

## High-pressure–high-temperature melting experiments on a SiO<sub>2</sub>-poor aphanitic kimberlite from the Wesselton mine, Kimberley, South Africa

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### ABSTRACT

Phase relations in a SiO<sub>2</sub>-poor aphanitic Group I kimberlite from the Wesselton mine, South Africa, were determined at 10–40 kbar and 1000–1525 °C. Experiments were done first with no additional H<sub>2</sub>O or CO<sub>2</sub>, equivalent to the initial amounts in the rock of 6.20 wt% H<sub>2</sub>O and 4.77 wt% CO<sub>2</sub>, and second with sufficient CO<sub>2</sub> added to bring the total to 10.34 wt% CO<sub>2</sub>. These amounts are equivalent to a mole fraction of CO<sub>2</sub> ( $X_{\text{CO}_2}$ ) of 0.24 and 0.52, respectively. Oxygen fugacities are difficult to predict but were likely less than the MW and greater than the IW buffer assemblages. All experiments are suprasolidus and apparently vapor absent. In addition to liquid, runs at  $X_{\text{CO}_2} = 0.24$  produced the following assemblages with decreasing pressure from 40 to 10 kbar and temperatures from 1400 to 1000 °C: olivine, olivine + spinel, olivine + spinel + clinopyroxene ± calcite ± perovskite, and olivine + spinel + monticellite + calcite + perovskite. At  $X_{\text{CO}_2} = 0.52$ , runs at 20–35 kbar produced olivine + spinel, olivine + clinopyroxene + spinel, and olivine + clinopyroxene + spinel + calcite. Above 35 kbar, the latter assemblage is replaced by olivine + clinopyroxene + dolomite. Comparison of the compositions of the minerals in the rock with those produced in the experiments indicates good agreement except for spinels that are highly oxidized in the experimental products relative to those in the rock. The run assemblages are comparable with the minerals in the aphanitic kimberlite except for clinopyroxene, which is absent in the rock, and ilmenite, apatite, and phlogopite, which are present in the rock but not in the experimental runs. Based on the  $X_{\text{CO}_2} = 0.24$  experiments, the inferred *P-T* path of ascent of the aphanitic kimberlite magma above about 40-km depth may have exceeded the temperature (1250–1300 °C) at which clinopyroxene is stable for this composition. The antipathy of clinopyroxene and monticellite in the  $X_{\text{CO}_2} = 0.24$  experiments may be used to explain the incompatibility of these minerals in kimberlite and suggests that monticellite need not be a product associated with crustal processes.

The aphanitic Wesselton kimberlite has lower SiO<sub>2</sub> and MgO and higher CaO than other Group I kimberlites and, when plotted on the CMS system, lies on the CaO-rich side of the olivine-clinopyroxene join whereas more SiO<sub>2</sub>-rich Group I kimberlites fall close to this join. These compositional differences may account for the absence of orthopyroxene in any of the experimental assemblages and possibly for the fact that calcite is the only carbonate mineral below 35 kbar and occurs only at high  $X_{\text{CO}_2}$  conditions. Most Group I kimberlite compositions are represented by the model carbonated lherzolite system (olivine-clinopyroxene-orthopyroxene-dolomite) for which a pseudo-eutectic melting relationship involving enstatite may occur. The absence of orthopyroxene in the present experiments does not preclude the more SiO<sub>2</sub>-undersaturated Wesselton kimberlite magma from

being the product of crystal fractionation at mantle depths of a more SiO<sub>2</sub>-rich kimberlite magma derived by partial melting of a carbonated lherzolite source. However, the absence of orthopyroxene in the experiments does indicate that the aphanitic kimberlite magma could have evolved from a source devoid of orthopyroxene and with calcite as the carbonate phase. The present experiments suggest that the aphanitic Wesselton kimberlite is not an evolved species but may represent a primitive kimberlite magma.

## INTRODUCTION

Experimental studies under pressure and temperature conditions compatible with crystallization and differentiation of kimberlite magmas are valuable in understanding the evolution of kimberlites (Mitchell, 1986). The only available studies using actual kimberlites are those of Egger and Wendlandt (1979) on a modified Lesotho kimberlite composition with 0–11 wt% H<sub>2</sub>O and that of Ito et al. (1968) on an anhydrous kimberlite from the Dutoitspan mine. Most experimental work pertinent to kimberlites has involved determination of the role of peridotite, particularly lherzolite and harzburgite with orthopyroxene as an essential mineral, and/or the significance of CO<sub>2</sub> in their genesis, using simplified model peridotite systems (cf. Egger and Wendlandt, 1979; Wyllie, 1979, 1980; Olafsson and Egger, 1983; Brey et al., 1984; Huang and Wyllie, 1984). Experiments on the crystallization and evolution of kimberlite magmas are hampered by the wide variation in kimberlite compositions and hence the difficulty in identifying compositions that may be reasonably representative of primitive kimberlite magma.

This paper describes suprasolidus, apparently vapor-absent experiments between 10 and 40 kbar on a Group I aphanitic kimberlite from the Wesselton mine, Kimberley, South Africa. The scarcity of xenoliths and xenocrysts, the fine-grained nature of this kimberlite, and its low SiO<sub>2</sub> content relative to other kimberlites suggest that the aphanitic kimberlite at Wesselton may represent a close to primitive, although not necessarily primary, kimberlite magma composition. If this assumption is correct, then the experiments can be used to determine possible crystallization paths during ascent of the aphanitic Wesselton kimberlite from depths corresponding to 40 kbar to those corresponding to 10 kbar by comparing the polybaric-polythermal mineral assemblages obtained in the experiments with those inferred from the petrography of the rock. Such experiments also indicate potential genetic relationships between extremely SiO<sub>2</sub>-undersaturated aphanitic varieties of kimberlite, such as the one used in this study, and the more common, relatively SiO<sub>2</sub>-enriched macrocrystic kimberlites, such as the macrocrystic Wesselton kimberlite.

