedures of Bence and Albee (1968) and the data of Albee and Ray (1970). Except for the rims of ilmenite megacrysts, all minerals were found to be extremely homogeneous. When grain size permitted, four to ten analyses were made on each grain and an average analysis and 1 σ standard deviation computed. Representative average analyses of all minerals are included in Tables 1 through 3.

Ilmenite

Representative average analyses of ilmenite megacrysts from the Elliott County kimberlites are presented in Table 1. The compositional range of ilmenite megacrysts is shown in an expanded portion of the $\text{MgTiO}_3\text{--FeTiO}_3\text{--Fe}_2\text{O}_3$ ternary in Figure 5. The compositions of the megacryst cores (31.6–46.3 mol% MgTiO_3 and 6.3–14.9 mol% Fe_2O_3) are similar to ilmenites reported from kimberlite pipes in West Africa and Lesotho (Fig. 6; Haggerty, 1975). The ilmenite megacrysts show a correlation of increasing Fe_2O_3 (7.14–16.4 wt.%) with decreasing $\text{Mg}/(\text{Mg}+\text{Fe})$ (50.6–36.7) (Fig. 7) and decreasing MgO (13.2–8.63 wt.%). This correlation of decreasing MgO and $\text{Mg}/(\text{Mg}+\text{Fe})$ with increasing Fe_2O_3 suggests that the ilmenite megacrysts are related by crystal fractionation. As crystallizing silicates and ilmenites deplete the melt in MgO and decrease $\text{Mg}/(\text{Mg}+\text{Fe})$, the preferential incorporation of Fe^{+2} into the silicate phases increases the $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio in the remaining melt. Since ilmenite is the only major crystallizing phase that can incorporate substantial Fe^{+3} , the ilmenites may be expected to show an increase in Fe_2O_3 with differentiation (*i.e.*, decreasing $\text{Mg}/(\text{Mg}+\text{Fe})$).

The rims of ilmenite megacrysts have higher MgTiO_3 content (44.3–53.1 mol% MgTiO_3) than the megacryst cores (Table 1; Fig. 5); however, the rims have a similar hematite content (4.4–13.3 mol% Fe_2O_3). The megacryst rims exhibit a strong correlation of increasing Fe_2O_3 (5.15–15.0 wt.%) with decreasing MgO (15.6–12.6 wt.%); there appears to be no correlation between $\text{Mg}/(\text{Mg}+\text{Fe})$

Table 1. Representative average analyses of ilmenite megacrysts

	Pipe 1				Pipe 2				Cpx-ilmenite intergrowth
	megacryst core	megacryst rim	megacryst core	megacryst rim	megacryst core	megacryst rim	megacryst core	megacryst rim	
TiO ₂	52.3 (4)*	53.4 (2)	48.2 (2)	48.9 (5)	53.0 (4)	53.7 (2)	52.0 (2)	53.5 (5)	54.2 (3)
Al ₂ O ₃	0.63(4)	0.62(2)	0.39(2)	0.52(4)	0.65(3)	0.66(3)	0.61(1)	0.53(1)	0.57(4)
Cr ₂ O ₃	0.07(1)	0.07(4)	0.27(2)	0.30(1)	0.09(2)	0.09(1)	n.d.**	0.35(3)	0.33(2)
Fe ₂ O ₃ ***	9.44	8.95	16.4	15.0	8.86	9.29	9.22	7.58	6.71
FeO	24.6 (6)	23.5 (8)	25.7 (6)	21.5 (9)	25.2 (4)	21.5 (7)	25.9 (8)	21.8 (6)	25.7 (2)
MnO	0.28(3)	0.43(5)	0.31(3)	0.41(1)	0.29(3)	0.39(3)	0.26(2)	0.44(2)	0.24(3)
MgO	12.5 (1)	13.5 (2)	9.33(2)	12.6 (6)	12.6 (1)	15.0 (3)	11.7 (4)	14.6 (1)	13.0 (1)
NiO	n.d.	0.04(3)	n.d.	0.10(1)	n.d.	0.04(2)	n.d.	0.07(6)	0.09(4)
Σ	99.82	100.51	100.60	99.33	100.69	100.67	99.69	98.87	100.84
Cation Basis	3	3	3	3	3	3	3	3	3
Al	0.017	0.017	0.011	0.014	0.018	0.018	0.017	0.014	0.015
Cr	0.001	0.001	0.005	0.006	0.002	0.002	---	0.006	0.005
Ti	0.908	0.913	0.853	0.856	0.910	0.913	0.909	0.923	0.927
Fe ⁺³	0.164	0.153	0.291	0.261	0.152	0.155	0.161	0.131	0.115
Mg	0.430	0.459	0.327	0.437	0.431	0.501	0.404	0.418	0.442
Ni	---	0.001	---	0.001	---	0.001	---	0.001	0.001
Fe ⁺²	0.475	0.448	0.506	0.417	0.480	0.404	0.504	0.418	0.490
Mn	0.005	0.008	0.006	0.008	0.006	0.007	0.005	0.009	0.005
Σ	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

* units in () represent 1σ standard deviation of replicate analyses in terms of least units cited.

** n.d. = not detected; less than 0.03 %.

*** Fe determined as FeO; oxides based on crystal chemistry.

Table 2. Representative analyses of Type III, IV, V, and VI ilmenites

	Pipe 1		Pipe 2		Inclusion in olivine	lamellae in rutile	rim of rutile	Type VI
	groundmass	groundmass	groundmass	groundmass				
TiO ₂	55.8	53.3	55.4	51.2	52.3	58.7	57.9	48.3
Al ₂ O ₃	0.29	0.66	0.32	0.96	0.89	n.d.**	0.34	0.41
Cr ₂ O ₃	1.69	0.13	2.71	0.34	4.42	0.06	0.21	0.96
Fe ₂ O ₃ *	5.72	8.72	5.15	12.5	7.86	---	1.86	11.3
FeO	19.8	23.6	20.6	21.5	18.4	28.1	24.4	27.0
MnO	0.54	0.34	0.51	0.45	0.26	0.39	0.60	8.69
MgO	16.8	13.6	16.3	13.6	16.0	13.0	15.4	4.47
NiO	0.07	n.d.	0.14	0.12	0.16	n.d.	n.d.	n.d.
Σ	100.71	100.35	101.13	100.67	100.29	100.25	100.71	101.13
Cation Basis	3	3	3	3	3	3	3	3
Al	0.008	0.018	0.008	0.026	0.024	---	0.009	0.012
Cr	0.030	0.002	0.048	0.006	0.078	0.001	0.004	0.018
Ti	0.932	0.913	0.927	0.874	0.880	1.005	0.975	0.879
Fe ⁺³	0.096	0.150	0.086	0.214	0.133	---	0.031	0.207
Mg	0.556	0.461	0.538	0.462	0.533	0.537	0.513	0.161
Ni	0.001	---	0.002	0.002	0.002	---	---	---
Fe ⁺²	0.367	0.449	0.382	0.408	0.345	0.440	0.456	0.546
Mn	0.010	0.007	0.010	0.009	0.005	0.007	0.011	0.177
Σ	2.000	2.000	2.000	2.000	2.000	1.990	2.000	2.000

* Fe determined as FeO; oxides based on crystal chemistry.