## PETROGRAPHY AND CHEMISTRY OF GROUP I KIMBERLITES AT WESSELTON

Shee (1984, 1986) described the geology, petrography, classification, and chemistry of the hypabyssal facies Group I kimberlites at Wesselton. In the aphanitic kim-

berlite, olivine microphenocrysts occur in a matrix consisting of variable amounts of calcite, monticellite, ilmenite, spinel, perovskite, apatite, serpentine, and rare phlogopite. Olivine and phlogopite xenocrysts and xenoliths of country rock occur only in trace amounts. The aphanitic kimberlite used in this study (Table 1; analyses 1, 2) has lower SiO<sub>2</sub>, MgO, and K<sub>2</sub>O and higher TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO than the mean value for macrocrystic kimberlites from the same locality and from Group I kimberlites generally (Table 1; analyses 3, 4). This composition also differs considerably from that used by Egger and Wendlandt (1979) in their experiments.

## EXPERIMENTAL CONDITIONS AND TECHNIQUES

Experiments were done under two sets of CO<sub>2</sub>/H<sub>2</sub>O ratios. In the first set of experiments, between 10 and 40 kbar, no H<sub>2</sub>O or CO<sub>2</sub> other than that in the rock itself was used. These experi-

TABLE 1. Compositions of aphanitic, macrocrystic, and average Group I kimberlites

	1	2 (n = 7)	3 (n = 17)	4 (n = 44)
SiO <sub>2</sub>	25.60	24.46(22.80–26.00)	31.55(28.90–34.50)	30.26
TiO <sub>2</sub>	3.35	3.11(2.53–3.48)	2.00(1.73–2.32)	1.91
Al <sub>2</sub> O <sub>3</sub>	3.31	3.58(3.00–3.90)	2.57(1.70–4.45)	2.87
Fe <sub>2</sub> O <sub>3(T)</sub>	10.30	9.74(9.06–10.20)	9.01(8.58–9.46)	8.63
MnO	0.21	0.19(0.15–0.22)	0.15(0.12–0.19)	0.16
MgO	27.20	25.94(23.26–29.10)	31.30(27.10–33.40)	29.62
CaO	15.30	15.07(12.70–16.70)	8.14(6.40–9.59)	10.13
Na <sub>2</sub> O	0.28	0.26(0.10–0.80)	0.35(0.05–0.60)	0.39
K <sub>2</sub> O	0.70	0.68(0.13–1.23)	1.29(0.48–2.32)	1.31
P <sub>2</sub> O <sub>5</sub>	1.83	1.74(1.45–2.56)	1.00(0.46–1.58)	1.48
CO <sub>2</sub>	4.77	6.92(3.45–10.86)	4.26(1.45–5.97)	5.24
H <sub>2</sub> O <sup>+</sup>	6.20	7.56(4.92–9.39)	7.71(3.96–10.09)	7.64
Total	99.05	99.25	99.33	99.64
	Trace elements (ppm)			
F	2500	2225	1784	1917
Cl	800	—	—	—
S	—	671	271	367
V	—	170	105	123
Cr	2410	2007	1291	1517
Co	—	87	110	94
Ni	810	729	1233	1061
Cu	—	105	60	66
Zn	—	111	88	86
Rb	20	60	78	77
Sr	1180	1256	905	1186
Y	10	26	12	16
Zr	580	502	258	318
Nb	250	284	146	171
Ba	1000	1578	1198	1399

Note: Columns are (1) aphanitic kimberlite used in this study (after Shee, 1986, and by X-ray fluorescence techniques by X-ray Assay Laboratories, Don Mills, Ontario); (2) mean and ranges of 7 aphanitic kimberlites from Wesselton (after Shee, 1986); (3) mean and ranges of 17 macrocrystic kimberlites from Wesselton (after Shee, 1986); (4) mean of 44 Group I kimberlites from Wesselton, DeBeers, Benfontein, Dutoitspan (after Shee, 1986).

ments represent the minimum  $\text{H}_2\text{O} + \text{CO}_2$  prior to crystallization, and the results assume that loss of these volatiles during ascent was minimal and that neither  $\text{H}_2\text{O}$  nor  $\text{CO}_2$  was added by secondary processes. Probably some loss of volatiles occurred during ascent, and the presence of serpentine in the groundmass suggests that some of the volatiles may not be of magmatic origin. However, the degree of serpentinization in the aphanitic sample (12–15%) is less than the 20–50% for many kimberlites (Skinner and Clement, 1979). Experiments done with only the volatiles present in the bulk-rock composition correspond to  $X_{\text{CO}_2} = 0.24$  [where mole fraction  $\text{CO}_2 = X_{\text{CO}_2} = \text{CO}_2 / (\text{CO}_2 + \text{H}_2\text{O})$ ], representing 6.20 wt%  $\text{H}_2\text{O}$  and 4.77 wt%  $\text{CO}_2$  (Table 1). After each run, capsules were punctured and examined under the microscope, but no vapor was observed. We therefore assume that these experiments were done under vapor-absent conditions. If vapor was absent, then the  $X_{\text{CO}_2}$  values for the bulk rock are also those of the liquid in the experiments.

The second set of experiments was done with sufficient added  $\text{CO}_2$  so that  $X_{\text{CO}_2} = 0.52$ . The rationale for doing experiments with higher  $X_{\text{CO}_2}$  was to compensate for any  $\text{CO}_2$  lost during ascent of the kimberlite magma and to promote the crystallization of carbonate phases, postulated to be key minerals in kimberlite magma generation and evolution (cf. Wyllie and Huang, 1976). Experiments between 20 and 35 kbar with  $X_{\text{CO}_2} = 0.52$  also appear to have been vapor-absent on the basis of optical examination.

A number of other constraints might have been imposed in these experiments, including variation in the  $f_{\text{O}_2}$ . However, the close correspondence between the assemblages in these supra-solidus experiments and the paragenesis of the kimberlite inferred from its petrography and, in some instances, the correspondence in mineral chemistry suggest that the experimental  $f_{\text{O}_2}$  conditions used may be reasonable approximations of the conditions under which the aphanitic kimberlite evolved.

All experiments were done in a 1.27-cm-diameter piston-cylinder apparatus (Boyd and England, 1960) with talc-Pyrex glass assemblages using the hot, piston-out method. The starting material was crushed to <200 mesh, preheated at 110 °C for 24 h to remove absorbed  $\text{H}_2\text{O}$  (additional to the  $\text{H}_2\text{O}^+$  given in Table 1), and loaded into sealed Fe-soaked Pt capsules (Ford, 1978) for runs above 1250 °C or into  $\text{Ag}_{50}\text{Pd}_{50}$  capsules for lower-temperature experiments. For runs at  $X_{\text{CO}_2} = 0.52$ , additional  $\text{CO}_2$  was attained by adding  $\text{Ag}_2\text{C}_2\text{O}_4$  (Boettcher et al., 1973).

Runs were made between 10 and 40 kbar for experiments at  $X_{\text{CO}_2} = 0.24$  and between 20 and 35 kbar for experiments at  $X_{\text{CO}_2} = 0.52$ . Temperatures were maintained by a graphite furnace and ranged from 1000 to 1525 °C. Pressures and temperatures were calibrated at the kyanite-sillimanite transition at 22 kbar and 1300 °C (Richardson et al., 1968) and at the jadeite + quartz → albite reaction at 16.3 kbar and 600 °C (Johannes et al., 1971; Holland, 1980). Results were within accepted values, and consequently the experiments are believed to be accurate to  $\pm 0.5$  kbar and  $\pm 5$  °C of the values stated. No frictional correction was applied to pressure, and no pressure correction was applied to the emf of the Pt-Pt<sub>90</sub>Rh<sub>10</sub> thermocouples used to measure temperatures.

As all experiments are assumed to have been done under vapor-absent conditions, the  $f_{\text{O}_2}$  and  $f_{\text{H}_2}$  within the capsule cannot be estimated. In a graphite-talc-Pyrex assembly, a C-O-H fluid is produced over a range of  $f_{\text{O}_2}$  values ranging from below the MW to the IW buffers. No experiments were done to assess the actual  $f_{\text{O}_2}$  as this was beyond the scope of this study.

To assess whether equilibrium was achieved, selected runs were isobarically reversed over liquidus boundaries by holding

charges at previous run conditions and reducing or increasing the temperature by 25 °C. In all cases, these runs produced the same assemblages as the runs done on the low- or high-temperature side of the liquidus (Table 2).

Products of the experiments consisted of combinations of olivine, spinel, monticellite, clinopyroxene, perovskite, calcite, and dolomite. All assemblages contained glass, and no optical evidence of vapor was found in any run product when the capsule was punctured and the contents examined under 40× magnification. Products were identified optically, by X-ray diffraction, and by electron microprobe. Analyses of minerals were done on an automated MAC-400 electron microprobe at an accelerating voltage of 15 kV and an approximate sample current of 0.025  $\mu\text{A}$ .

## RESULTS

### Distinction between primary and quench phases

Primary and quench phases occurred in all experiments and were distinguished on the basis of their morphology and composition. Euhedral olivine and clinopyroxene are considered to be primary, whereas quench varieties are acicular and have high  $\text{TiO}_2$ ,  $\text{FeO}$ , and  $\text{CaO}$ . Primary spinels form large cubic crystals whereas quench varieties are much finer grained with less-well-defined cubic habit. In the  $X_{\text{CO}_2} = 0.24$  experiments, primary calcite forms euhedral, clear crystals whereas quench calcite is anhedral and contains fine-grained inclusions (cf. Eggler and Wendlandt, 1979). Distinction between primary and quench carbonate minerals in the  $X_{\text{CO}_2} = 0.52$  runs is impossible because of the much finer grain sizes in these runs. A theoretical consideration of probable quench and primary carbonate minerals in these experiments is discussed below.

### Experiments at $X_{\text{CO}_2} = 0.24$

Experiments at  $X_{\text{CO}_2} = 0.24$  (6.20 wt%  $\text{H}_2\text{O}$  and 4.77 wt%  $\text{CO}_2$ ) represent probable vapor-absent conditions; liquid is present in all run products. Olivine is the liquidus phase up to 40 kbar with spinel being the next mineral to crystallize at 5 °C (at 40 kbar) to 65 °C (at 10 kbar) below the liquidus. The “spinel in” curve (Fig. 1a) may be affected by Fe loss to the Pt capsules and by  $f_{\text{O}_2}$ ; hence the pressure at which it intersects the liquidus—just above 40 kbar—may not necessarily be a reasonable pressure corresponding to the depth for spinel crystallization in the natural magma. With decreasing temperature, clinopyroxene crystallizes between 40 and 13 kbar at 60–135 °C below the liquidus. Above 25 kbar, the “calcite in” curve occurs at slightly lower temperatures (10–15 °C) than those of the “clinopyroxene in” curve, but at lower pressures, calcite has decreasing temperature stability down to >300 °C below the liquidus at 10 kbar (Fig. 1a). Calcite is the only carbonate present in the  $X_{\text{CO}_2} = 0.24$  experiments as confirmed by X-ray diffraction and by microprobe analysis.

Monticellite crystallizes from about 1250 °C at 13 kbar to 1000 °C at 10 kbar, producing a wedge-shaped field on the  $P$ - $T$  diagram (Fig. 1a). On the basis of runs at 14 kbar, 1250 °C and 12 kbar, 1150 °C (Table 2), the “clinopy-