** n.d. = not detected; less than 0.03 %.

Table 3. Representative analyses of spinels, rutile, and perovskite

	Type I spinel		Type II spinel		Type III spinel		perovskite	rutile
SiO ₂	n.a.*	n.a.	n.a.	n.a.	n.a.	n.a.	0.09	n.a.
TiO ₂	1.52	3.85	2.05	3.27	21.5	21.0	57.6	97.6
Al ₂ O ₃	8.02	8.70	50.5	46.1	8.48	10.0	0.33	0.11
Cr ₂ O ₃	51.3	49.8	5.78	6.07	2.07	0.46	0.16	n.d.***
Fe ₂ O ₃ **	9.55	8.24	9.78	12.1	27.8	25.5	---	n.d.
FeO	17.0	18.2	11.0	10.1	17.4	22.7	1.40	0.05
MnO	0.52	0.53	0.21	0.11	0.87	0.89	0.13	n.d.
MgO	11.0	12.2	19.8	20.4	22.6	18.4	0.23	n.d.
NiO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	38.6	n.a.
Σ	98.91	101.52	99.12	98.15	100.72	98.95	98.54	97.76
Cation Basis	4	4	4	4	4	4	3	2
Si	---	---	---	---	---	---	0.001	---
Al	0.317	0.333	1.596	1.488	0.306	0.376	0.008	0.001
Cr	1.363	1.273	0.123	0.131	0.050	0.012	0.002	---
Ti	0.038	0.095	0.041	0.066	0.502	0.498	0.994	0.999
Fe ⁺³	0.241	0.200	0.197	0.249	0.642	0.610	---	---
Mg	0.549	0.590	0.793	0.832	1.034	0.874	0.007	---
Ni	---	---	---	---	---	---	---	---
Fe ⁺²	0.478	0.493	0.245	0.231	0.443	0.605	0.026	---
Mn	0.015	0.015	0.005	0.003	0.023	0.024	0.002	---
Ca	---	---	---	---	---	---	0.951	---
Σ	3.000	3.000	3.000	3.000	3.000	3.000	1.991	1.000

* n.a. = not analyzed. ** Fe determined as FeO; oxides based on crystal chemistry. *** n.d. = not detected.

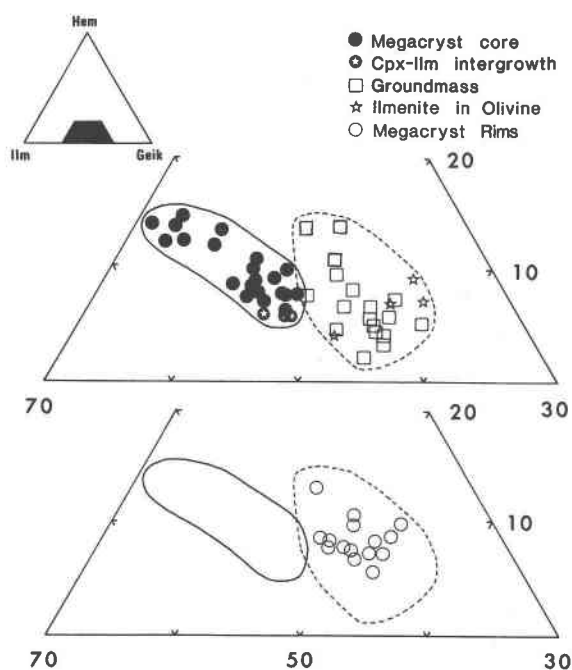


Fig. 5. Compositions of the ilmenite textural types plotted in an expanded portion of the FeTiO₃-MgTiO₃-Fe₂O₃ ternary. All data plotted as mol%.

and Fe₂O₃ such as that observed for the megacryst cores (Fig. 7).

There occurs a regular, well-developed compositional gradient between the megacryst core and the high-MgO rim (Fig. 8). This profile is developed over a distance of at least 75–100 μm, although the true extent cannot be determined due to the extensive reaction rim of perovskite + titanomagnetite + Mn ilmenite. In many cases, the profiles can be

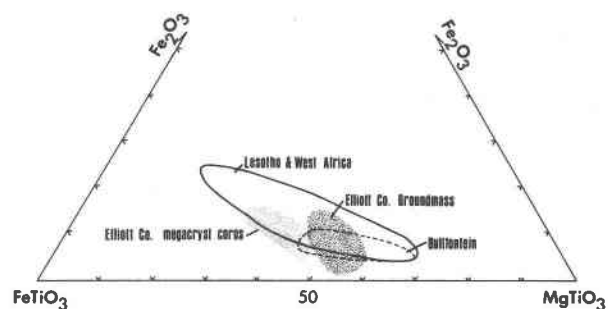


Fig. 6. Ternary FeTiO₃-MgTiO₃-Fe₂O₃ plot showing the compositions of the Elliott County megacryst and groundmass ilmenites relative to ilmenites from Africa (Haggerty, 1975; Mitchell, 1977).

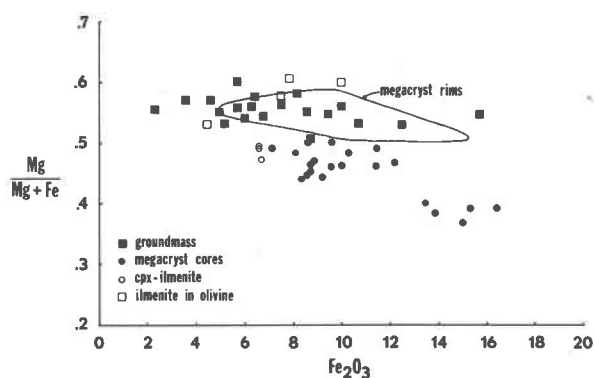


Fig. 7. A plot of $\text{Mg}/(\text{Mg}+\text{Fe})$ vs. wt.% Fe_2O_3 for the Elliott County ilmenites.

extended into the reaction zone by analyzing the remnant islands of ilmenite within the reaction zones (Fig. 4b). Haggerty *et al.* (1979) noted similar compositional gradients in megacrysts from the Monastery Mine, South Africa; they referred to it as the magmatic reaction trend. Elthon and Ridley (1979) also found an increase in MgO near the rims of ilmenites from the Premier Mine, South Africa. Bector and Boyd (1980) reported similar compositional gradients developed within the outer 300–400 μm of discrete ilmenite megacrysts from the Lihobong kimberlite, Lesotho. Since the perovskite + titanomagnetite + Mn-ilmenite reaction zone is rarely over 100 μm wide, it appears that the compositional gradients near the rims of the Elliott County ilmenite megacrysts probably cannot be extended over 200 μm inward, a distance somewhat less than observed for the Lihobong ilmenite megacrysts. These compositional gradients to the high-MgO rims probably developed as the result of reaction of the ilmenite megacrysts with a MgO-enriched melt; therefore, they represent a diffusion profile between the megacryst core and an overgrowth with a higher MgO content.

Ilmenites from the clinopyroxene-ilmenite intergrowths (44.7–44.6 mol% MgTiO_3 and 5.4–5.8 mol% Fe_2O_3) have compositions similar to the more MgO-rich megacryst cores (Table 1; Figs. 5 and 7). Although lower in Cr_2O_3 (0.06–0.38 wt.%), the clinopyroxenes from the intergrowths have compositions similar to the clinopyroxene megacrysts from Elliott County (0.56–0.88 wt.%); the clinopyroxenes from the intergrowths have estimated equilibration temperatures of 1295°–1335° C which overlap the range of temperatures estimated for the Pipe 1 clinopyroxene megacrysts (1305°–1390° C), using the diopside-enstatite solvus of Lindsley and

Dixon (1976) with $\text{mol\% Di} = 2\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe})$ (Garrison and Taylor, 1980; 1981). Using the clinopyroxene-ilmenite geothermometer of Bishop (1980), with $X_{\text{Fe}}^{\text{il}} = \text{Fe}^{+2}/(\text{Fe}^{+2}+\text{Mg}^{+2}+0.5\text{Fe}^{+3})$ and $X_{\text{Di}}^{\text{cpx}} = [2\text{Ca}/(\text{Ca}+\text{Mg}+\text{Fe})][\text{Mg}/(\text{Mg}+\text{Fe})]$, Garrison and Taylor (1981) estimated the equilibration temperatures (at $P = 50$ kbar) of the clinopyroxene-ilmenite pairs at 1210°–1245° C; these equilibration temperatures are generally consistent with the diopside-enstatite solvus temperature estimates considering the uncertainties associated with applying these geothermometers. The compositional similarities between the clinopyroxenes and ilmenites from the intergrowths and the discrete ilmenite and clinopyroxene megacrysts from Elliott County suggest that the clinopyroxene-ilmenite intergrowths and the clinopyroxene and ilmenite megacrysts are genetically related (Garrison and Taylor, 1981).

The Elliott County *Type IV* groundmass ilmenites are distinctly richer in MgTiO_3 (46.8–57.3 mol% MgTiO_3) than the ilmenite megacryst cores, although quite similar in MgTiO_3 content to the MgO-enriched rims of the ilmenite megacrysts (Fig. 5; Table 2). The groundmass ilmenites show a wide range of Fe_2O_3 (1.9–13.9 mol% Fe_2O_3). Analogous to the MgO-enriched megacryst rims, the groundmass ilmenites exhibit a correlation of increasing Fe_2O_3 (2.29–15.7 wt.%) with decreasing MgO (15.7–13.5 wt.%), but no correlation between Fe_2O_3 and $\text{Mg}/(\text{Mg}+\text{Fe})$. The groundmass ilmenites exhibit a wider range of Cr_2O_3 (0.12–3.76 wt.%) than either the megacryst cores (<0.03–1.30 wt.% Cr_2O_3) or the megacryst rims (0.04–2.22 wt.% Cr_2O_3). The similarity in chemical systematics between the MgO-enriched rims of the megacrysts and the *Type IV* groundmass ilmenites suggests that both may have equilibrated with the same MgO-enriched

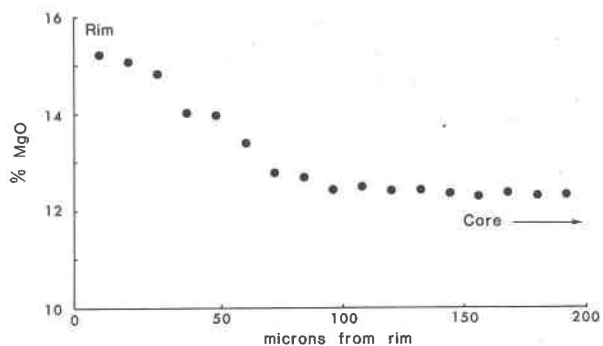


Fig. 8. Electron microprobe traverse from rim to core of a *Type I* ilmenite megacryst showing the smooth MgO compositional gradient.

melt. The core-rim-groundmass pattern of the Elliott County ilmenites is analogous to the chemical systematics displayed by the Elliott County olivine megacrysts and groundmass olivines; the rims of olivine megacrysts have $\text{Mg}/(\text{Mg}+\text{Fe})$ ratios of 0.89–0.90, regardless of the core compositions which range in $\text{Mg}/(\text{Mg}+\text{Fe})$ from 0.85 to 0.93. The rims of these olivine megacrysts are similar to the low-NiO groundmass olivines in $\text{Mg}/(\text{Mg}+\text{Fe})$, CaO, and NiO, reflecting a later-stage reaction of the olivine megacrysts with a liquid more enriched in MgO than the liquid in equilibrium with the most fractionated megacrysts (*i.e.*, with the lowest $\text{Mg}/(\text{Mg}+\text{Fe})$).

The ilmenites occurring as inclusions in groundmass olivines (50.9–56.4 mol% MgTiO_3 and 3.9–9.1 mol% Fe_2O_3) have compositions that overlap the more MgO-rich groundmass ilmenites, although they are slightly higher in Cr_2O_3 (4.00–4.42 wt.%) (Figs. 5 and 7; Table 2). This similarity suggests that these inclusions are genetically related to at least some of the *Type IV* groundmass ilmenites. Furthermore, this also suggests that at least some of the groundmass ilmenites belong to a compositionally distinct population of ilmenites formed during a later stage of ilmenite crystallization and are, in fact, not MgO-enriched fragments of disaggregated recrystallized megacrysts. These high- Cr_2O_3 ilmenites actually approach the composition of the small idiomorphic groundmass ilmenites reported from the Lihobong kimberlite by Boctor and Boyd (1980), although somewhat more variable in Fe_2O_3 . The Fe–Mg equilibria between groundmass olivine ($\text{Fo}_{89.6}$) and ilmenite inclusions, using the geothermometer of Andersen and Lindsley (1979), suggest equilibration of these groundmass phases at 965° C (at $P = 50$ kbar). A 5 kbar change in the assumed pressure will change the estimated temperature by only 9.5° C.