TABLE 2. Experimental results

Temp (°C)	Pressure (kbar)	Time (min)	Capsule	Results**
$X_{\text{CO}_2} = 0.24$ (6.20 wt% H <sub>2</sub> O, 4.77 wt% CO <sub>2</sub> )				
1400	10	10	Pt	Tr. ol (97), L
1375	10	20	Pt*	ol, L
1340	10	60	Pt*	ol (97), sp, L
1300	12	60	Pt*	ol (96), sp, L
1270	10	60	Pt*	ol, sp, L
1225	10	180	Ag <sub>50</sub> Pd <sub>50</sub>	ol (91), mo, sp, pv, L
1150	10	360	Ag <sub>50</sub> Pd <sub>50</sub>	ol (90), mo, sp (46), pv, L
1000	10	360	Ag <sub>50</sub> Pd <sub>50</sub>	ol (89), mo, sp, pv, ct, L(?)
1150	12	360	Pt*	ol, mo, sp, pv, L
1240	14	180	Pt*	ol (96), sp, cpx, pv(?), L
1225	15	180	Pt*	ol, sp, cpx, pv, L
1175	15	360	Pt*	ol (95), sp (44), cpx, pv, L
1150	15	300	Ag <sub>50</sub> Pd <sub>50</sub>	ol (94), sp (45), cpx, ct, pv, L
1425	20	20	Pt*	L
1400	20	10	Pt*	ol (97), L
1325	20	60	Pt*	ol (95), sp, L
1300	20	60	Pt*	ol, sp (48), cpx, L
1280	20	60	Pt*	ol, sp, cpx, L
1250	20	40	Pt*	ol, sp (50), cpx, L
1150	20	360	Ag <sub>50</sub> Pd <sub>50</sub>	ol (95), sp (37), cpx, ct, pv, L
1000	20	360	Ag <sub>50</sub> Pd <sub>50</sub>	ol (93), sp, cpx, ct, pv, L(?)
1300	25	20	Pt*	ol (95), sp, cpx, ct, pv, L
1450	30	10	Pt*	L
1425	30	20	Pt	Tr. ol, L
1400	30	10	Pt	ol (96), sp, L
1350	30	10	Pt	ol (96), sp, L
1300	30	20	Pt*	ol (95), sp (54), cpx(?), ct, L
1250	30	30	Pt*	ol (95), sp, cpx, ct, pv, L
1200	30	200	Ag <sub>50</sub> Pd <sub>50</sub>	ol (94), sp (38), cpx, ct, pv, L
1150	30	300	Ag <sub>50</sub> Pd <sub>50</sub>	ol (94), sp (38), cpx, ct, pv, L
1050	30	360	Ag <sub>50</sub> Pd <sub>50</sub>	ol (92), sp, cpx, ct, pv, L(?)
1000	30	360	Ag <sub>50</sub> Pd <sub>50</sub>	ol (92), sp (32), cpx, ct, pv, L(?)
1430	35	10	Pt*	ol (95), L
1350	35	10	Pt*	ol (94), sp, cpx, pv, ct(?), L
1425	40	10	Pt*	ol, sp, L
Reversal runs				
1425 (1400)	20	20 (10)	Pt*	L
1400 (1425)	20	10 (20)	Pt*	ol, L
1425 (1400)	30	20 (10)	Pt*	L
1400 (1425)	30	10 (20)	Pt*	ol, L
$X_{\text{CO}_2} = 0.52$ (6.20 wt% H <sub>2</sub> O, 10.34 wt% CO <sub>2</sub> )				
1485	20	10	Pt*	L
1450	20	10	Pt*	ol, L
1400	20	10	Pt*	ol, sp, cpx(?), L
1350	20	60	Pt*	ol (94), sp, cpx, pv, L
1300	20	40	Pt*	ol (93), cpx, sp, pv, ct, L
1525	30	10	Pt*	L
1475	30	10	Pt*	ol (97), L
1450	30	15	Pt*	ol, sp, cpx, L
1425	30	20	Pt*	ol (95), sp, cpx, pv(?), L
1400	30	10	Pt*	ol (94), sp, cpx, L
1350	30	10	Pt*	ol, sp, cpx, ct, L
1300	30	20	Pt*	ol (91), sp, cpx, ct, L
1500	35	10	Pt*	ol (95), sp, cpx(?), L
1450	35	10	Pt*	ol, cpx, dol, L
1350	35	10	Pt*	ol, cpx, dol, L(?)

\* Fe-soaked Pt capsule; Pt without asterisk indicates untreated Pt capsule.

\*\* Abbreviations: ol = olivine, L = liquid, sp = spinel, mo = monticellite, pv = perovskite, ct = calcite, cpx = clinopyroxene, dol = dolomite, tr = trace.

† Parenthetical numbers after ol and sp are 100Mg/(Mg + Fe<sub>tot</sub>) values.

roxene in–monticellite out” curve (Fig. 1a) is well established. There are no assemblages containing both monticellite and clinopyroxene.

Because of difficulties in identification of primary perovskite, no “perovskite in” curve is shown in Figure 1a.

Above 25 kbar, perovskite occurs in most runs containing olivine + spinel + clinopyroxene + calcite + liquid, but is absent in runs at higher temperature with olivine + liquid and olivine + spinel + liquid. Below 25 kbar, perovskite is always present with olivine + spinel + clino-

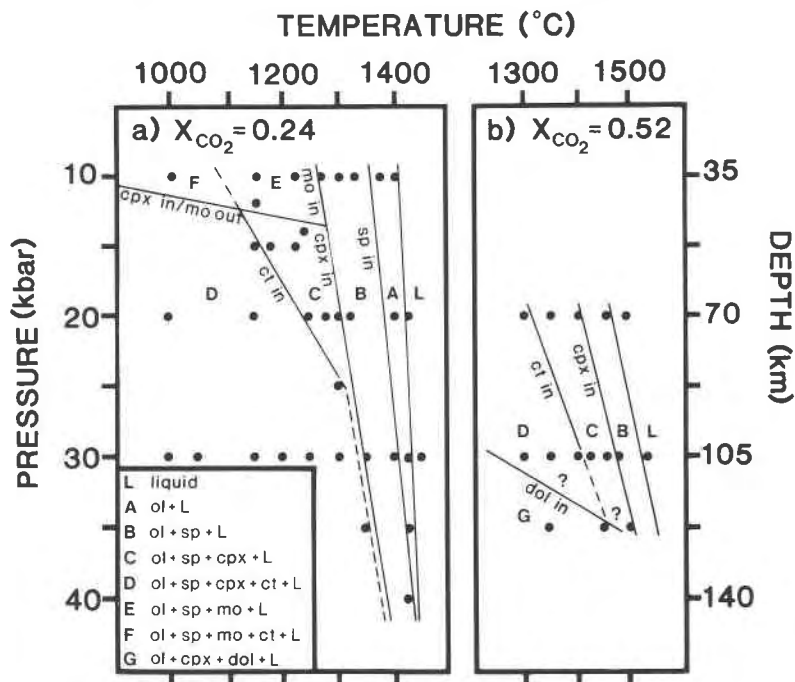


Fig. 1. Results of experiments on Wesselton aphanitic kimberlite at (a)  $X_{\text{CO}_2} = 0.24$  and (b)  $X_{\text{CO}_2} = 0.52$  (see text for wt%  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ). Phase assemblages are shown at bottom of Fig. 1. Vapor is absent in all runs. Abbreviations: ol, olivine; sp, spinel; cpx, clinopyroxene; mo, monticellite; ct, calcite; dol, dolomite; L, liquid.

pyroxene + calcite + liquid, olivine + spinel + monticellite + liquid, and olivine + spinel + monticellite + calcite + liquid; but its presence in the olivine + spinel + clinopyroxene + liquid assemblage is random (Fig. 1a, Table 2).