The ilmenite from the ilmenite-rutile intergrowth (55.0 mol% MgTiO_3) contains no Fe_2O_3 (Table 2). The ilmenite that rims the rutile-ilmenite intergrowth is similar in composition (52.0 mol% MgTiO_3 and 1.5 mol% Fe_2O_3) to the low- Fe_2O_3 groundmass ilmenites. The absence of Fe_2O_3 in the ilmenite lamellae in the rutile suggests that they are not related to the rim ilmenite. The rim ilmenite is probably related to the *Type IV* groundmass ilmenites and the MgO-enriched rims of the ilmenite megacrysts, reflecting reaction of the rutile phenocryst with the MgO-enriched liquid. The ilmenite lamellae within the rutile were probably formed by

exsolution from the rutile. Energy Dispersive Analysis (EDA) of the rutile indicates the presence of substantial Nb; this is also reflected in the low sum of the rutile analysis in Table 3.

The high-MnO *Type VI* ilmenites found within the perovskite + titanomagnetite + Mn-ilmenite reaction rims around the ilmenite megacrysts and *Type IV* groundmass ilmenites contain 17.9 mol% MnTiO_3 , 16.3 mol% MgTiO_3 , and 10.5 mol% Fe_2O_3 . They are quite distinct from either megacryst or groundmass ilmenite (Table 2). Their distinctive composition and textural relationship to perovskites and titanomagnetites indicate that these MnO-rich *Type VI* ilmenites are clearly of secondary origin. High-MnO ilmenites have been described in kimberlite by Haggerty *et al.* (1979), Hsu and Taylor (1978), Boctor and Meyer (1979), and Wyatt (1979). In each case, they are associated with late-stage reaction rims or occur in cracks within ilmenite megacrysts.

Spinel

Representative analyses of spinels from the Elliott County kimberlites are presented in Table 3. The *Type I* chromites contain 63.6–68.1 mol% $(\text{Fe,Mg})\text{Cr}_2\text{O}_4$, 10.0–12.1 mol% $(\text{Fe,Mg})\text{Fe}_2\text{O}_4$, 3.8–11.0 mol% $(\text{Fe,Mg})_2\text{TiO}_4$, and 15.9–16.7 mol% $(\text{Fe,Mg})\text{Al}_2\text{O}_4$. The *Type II* pleonastes that occur as overgrowths on *Type I* chromites and as discrete groundmass grains contain 74.3–79.8 mol% $(\text{Fe,Mg})\text{Al}_2\text{O}_4$, 6.2–6.6 mol% $(\text{Fe,Mg})\text{Cr}_2\text{O}_4$, 8.9–12.5 mol% $(\text{Fe,Mg})\text{Fe}_2\text{O}_4$, and 4.1–6.6 mol% $(\text{Fe,Mg})\text{TiO}_4$. *Type III* titanomagnetites that occur within the perovskite + titanomagnetite + Mn-ilmenite reaction zones and as discrete grains in the groundmass are distinctly higher in TiO_2 than the other spinels (38.0–53.0 mol% $(\text{Fe,Mg})_2\text{TiO}_4$, 17.5–26.3 mol% $(\text{Fe,Mg})\text{Al}_2\text{O}_4$, and 3.0–6.1 mol% $(\text{Fe,Mg})\text{Cr}_2\text{O}_4$). The compositional ranges for spinels from the Elliott County kimberlites are plotted in the spinel prism of Figure 9 (Irvine, 1965). The typical kimberlite trend (Haggerty, 1976) of early Cr- and Al-rich spinels followed by late-stage crystallization of spinels enriched in Fe^{+3} and Ti is readily seen at Elliott County. This compositional change from groundmass *Type I* Cr-spinel and *Type II* pleonaste crystallization to the precipitation of *Type III* titanomagnetite reflects the breakdown of ilmenite in the presence of a CaO-enriched fluid. From the Elliott County data, it is not clear whether the change from Cr-spinel to pleonaste crystallization is continuous or discontinuous.

Perovskite

The composition of perovskite shows little variation whether in the reaction rim around ilmenite or as discrete groundmass grains (Table 3). Perovskite has only minor FeTiO_3 (2.6 mol%) and MgTiO_3 (0.7 mol%) in solid solution. Energy dispersive analysis (EDA) indicates the presence of substantial Nb and REEs. Bector and Meyer (1979) considered the abundance of Nb and REEs in perovskite to be the result of carbonate complexing of the REEs; this complexing stabilizes the REEs in the late-stage kimberlitic fluids.

Discussion

Previous investigations of oxide minerals in kimberlite (e.g., Haggerty, 1973; 1975; Danchin *et al.*, 1975) have dealt with the mineralogy of the megacrysts and/or groundmass, as well as compilations of data from many localities. The Elliott County kimberlite is well-preserved and permits a detailed investigation of both megacrysts and groundmass phases from the same kimberlite. The relationship between these different generations of minerals is complex; however, when the oxide data are combined with the data on megacryst and groundmass silicates by Garrison and Taylor (1980), the evolution of the Elliott County kimberlite can be divided into four distinct stages: (I) the crystallization of the megacryst phases, (II) an increase in the MgO/FeO ratio in the kimberlitic liquid, (III) the crystallization of the groundmass phases with the accompanying back-reaction of the megacrysts with the MgO -enriched liquid, and (IV) a late-stage "autometasomatic" reaction of ilmenite with a CaO -enriched fluid to form perovskite + titanomagnetite + Mn-ilmenite.

The ilmenite, as well as the silicate, megacrysts could have formed as the result of (1) disaggregation of peridotite to form discrete mineral grains, or (2) direct precipitation from a "proto-kimberlitic" liquid (Eggler *et al.*, 1979; Garrison and Taylor, 1980). The latter origin was suggested for the Elliott County silicate megacrysts (Garrison and Taylor, 1980) because: (1) the large grain size of the megacrysts is generally larger than the grain size expected from disaggregated peridotite; (2) the common intergrowths of the minerals is typical for phases co-precipitated from a liquid; (3) the megacrysts do not show complete or nearly complete compositional overlap with the phases of included peridotite xenoliths; and (4) the garnets, clinopyroxenes, olivines,

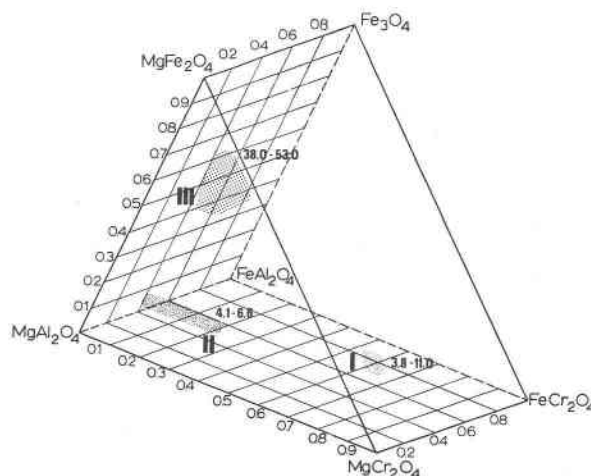


Fig. 9. Compositional fields of the different spinel types plotted in the spinel prism (Irvine, 1965). The range of mol% Fe_2TiO_4 is given for each spinel type. I = Type I chromite; II = Type II pleonaste; III = Type III titanomagnetite.

and to a lesser extent, the orthopyroxenes of the megacryst assemblage exhibit compositional trends generally attributed to precipitation from a fractionating liquid.

The silicate megacrysts from Elliott County exhibit well-defined chemical trends which Garrison and Taylor (1980) attribute to fractional crystallization from a "proto-kimberlitic" liquid. Garnet megacrysts show correlation of $\text{Mg}/(\text{Mg}+\text{Fe})$ (0.79–0.86) and CaO (4.54–7.10 wt.%) with Cr_2O_3 (0.21–9.07 wt.%); the more magnesian garnets have more uvarovite in solution. Olivine megacrysts show a decrease in NiO (0.5–0.05 wt.%) with decreasing $\text{Mg}/(\text{Mg}+\text{Fe})$ (0.93–0.85). The clinopyroxene megacrysts show increasing TiO_2 (0.38–0.56 wt.%) and decreasing Cr_2O_3 (0.88–0.56 wt.%) with decreasing $\text{Mg}/(\text{Mg}+\text{Fe})$ (0.91–0.87). The high- Al_2O_3 , high T (1165°–1255° C) orthopyroxene megacrysts exhibit a general trend of decreasing TiO_2 and Cr_2O_3 with decreasing $\text{Mg}/(\text{Mg}+\text{Fe})$.

An origin by precipitation from a "proto-kimberlitic" liquid is also preferred for the Elliott County ilmenite megacrysts because: (1) ilmenite is an extremely rare minor constituent of mantle peridotite, (2) the size of the ilmenite megacrysts (0.5–1.5 cm) is much larger than the grain size expected from disaggregated peridotite, and (3) the ilmenite megacrysts display a correlation of increasing Fe_2O_3 with decreasing MgO and $\text{Mg}/(\text{Mg}+\text{Fe})$, which can be attributed to fractional crystallization.

Gurney *et al.* (1979) studied a large number of coexisting ilmenite-silicate pairs from the Monastery Mine and demonstrated a co-variance of MgO in ilmenite and $\text{Mg}/(\text{Mg}+\text{Fe})$ in the coexisting silicate phases. They suggested that the Fe_2O_3 variation of the ilmenites could be due to increases in f_{O_2} as the kimberlitic liquid evolves. As discussed earlier, we believe the increase in Fe_2O_3 with decreasing MgO and $\text{Mg}/(\text{Mg}+\text{Fe})$ in the Elliott County ilmenite megacrysts can be produced, as a result of crystallizing silicates and ilmenites, depleting the liquid in MgO and decreasing $\text{Mg}/(\text{Mg}+\text{Fe})$ slowly with fractionation. The preferential incorporation of Fe^{+2} into the abundant silicate phases will produce an increase in $\text{Fe}^{+3}/\text{Fe}^{+2}$ ratio in the remaining melt. Since both mechanisms would progressively enrich ilmenite in Fe_2O_3 , the $\text{MgO}-\text{Fe}_2\text{O}_3$ and $\text{Mg}/(\text{Mg}+\text{Fe})-\text{Fe}_2\text{O}_3$ systematics may prove valuable indicators of the $T-X$ trajectory of the evolving kimberlite liquid.

The silicate megacrysts from Elliott County are considered to be derived from a fractionating proto-kimberlitic liquid, representing the earliest stages of kimberlite development (Garrison and Taylor, 1980; 1981); the data presented above suggest that the Elliott County ilmenite megacrysts probably crystallized from the same liquid. The compositional similarities of ilmenite and clinopyroxene in the nodular graphic intergrowths to megacryst clinopyroxene and ilmenite in the host kimberlite support co-precipitation of clinopyroxene and ilmenite, at least during a portion of kimberlite crystallization. The clinopyroxene megacrysts generally have higher estimated equilibration temperatures (1305°–1390° C), by as much as 50° C, than the clinopyroxenes from the nodular graphic intergrowths (1295°–1335° C) suggesting that clinopyroxene crystallized over a short temperature interval before being joined by ilmenite. This sequence of events is consistent with phase relations outlined by Wyatt (1977). The high $\text{Mg}/(\text{Mg}+\text{Fe})$ ratios (0.47–0.50) and MgO content (13.0–13.5 wt.%) and low Fe_2O_3 content (6.14–6.71 wt.%) of the ilmenites from the graphic intergrowths is consistent with the ilmenites from the intergrowths representing some of the earliest formed ilmenites (*i.e.*, least fractionated). The clinopyroxenes from the intergrowths have chemical systematics that suggest they represent some of the more fractionated members of the clinopyroxene population (Garrison and Taylor, 1980). Ilmenite and clinopyroxene probably crystallized together over only a short temperature inter-

val. Data from the Elliott County high- T orthopyroxene megacrysts (*i.e.*, with estimated equilibration temperatures of 1165°–1255° C) suggest that Stage I megacryst crystallization continued to about 1165° C at pressures of 51–53 kbar. It is not clear whether ilmenite megacrysts crystallized throughout this interval, along with orthopyroxene, garnet, phlogopite, and olivine.

Crystallization of groundmass phases

The high-MgO *Type IV* groundmass ilmenites from the Elliott County kimberlite pipes could have two possible origins: (1) they may represent MgO-enriched fragments of disaggregated recrystallized ilmenite megacrysts, and/or (2) they may represent a compositionally distinct second generation of ilmenite that crystallized with the other groundmass phases. The similarity in chemical systematics between the MgO-enriched rims of the ilmenite megacrysts and the *Type IV* groundmass ilmenites suggests that, regardless of their initial mode of origin, both probably equilibrated with the same MgO-enriched liquid.