Glass was clearly identified in runs at 1150 °C and strongly suspected in run products at 1000 °C, indicating that all experiments were suprasolidus. No phlogopite was observed in any of these experiments, even those near the probable solidus (<1000 °C).

#### Experiments at $X_{\text{CO}_2} = 0.52$

The higher liquidus temperature in the  $X_{\text{CO}_2} = 0.52$  experiments relative to the runs at lower  $X_{\text{CO}_2}$  (Fig. 1) reflects the different  $\text{CO}_2/\text{H}_2\text{O}$  in the liquids present above the liquidus. Unlike the  $X_{\text{CO}_2} = 0.24$  experiments, olivine was not the sole near-liquidus mineral in any run but was always accompanied by spinel (Fig. 1b). However, the possibility of an olivine + liquid assemblage near the liquidus cannot be discounted. Clinopyroxene crystallizes closer to the liquidus in the higher  $X_{\text{CO}_2}$  experiments than in those at  $X_{\text{CO}_2} = 0.24$ , and the olivine + clinopyroxene + spinel + liquid assemblage is stable over a much wider temperature range (Figs. 1a, 1b). This field appears to be constrained by the "calcite in" curve extending up to 30 kbar and 1400 °C and by the absence of calcite at 35 kbar, 1450 °C. Analyzable calcite is present at 1500 °C and 35 kbar (Table 2, Fig. 1b).

Dolomite is present only in the 35-kbar, 1350 °C and 1450 °C runs where calcite and spinel are absent. Perov-

skite was detected in some runs (Table 2), but its distribution from run to run was unsystematic.

#### Analyses of run products

**Olivine.** Microprobe analyses for olivine were obtained for many of the run products. Except for their 100Mg/(Mg + Fe) ratios, these are fairly uniform. The average of the 100Mg/(Mg + Fe) ratios, usually from several grains, is given in Table 2. These show a small decrease with decreasing temperature, but all 100Mg/(Mg + Fe) ratios are high because of some loss of Fe even to the Fe-soaked Pt capsules used at high temperatures and the  $\text{Ag}_{50}\text{Pd}_{50}$  capsules used at lower temperatures. The small range of 100Mg/(Mg + Fe) ratios (97–89) over 400 °C in the 10-kbar runs (Table 2, Fig. 1a) probably reflects the increased loss of Fe to the sample capsules in lower-temperature experiments done for longer times and the possible higher  $f_{\text{O}_2}$  in these experiments.

**Clinopyroxene, monticellite, and perovskite.** All of these phases, particularly clinopyroxene, were difficult to analyze because of their fine grain size. The single run for which a satisfactory clinopyroxene analysis was obtained (Table 2) indicates an  $\text{Al}_2\text{O}_3$ - and CaO-rich variety, probably a fassaite. Both analyses of monticellite have comparable compositions. Two of the perovskite analyses have low totals (Table 3) that may be due to the very fine grain size of these samples or to unidentified REEs and Nb (cf. Mitchell, 1984; Shee, 1984).

**Spinel.** Only semiquantitative analyses of spinels were obtained owing to their fine-grained nature. No analyses

TABLE 3. Clinopyroxene, monticellite, and perovskite analyses;  $X_{\text{CO}_2} = 0.24$ 

Minerals (no. of analyses):	Cpx (2)	mo (1)	mo (1)	pv (1)	pv (2)	pv (2)
SiO <sub>2</sub>	48.66	37.25	37.12	1.39	1.27	1.37
TiO <sub>2</sub>	0.98	0.27	0.36	53.67	53.81	51.93
Al <sub>2</sub> O <sub>3</sub>	4.90	0.19	0.71	0.57	0.35	0.38
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.12	0.22	0.10	0.09	0.32
FeO	3.66	4.16	5.03	1.85	1.56	1.58
MnO	0.00	0.23	0.41	0.00	0.11	0.21
MgO	15.68	24.64	25.30	0.38	0.10	0.45
CaO	25.45	33.82	30.52	40.82	36.67	38.26
Na <sub>2</sub> O	0.09	—	—	0.55	0.42	0.11
K <sub>2</sub> O	0.00	—	—	0.05	0.06	0.06
NiO	—	0.12	0.22	—	—	—
Total	99.42	100.80	99.90	99.38	94.44	94.67
100Mg/(Mg + Fe)	88	91	90	—	—	—
Pressure (kbar):	30	10	10	30	25	20
Temp (°C):	1050	1225	1150	1050	1300	1000
Capsule:	Ag <sub>50</sub> Pd <sub>50</sub>	Ag <sub>50</sub> Pd <sub>50</sub>	Ag <sub>50</sub> Pd <sub>50</sub>	Ag <sub>50</sub> Pd <sub>50</sub>	Fe-soaked Pt	Ag <sub>50</sub> Pd <sub>50</sub>
Coexisting phases:	ol, sp, cpx, pv, ct, L(?)	ol, sp, mo, pv, L	ol, sp, mo, pv, L	ol, sp, pv, cpx, ct, L(?)	ol, sp, pv, cpx, ct, L	ol, sp, pv, cpx, ct, L

Note: For abbreviations, see Table 2.

were possible in runs at 10 kbar or those above 30 kbar. Analyses of discrete grains of spinel at 30 kbar, 1300 °C yielded an aluminous magnesiochromite coexisting with an aluminous magnesioferrite. As only the latter was found in other run products at 30 and 20 kbar, the significance of both spinel compositions at 30 kbar, 1300 °C is not known. The 100Mg/(Mg + Fe) ratio in spinels shows a decreasing trend with decreasing temperature (Table 2). No correlation was found between Cr<sub>2</sub>O<sub>3</sub> contents and the crystallization temperature (cf. Osborn and Doctor, 1981) or between TiO<sub>2</sub> contents and pressure (cf. Osborn, 1983; Shee, 1984).

Recalculation of the spinel analyses (Carmichael, 1967) gave high proportions of the Fe<sub>3</sub>O<sub>4</sub> molecule as indicated by Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratios of 0.40–0.66; these values are higher than those of the natural spinels from the Wesselton kimberlites (Shee, 1984). These high Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratios may be due to different  $f_{\text{O}_2}$  conditions in the experiments relative to those in the natural system. No consistent variation in the Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratios with temperature or pressure was found, probably as a result of the semiquantitative nature of the analyses.