By examining the Cr_2O_3 content of the *Type IV* groundmass ilmenites, it is possible to delineate the second generation groundmass ilmenites from the MgO-enriched fragments of disaggregated megacrysts. Since the *Type V* ilmenite inclusions in groundmass olivines are high in Cr_2O_3 (4.00–4.42 wt.%), it is most probable that the ilmenites that crystallized in equilibrium with the groundmass assemblage are high in Cr_2O_3 . Over 90% of the analyzed megacryst cores have between 0.03 and 0.40 wt.% Cr_2O_3 ; over 86% of the analyzed megacryst rims have between 0.04 and 0.73 wt.% Cr_2O_3 . This suggests that the megacryst ilmenites, as well as their MgO-enriched rims, are dominantly of the low- Cr_2O_3 variety. The low- Cr_2O_3 nature of the MgO-enriched megacryst rims probably reflects incomplete equilibration with the MgO- and Cr_2O_3 -enriched liquid. Only 54% of the analyzed *Type IV* groundmass ilmenites have Cr_2O_3 contents less than 0.73 wt.%; the remaining 46% have between 1.43 and 3.76 wt.% Cr_2O_3 . These high- Cr_2O_3 *Type IV* groundmass ilmenites are similar in Fe_2O_3 (4.58–8.58 wt.%) to the *Type V* ilmenite inclusions in groundmass olivines (4.43–10.0 wt.% Fe_2O_3), further substantiating a genetic relationship with the groundmass mineral assemblage. As discussed above, these high- Cr_2O_3 *Type V* and *Type IV* ilmenites have compositions that approach the composi-

tions of the small idiomorphic groundmass ilmenites reported by Boctor and Boyd (1980) from the Likhobong kimberlite. In contrast to the Likhobong groundmass ilmenites, the high-Cr₂O₃ *Type IV* groundmass ilmenites from Elliott County do have a well-developed reaction assemblage of titanomagnetite + perovskite + Mn-ilmenite. This may simply reflect the evolution of the late-stage kimberlitic fluid in time and *P-T-X* space. We suggest that kimberlite groundmass ilmenites *sensu stricto* can be distinguished from small MgO-enriched fragments of disaggregated megacrysts by their distinctly higher Cr₂O₃ content (*i.e.*, generally greater than 1.00 wt.% Cr₂O₃).

In the Elliott County kimberlites, the groundmass phases orthopyroxene (*i.e.*, the low-*T*, high-*mg* Group II orthopyroxenes of Garrison and Taylor, 1980), olivine ($Mg/(Mg+Fe) = 0.88-0.90$), and high-Cr₂O₃ *Type IV* ilmenite are generally more magnesian than the more fractionated members of the corresponding megacryst phases (*i.e.*, those with the lowest $Mg/(Mg+Fe)$ ratios). Both ilmenite and olivine megacrysts exhibit MgO-enriched rims similar in composition to the groundmass phases. Both groundmass ilmenite and orthopyroxene in the Elliott County groundmass assemblage are higher in Cr₂O₃ than megacryst ilmenite and orthopyroxene suggesting that the MgO-enriched liquid from which the groundmass assemblage crystallized was also enriched in Cr₂O₃. These chemical systematics indicate that the crystallization of groundmass phases and the back-reaction of megacryst phases (*i.e.*, Stage III) was preceded by an effective increase in the MgO/FeO ratio (and Cr₂O₃) in the kimberlitic liquid (*i.e.*, Stage II).

Garrison and Taylor (1980) have suggested that the Stage II increase in MgO/FeO ratio of the kimberlitic liquid was related to an increase in f_{O_2} and/or assimilation of carbonated peridotite. They suggested that the assimilation of a carbonated peridotite such as dolomite or magnesite peridotite would have the effect of adding the gaseous species CO₂ to the liquid. In the absence of graphite or diamond (Eggler *et al.*, 1980), this CO₂ would be an oxidizing agent and would subsequently increase the f_{O_2} and the Fe³⁺/Fe²⁺ ratio of the liquid. This increase in Fe³⁺ would have the effect of increasing the MgO/FeO ratio. This mechanism seems inconsistent with the observation that the high-Cr₂O₃ *Type IV* and *V* ilmenites have Fe₂O₃ contents which are generally lower than the Fe₂O₃ content of the more fractionated (*i.e.*, lowest $Mg/(Mg+Fe)$ ratio)

members of the ilmenite megacrysts. If the carbonated peridotite contains substantial MgO, in the form of easily assimilated dolomite or magnesite, assimilation would also add substantial MgO and subsequently increase MgO/FeO. This increase in the availability of divalent species may explain the observed low-Fe₂O₃ content of the high-Cr₂O₃ *Type IV* and *V* ilmenites. It should be realized that any such model invoked to explain the increase in MgO in the kimberlitic liquid at Elliott County should also explain the apparently ubiquitous MgO-enrichment observed in kimberlite in other localities.

Temperature estimates for various pairs of Stage III groundmass minerals suggest equilibration of the groundmass assemblage at temperatures as low as 965° C. The Fe-Mg equilibria between groundmass olivine (Fo_{89.6}) and an ilmenite inclusion, using the geothermometer of Andersen and Lindsley (1979), suggests equilibration at 965° C (at *P* = 50 kbar). This is consistent with the temperature estimates of 970°–1020° C reported by Garrison and Taylor (1980) for the low-*T*, high-*mg* (Group II) orthopyroxenes in the Elliott County kimberlite. Using the olivine-spinel geothermometer of Fabries (1979), the Fe-Mg equilibria between the *Type I* chromites and groundmass olivines (Fo_{87.9} to Fo_{90.0}), representing the entire range of observed groundmass olivine compositions, suggest equilibration at temperatures of 990°–1085° C; this range is consistent with both of the previous temperature estimates for groundmass phases.

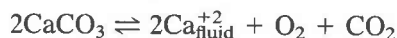
If the Stage III groundmass mineral assemblage indeed crystallized from the MgO-enriched kimberlitic liquid at 965°–1085° C, it is possible to place a constraint on the depth at which this event occurred. From the position of the univariant solidus for kimberlite, as outlined by Eggler and Wendlandt (1979), it is clear that Stage III groundmass crystallization probably occurred at pressures not greater than 25–35 kbar. This suggests that Stage III groundmass crystallization occurred at depths shallower than about 100 km, 50 km shallower than the depth at which Stage I megacryst crystallization occurred. Assuming that the Group II low-*T* orthopyroxenes at Elliott County were in equilibrium with garnet, Garrison and Taylor estimated that the Group II orthopyroxenes crystallized at pressures of 47–50 kbar using the geobarometer of Wood (1974). Since garnet does not belong to the Stage III groundmass mineral assemblage, we feel that the geobarometer of Wood (1974) is not applicable and that the above maximum pressure estimate of 25–35

kbar for the Stage III groundmass crystallization is more reasonable.