## DISCUSSION

### Comparison of mineral assemblages in the aphanitic kimberlite with those inferred from the experiments

The aphanitic kimberlite used in this study, excluding traces of olivine and phlogopite xenocrysts and xenoliths of country rocks, contains olivine and spinel as microphenocrysts in a matrix of olivine, calcite, monticellite, ilmenite, spinel, perovskite, apatite, serpentine, and rare phlogopite (Shee, 1984, 1986). Within the matrix, olivine is coarser than monticellite and from its chemistry and association appears to have crystallized prior to monticellite. Clinopyroxene is absent in the natural kimberlite, and ilmenite, apatite, and phlogopite are not observed among the experimental assemblages (Fig. 1). From the

petrography of the rock it can be inferred that the olivine microphenocrysts and spinel crystallized prior to the later matrix-mineral assemblage in which the paragenetic sequence is likely olivine, spinel, perovskite, monticellite, phlogopite, apatite, calcite, and finally serpentine, comparable to that proposed by Mitchell (1986, p. 57) for hypabyssal-facies kimberlites.

The paragenesis based on the petrography can be compared with polybaric-polythermal crystallization courses in the experiments (Fig. 1a) with the notable exception that the matrix in the natural kimberlite minerals probably formed in the absence of liquid, as suggested by the proposed low temperatures of formation of many of these minerals in kimberlites (cf. Mitchell, 1986, Fig. 3–11). From the absence of clinopyroxene in the rock it may be inferred that the aphanitic kimberlite magma may not have ascended under the  $P$ - $T$  conditions of clinopyroxene stability defined by the experiments. For the  $X_{\text{CO}_2} = 0.24$  experiments (Fig. 1a), this implies that the cooling path remained above 1250–1300 °C at depths in excess of 50 km above which rapid emplacements may have allowed high temperatures to persist to fairly shallow levels (cf. Skinner, 1986). If this is correct, then the occurrence of olivine ± spinel as near-liquidus assemblages in the  $X_{\text{CO}_2} = 0.24$  experiments between 10 and 40 kbar (Fig. 1a) is in accordance with these minerals as early-formed microphenocrysts in the rock. At depths of 45–50 km, corresponding to pressures of less than 10–14 kbar, a more pronounced degree of cooling would result in crystallization of assemblages characteristic of those found in the kimberlite matrix except for ilmenite, phlogopite, apatite, and serpentine. Of these minerals it is likely that phlogopite crystallized by reaction with olivine and liquid (Luth, 1967) at some depth corresponding to a pressure less than that employed in the  $X_{\text{CO}_2} = 0.24$  experiments. In the aphanitic kimberlite, phlogopite crystallized later than monticellite, forming poikilitic plates flanking the monticellite (Shee, 1986). Based on the model of  $P$ - $T$  cooling

at  $X_{\text{CO}_2} = 0.24$ , calcite would form in the aphanitic kimberlite below 1100 °C at a maximum depth slightly greater than 35 km. This is in agreement with the temperatures of formation of calcite in other kimberlites (McMahon et al., 1979).

The mechanism for the disappearance of clinopyroxene and incoming of monticellite with decreasing temperatures in the experimental runs is unknown. The apparent incompatibility of clinopyroxene and monticellite in the  $X_{\text{CO}_2} = 0.24$  experiments may explain why these minerals do not occur together in natural kimberlites (Mitchell, 1986, p. 245). Mitchell (1986, p. 353, 377) attributed the appearance of either mineral to local variation in silica activity. The results of the  $X_{\text{CO}_2} = 0.24$  experiments suggest that monticellite may form as deep as 45 km and between about 1100 and 1250 °C—values greater than those likely for monticellite to have formed under crustal conditions in which the  $\text{SiO}_2$  activity is higher.

The composition of the minerals in the rock and the phases that crystallized in the experiments is dissimilar as the majority of the kimberlite minerals, except for the olivine microphenocrysts, probably equilibrated at lower-pressure and lower-temperature conditions than those of the experiments in which all crystals formed in the presence of liquid. Variations in the  $f_{\text{O}_2}$  conditions in the experiments relative to those under which the natural kimberlite formed also affect the chemistry of the phases. The experimental  $f_{\text{O}_2}$  used is within the range of that of the experiments on peridotite composition (cf. Olafsson and Eggler, 1983) but may be higher than those suggested for the Benfontein kimberlite sills (McMahon et al., 1979).

**Olivine.** The 100Mg/(Mg + Fe) ratios of the olivines in the experiments (Table 2) are higher than those of microphenocryst olivines in the aphanitic kimberlite in which the olivine cores are about 91 and the rims are 89 (Shee, 1986). In contrast, olivines in the experiments at  $X_{\text{CO}_2} = 0.24$  have 100Mg/(Mg + Fe) ratios ranging from about 95–96 at high temperatures to 89–91 at lower temperatures (Table 2). The higher ratios of 100Mg/(Mg + Fe) in the olivines in the experiments may be caused by (1) loss of Fe from the charge by alloying of Fe with the Pt and AgPd capsules used in the experiments; (2) lower  $f_{\text{O}_2}$  in the experiments relative to that during the ascent of the kimberlite magma, which would result in a shift in the  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  equilibrium and thus in higher ratios of 100 Mg/(Mg + Fe) in the olivines; and (3) different  $P$ - $T$  conditions of crystallization of the olivine in the experiments relative to those in nature.

The effects of these variables are difficult to assess. However, loss of Fe by alloying was probably not appreciable for the short run times used, as five runs between 1400 and 1350 °C at 10 kbar done with Pt capsules that had not been Fe-soaked gave 100Mg/(Mg + Fe) ratios for olivine that were similar to those of olivines in other runs in Fe-soaked Pt capsules.

**Monticellite.** The composition of the monticellite crystallized in the experiments is comparable to the few mon-

ticellite analyses from kimberlites listed by Mitchell (1986). The 100 Mg/(Mg + Fe) ratios in monticellite in the experiments are slightly lower than those for monticellite from the aphanitic kimberlite in which core and rim analyses gave  $100\text{Mg}/(\text{Mg} + \text{Fe}) = 93$  (Shee, 1986). These slightly lower ratios of 100Mg/(Mg + Fe) cannot be attributed either to Fe loss or  $f_{\text{O}_2}$  effects during the experiments. Analyses of monticellite crystallized in the experiments have slightly greater FeO,  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  than the analyses for monticellite in the rock (Shee, 1984).