The presence of rutile in kimberlite has been attributed to the breakdown of armalcolite ((Fe,Mg)Ti₂O₅) when it is found in intergrowths containing approximately equal amounts of rutile and ilmenite (Haggerty, 1975). The rutile-ilmenite intergrowth from Elliott County contains less than 2% ilmenite lamellae and cannot be explained by this mechanism. This intergrowth is best explained as the result of exsolution of ilmenite from a rutile that contained a small amount of FeO and MgO in solution. Haggerty (1976) and Mitchell (1973; 1979) have noted similar intergrowths in kimberlites in South Africa and Canada; as in the case of the Elliott County kimberlite, these intergrowths were also rimmed by high-MgO ilmenite. This ilmenite rim probably formed at the time of Stage III groundmass crystallization as the rutile reacted with the MgO-enriched liquid. The rutile host could be (1) a xenocryst, or (2) a primary phase precipitated from the kimberlitic liquid.

Formation of the late-stage reaction assemblage

At Elliott County, the final recorded stage of kimberlite evolution (Stage IV) is the reaction of ilmenite to form the assemblage perovskite + titanomagnetite + Mn-ilmenite. This reaction suggests the presence of a late-stage CaO-enriched fluid; the presence of Mn-ilmenite also suggests an increase in the availability of MnO in the fluid. The late-stage reaction of ilmenite with a CaO-enriched fluid to form perovskite and titanomagnetite may occur according to the following reactions:



These reactions explain the major element systematics of the phases involved; minor elements such as Al₂O₃, Cr₂O₃, and MnO are easily accommodated into the reaction scheme. The availability of Ca⁺² is controlled by the breakdown of calcite. Garrison (1981) has suggested that the breakdown of earlier-formed groundmass calcite may have increased the availability of Ca⁺² in the kimberlitic fluid; textural evidence suggests that the breakdown of groundmass calcite may have been extensive in the Elliott County kimberlite. The early-formed groundmass calcite probably became unstable as the late-stage kimberlitic fluid evolved in *P*-

T-*X* space. Thus, it appears that the metasomatic reaction of ilmenite to form the assemblage perovskite + titanomagnetite + Mn-ilmenite may be a natural consequence of the evolution of the late-stage kimberlitic fluid in time and *P*-*T*-*X* space.

The discrete grains of perovskite and titanomagnetite found throughout the groundmass of the Elliott County kimberlite could be: (1) primary phases precipitated from the late-stage kimberlitic fluid, (2) disaggregated fragments of reaction zone assemblages, and/or (3) the completely reacted remnants of very small groundmass ilmenite grains. These discrete groundmass grains are compositionally similar to the phases within the reaction zone assemblage suggesting that, regardless of mode of origin, both textural types probably equilibrated with the same fluid.

Since Mn-ilmenite is present in the reaction assemblage around ilmenite, the activity of Mn⁺² must have also increased in the late-stage kimberlitic fluid. Wyatt (1979) suggested that Mn-rich ilmenites can form by interaction of kimberlite with local meteoric waters. In a study of the Premier kimberlite, Wyatt (1979) found the MnTiO₃ content of ilmenites to increase toward the grain boundaries; these zoned grains were found only in the margins of the kimberlite pipe and small kimberlite dikes. Wyatt concluded that these Mn-ilmenites formed during post-magmatic interaction of the Premier kimberlite with local meteoric waters, the Mn source being the local country rock. The intimate textural relationship of the Elliott County *Type VI* Mn-ilmenites to the minerals of the reaction zone assemblage indicates a genetic relationship of Mn-ilmenite to the reaction zone perovskite and titanomagnetite. The ubiquitous occurrence of the perovskite + titanomagnetite reaction assemblage in kimberlites from other localities argues against a country rock controlled metasomatic event as a mechanism for the formation of the Mn-ilmenite, as well as perovskite and titanomagnetite.

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References

- Albee, A. L. and Ray, L. (1970) Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates, and sulfates. *Analytical Chemistry*, 42, 1408-1414.