**Spinel.** Spinel in the experiments are aluminous magnesioferrite and aluminous magnesiochromite and differ from the spinels in the aphanitic kimberlite, which have normal magmatic trends of Cr-rich, Ti-poor (chromite) cores to Ti-rich, Cr-poor (titanomagnetite) rims (Shee, 1984). In contrast to spinels in the aphanitic Wesselton and other kimberlites, there is no correlation between temperature or degree of evolution and Cr/Ti ratios in the spinels produced in the experiments. If the  $f_{\text{O}_2}$  in the experiments is higher than that involved in the evolution of the aphanitic kimberlite, the stabilization of  $\text{Fe}^{3+}$  might result in the reduction of Cr/(Cr + Al +  $\text{Fe}^{3+}$ ) in the octahedral site of the spinel crystallized in the experiments. The higher Al in the spinels in the experiments relative to those in the rock may be a consequence of spinel crystallizing in the experiments without any other major Al-bearing mineral. In contrast, spinel occurs with minor phlogopite in the matrix of the rock.

#### Implications for the genesis of the aphanitic kimberlite

The suprasolidus phase relations and the paragenesis given in this study have important implications to the genesis of the very  $\text{SiO}_2$ -poor aphanitic kimberlite (Table 1) found at Wesselton. The most significant differences in the chemistry of the aphanitic kimberlite and Group I kimberlites, including samples from Wesselton (Shee, 1986) are in CaO, MgO, and  $\text{SiO}_2$ . These differences are shown on the CMS system (cf. O'Hara, 1968) as plotted in Figure 2. This system includes most of the important mineral constituents in kimberlites and has been used in phase-equilibrium studies with added  $\text{CO}_2$  to model kimberlite magma genesis (Wyllie and Huang, 1976). The aphanitic kimberlite (Fig. 2, point A) plots on the CaO side of the olivine-clinopyroxene join whereas the more  $\text{SiO}_2$ -rich varieties plot close to this join (Fig. 2, area B). These differences are reflected in the phase relations in the present study relative to those inferred from experiments in the more  $\text{SiO}_2$ -rich parts of the CaO-MgO- $\text{SiO}_2$ - $\text{CO}_2$  system that involve orthopyroxene at 1150 °C and 30 kbar (Wyllie and Huang, 1976; Brey et al., 1984; Boettcher et al., 1980; Huang and Wyllie, 1984; shown in Fig. 3). The kimberlite composition used by Eggler and Wendlandt (1979) was richer in  $\text{SiO}_2$ , comparable to the  $\text{SiO}_2$ -rich varieties (Fig. 2, area B). In Figure 3, the majority of kimberlites, including the composition of Eggler and Wendlandt (1979), project within the olivine + or-

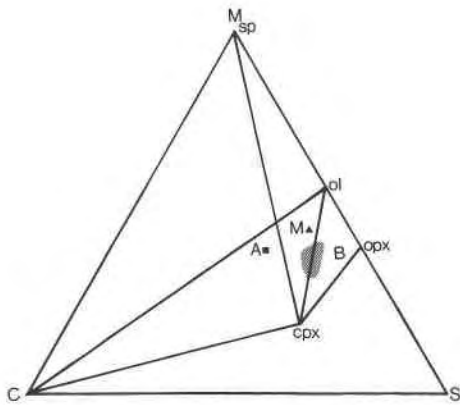


Fig. 2. Kimberlite compositions plotted on the CMS system (see O'Hara, 1968). A, aphanitic Wesselton kimberlite used in present study; M, macrocrystic Wesselton kimberlite; B, range of average kimberlite compositions from Mitchell (1986, Table 7.3, analyses 1, 3, 4, 5). Abbreviations: opx, orthopyroxene; others as in Fig. 1.

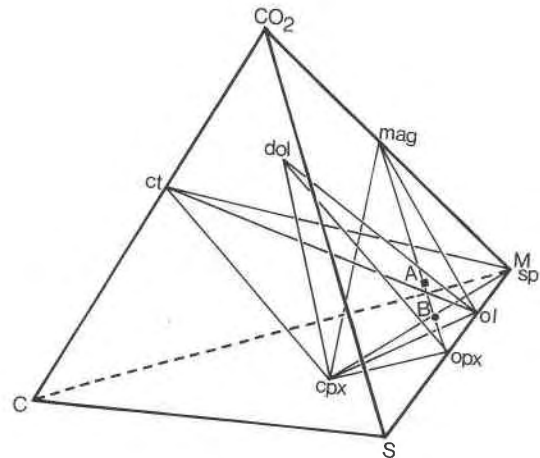


Fig. 3. Comparison of composition of aphanitic Wesselton kimberlite (A) and average kimberlite compositions (B) from Mitchell (1986, Table 7.3, analyses 1, 3, 4, 5) plotted in the CMS-CO<sub>2</sub> system. Inferred stable joins at 1150 °C, 30 kbar are taken from Wyllie and Huang (1976) and this study. Abbreviations: mag, magnesite; others as in Figs. 1 and 2.

thopyroxene + clinopyroxene + dolomite phase volume from the CO<sub>2</sub> apex whereas, on a similar projection, the aphanitic kimberlite plots within the olivine + clinopyroxene + spinel + calcite phase volume.

The SiO<sub>2</sub> undersaturation of the aphanitic kimberlite relative to many other kimberlites may account for the absence of orthopyroxene in all experiments on this composition (Fig. 1) and for the only carbonate mineral in the  $X_{\text{CO}_2} = 0.52$  runs being calcite up to 30 kbar and dolomite at 35 kbar (Fig. 1b). Experiments in the olivine + clinopyroxene + orthopyroxene + dolomite phase volume, representing a carbonate-bearing lherzolite, indicate a possible eutectic reaction relationship involving enstatite or enstatite + magnesite (Eggler and Wendlandt, 1979; Wyllie and Huang, 1976). Although this reaction does not preclude the more SiO<sub>2</sub>-undersaturated aphanitic kimberlite, plotting in the olivine + clinopyroxene + spinel + calcite phase volume (Fig. 3), from being derived by crystal fractionation of olivine ± orthopyroxene ± clinopyroxene from partial melts of carbonated lherzolite, it suggests an alternative possibility that the aphanitic kimberlite need not be a product of crystal fractionation of a liquid in equilibrium with orthopyroxene at mantle depths as suggested by Mitchell (1986, p. 13). Indeed the aphanitic kimberlite is not necessarily an evolved species as implied by Mitchell (1986, p. 46) on the basis of his textural genetic classification modified from the classifications of Skinner and Clement (1979) and Clement (1982). Our experiments and the composition of the aphanitic kimberlite relative to proposed stable mantle assemblages suggest that the aphanitic kimberlite is a primitive but not necessarily primary kimberlitic magma.

The composition of the macrocrystic kimberlite at Wesselton (Table 1; Fig. 2, point M) is comparable to that of the more SiO<sub>2</sub>-rich kimberlites (Table 1; Fig. 2,

area B) and plots near the olivine-clinopyroxene join in the CaO-MgO-SiO<sub>2</sub> system. These compositional relationships indicate that it is unlikely that fractionation of olivine, orthopyroxene, or clinopyroxene from the macrocrystic kimberlite magma would produce a composition as SiO<sub>2</sub> poor as that of the aphanitic kimberlite. However, the macrocrystic kimberlite could be a product of mixing of aphanitic kimberlite magma with a more SiO<sub>2</sub>-rich xenolithic material of crustal origin or could evolve by mixing and assimilation of aphanitic kimberlite magma with depleted harzburgitic mantle. The latter possibility implies that under CO<sub>2</sub> + H<sub>2</sub>O conditions different from those in the present experiments, olivine and orthopyroxene might be the stable phases.

#### Nature of carbonates and their role in the genesis of aphanitic kimberlites

Stable carbonate phases in upper mantle of lherzolite composition (i.e., containing orthopyroxene as an essential mineral) are dolomite and/or magnesite (Wyllie and Huang, 1976; Olafsson and Eggler, 1983; Brey et al., 1984). In the present experiments, calcite is the common carbonate phase coexisting with olivine, clinopyroxene, spinel, and liquid but never with orthopyroxene. The presence of calcite in these experiments may be a consequence of the extreme SiO<sub>2</sub> undersaturation of the aphanitic kimberlite relative to other varieties (Figs. 2, 3) or possibly to a reaction between dolomite and orthopyroxene to produce calcite, olivine, and CO<sub>2</sub> at higher pressures than we used.

In the  $X_{\text{CO}_2} = 0.52$  experiments, the occurrence of dolomite at 35 kbar may be due to a reaction such as dolomite + liquid to produce spinel + calcite, although this cannot be confirmed on the basis of the experiments. The absence of orthopyroxene + dolomite in these experi-



ments makes it improbable that dolomite is produced by reaction of clinopyroxene + magnesite to give dolomite + orthopyroxene at lower pressures as determined by Brey et al. (1984). Such a reaction implies that orthopyroxene occurs in these experiments at pressures greater than 35 kbar.

Wyllie (1980), Eggler and Wendlandt (1979), Wendlandt and Eggler (1980), and Olafsson and Eggler (1983) have proposed that partial melting of a magnesite-phlogopite-bearing garnet lherzolite at depths greater than 150 km might produce a kimberlitic magma. The composition of such a source is represented by the olivine + orthopyroxene + clinopyroxene + magnesite phase volume in the MCSCO<sub>2</sub> system (Fig. 3). If partial melting of a magnesite-phlogopite-bearing garnet lherzolite source is of eutectic type in which magnesite and phlogopite may be the early-melting phases (Eggler and Wendlandt, 1979; Olafsson and Eggler, 1983), the melt would coexist with a residual lherzolite assemblage (olivine + orthopyroxene + clinopyroxene + garnet) and would be represented by the olivine + orthopyroxene + clinopyroxene + magnesite phase volume (Fig. 3). Between 30 and 40 kbar, dolomite replaces magnesite by reaction with clinopyroxene (Brey et al., 1984) as discussed above, and the composition would then be represented by the olivine + orthopyroxene + clinopyroxene + dolomite phase volume, which may also melt to a pseudo-eutectic composition (Eggler and Wendlandt, 1979).

The present experiments were done at too low a pressure to permit us to establish unequivocally the source of the aphanitic kimberlite magma. However, on the basis of the absence of orthopyroxene in the present runs and its presence in those of systems used to model kimberlites at higher pressure (Eggler and Wendlandt, 1979; Wendlandt and Eggler, 1980; Olafsson and Eggler, 1983), it is possible that the aphanitic kimberlite, with a composition plotting outside of the olivine + orthopyroxene + clinopyroxene + dolomite or olivine + orthopyroxene + clinopyroxene + magnesite phase volume (Fig. 3), did not originate as a partial melt of a carbonate-bearing garnet lherzolite source.

Neither magnesite nor dolomite has been reported in xenoliths of mantle origin, but the presence of calcite as an inclusion in diamond (Leung, 1984) and as inclusions in pyrope xenocrysts (McGetchin and Besancon, 1973) precludes the possibility that all calcite in kimberlites is a late-stage mineral and suggests that CaCO<sub>3</sub> may be present in the upper mantle. Calcite is also present in veined peridotite and pyroxenite nodules, with the veining considered to be produced under mantle conditions (cf. Harte, 1978; Lloyd and Bailey, 1975). The pyroxenite nodules are often without orthopyroxene. Calcite is also the most common carbonate in the Benfontein sill kimberlites (Dawson and Hawthorne, 1973), which have very low SiO<sub>2</sub> contents similar to the aphanitic kimberlite.

The present study suggests that it is possible to derive SiO<sub>2</sub>-poor kimberlite magma from a calcite-bearing source that does not include orthopyroxene. On the basis of the

correlation of CaO and CO<sub>2</sub> in kimberlites, Bailey (1984) proposed that kimberlite magmas formed from sources that had CaCO<sub>3</sub> added prior to melting. Our study and the composition of the aphanitic kimberlite support Bailey's (1984) concept that an ultrametasomatized mantle source, in which CaCO<sub>3</sub> + olivine can coexist, may melt to form very SiO<sub>2</sub>-undersaturated kimberlite magma as represented by the aphanitic Wesselton kimberlite.

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