- Andersen, D. J. and Lindsley, D. H. (1979) The olivine-ilmenite thermometer. *Proceedings of the Lunar and Planetary Science Conference 10th*, 493–507.
- Bence, A. E. and Albee, A. L. (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *Journal of Geology*, 76, 382–403.
- Bishop, F. C. (1980) The distribution of Fe^{2+} and Mg between coexisting ilmenite and pyroxene with applications to geothermometry. *American Journal of Science*, 280, 46–77.
- Boctor, N. Z. and Boyd, F. R. (1980) Oxide minerals in the Likhobong kimberlite, Lesotho. *American Mineralogist*, 65, 631–638.
- Boctor, N. Z. and Meyer, H. O. A. (1979) Oxide and sulphide minerals in kimberlite from Green Mountain, Colorado. In F. R. Boyd and H. O. A. Meyer, Eds., *Kimberlites, diatremes, and diamonds: Their geology, petrology, and geochemistry*, p. 217–228. American Geophysical Union, Washington, D. C.
- Bolivar, S. L. (1972) Kimberlite of Elliott County, Kentucky. M. A. Thesis, Eastern Kentucky University, 61 p.
- Boyd, F. R. and Nixon, P. H. (1973) Origin of the ilmenite-silicate nodules in kimberlites from Lesotho and South Africa. In P. H. Nixon, Ed., *Lesotho Kimberlites*, p. 254–268. Lesotho National Development Corporation, Maseru.
- Danchin, R. V. and D'Orey, F. (1972) Chromian spinel exsolution in ilmenite from the Premier Mine, Transvaal, South Africa. *Contributions to Mineralogy and Petrology*, 35, 43–49.
- Danchin, R. V., Ferguson, J., McIver, J. R. and Nixon, P. H. (1975) The composition of late-stage kimberlite liquids as revealed by nucleated autoliths. *Physics and Chemistry of the Earth*, 9, 235–245.
- Dawson, J. B. and Reid, A. M. (1970) A pyroxene-ilmenite intergrowth from the Monastery Mine, South Africa. *Contributions to Mineralogy and Petrology*, 26, 296–301.
- Eggler, D. H. and Wendlandt, R. F. (1979) Experimental studies on the relationship between kimberlite magmas and partial melting of peridotite. In F. R. Boyd and H. O. A. Meyer, Eds., *Kimberlites, diatremes, and diamonds: Their geology, petrology, and geochemistry*, p. 330–338. American Geophysical Union, Washington, D. C.
- Eggler, D. H., McCallum, M. E., and Smith, C. B. (1979) Megacryst assemblages in kimberlite from northern Colorado and southern Wyoming: petrology, geothermometry-barometry, and areal distribution. In F. R. Boyd and H. O. A. Meyer, Eds., *The Mantle Sample: Inclusions in kimberlites and other volcanics*, p. 213–226. American Geophysical Union, Washington, D. C.
- Eggler, D. H., Baker, D. R. and Wendlandt, R. F. (1980) f_{O_2} of the assemblage graphite-enstatite-forsterite-magnesite: experiment and application to mantle f_{O_2} and diamond formation. *Geological Society of America Abstracts with Programs* 12, 420 (abstract).
- Elthon, D. and Ridley, W. I. (1979) The oxide and silicate mineral chemistry of a kimberlite from the Premier Mine: implications for the evolution of kimberlitic magmas. In F. R. Boyd and H. O. A. Meyer, Eds., *Kimberlites, diatremes, and diamonds: Their geology, petrology, and geochemistry*, p. 206–216. American Geophysical Union, Washington, D. C.
- Fabries, J. (1979) Spinel-olivine geothermometry in peridotites from ultramafic complexes. *Contributions to Mineralogy and Petrology*, 69, 329–336.
- Frick, C. (1973) Intergrowths of orthopyroxene and ilmenite from Frank Smith Mine, near Rarkly West, South Africa. *Transactions of the Geological Society of South Africa*, 76, 195–200.
- Garrison, J. R., Jr. and Taylor, L. A. (1980) Megacrysts and xenoliths in kimberlite, Elliott County, Kentucky: A mantle sample from beneath the Permian Appalachian Plateau. *Contributions to Mineralogy and Petrology*, 75, 27–42.
- Garrison, J. R., Jr. and Taylor, L. A. (1981) Petrogenesis of pyroxene-oxide intergrowths from kimberlite and cumulate rocks: co-precipitation or exsolution? *American Mineralogist*, 66, 723–740.
- Garrison, J. W. (1981) Mineralogy and petrology of hydrous groundmass minerals and altered crustal clasts in kimberlite, Elliott County, Kentucky. M.A. Thesis, University of Tennessee, 76 p.
- Garrison, J. W., Garrison, J. R., Jr. and Taylor, L. A. (1980) Kimberlite metasomatism: wallrock alterations from a hot intrusive at Elliott County, Kentucky. *EOS*, 61, 1156 (abstract).
- Gurney, J. J., Fesq, H. W. and Kable, E. J. D. (1973) Clinopyroxene-ilmenite intergrowths from kimberlite; a re-appraisal. In P. H. Nixon, Ed., *Lesotho Kimberlites*, p. 238–253. Lesotho National Development Corporation, Maseru.
- Gurney, J. J., Jakob, W. R. O. and Dawson, J. B. (1979) Megacrysts from the Monastery kimberlite pipe, South Africa. In F. R. Boyd and H. O. A. Meyer, Eds., *The Mantle Sample: Inclusions in kimberlites and other volcanics*, p. 227–243. American Geophysical Union, Washington, D. C.
- Haggerty, S. E. (1973) Spinel of unique composition associated with ilmenite reaction mantles in the lighobond kimberlite pipe, Lesotho. In P. H. Nixon, Ed., *Lesotho Kimberlites*, p. 149–158. Lesotho National Development Corporation, Maseru.
- Haggerty, S. E. (1975) The chemistry and genesis of opaque minerals in kimberlites. *Physics and Chemistry of the Earth*, 9, 295–307.
- Haggerty, S. E. (1976) Opaque mineral oxides in terrestrial igneous rocks. In D. Rumble, Ed., *Oxide Minerals, Short Course Notes*, Mineralogical Society of America, Washington, D. C.
- Haggerty, S. E., Hardie, R. B. III and McMahon, B. M. (1979) The mineral chemistry of ilmenite nodule associations from the Monastery diatreme. In F. R. Boyd and H. O. A. Meyer, Eds., *The Mantle Sample: Inclusions in kimberlites and other volcanics*, p. 249–256. American Geophysical Union, Washington, D. C.
- Hsu, J. A. and Taylor, L. A. (1978) An unusual mineralogy in the Norris kimberlite of Tennessee. *Geological Society of America Abstracts with Programs*, 10, 172 (abstract).
- Irvine, T. N. (1965) Chromian spinel as a petrogenetic indicator. Part I. *Canadian Journal of Earth Science*, 2, 648–672.
- Lindsley, D. H. and Dixon, S. A. (1976) Diopside-enstatite equilibria at 850° C to 1,400° C, 5 to 35 kb. *American Journal of Science*, 276, 1285–1301.
- Mitchell, R. H. (1973) Magnesian ilmenite and its role in kimberlite petrogenesis. *Journal of Geology*, 81, 301–311.
- Mitchell, R. H. (1977) Geochemistry of magnesian ilmenites from kimberlites from South Africa and Lesotho. *Lithos*, 10, 29–37.
- Mitchell, R. H. (1979) Mineralogy of the Tunraq kimberlite, Somerset Island, N. W. T. Canada. In F. R. Boyd and H. O. A. Meyer, Eds., *Kimberlites, diatremes, and diamonds:*

- Their geology, petrology, and geochemistry, p. 161–171. American Geophysical Union, Washington, D. C.
- Pasteris, J. D. (1980) The significance of groundmass ilmenite and megacryst ilmenite in kimberlites. *Contributions to Mineralogy and Petrology*, 75, 315–325.
- Wood, B. J. (1974) The solubility of alumina in orthopyroxene coexisting with garnet. *Contributions to Mineralogy and Petrology*, 46, 1–15.
- Wyatt, B. A. (1977) The melting and crystallization behavior of a natural clinopyroxene-ilmenite intergrowth. *Contributions to Mineralogy and Petrology*, 61, 1–9.
- Wyatt, B. A. (1979) Mangoan ilmenite from the Premier kimberlite. *Geological Society of South Africa, Geokongres*, 456–460.
- Zartman, R. E., Brock, M. R., Heyl, A. V., and Thomas, H. H. (1972) K–Ar and Rb–Sr ages of some alkalic intrusive rocks from central and eastern United States. *American Journal of Science*, 265, 884–870.

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