Petrochemical and Thermodynamic Evidence on the Origin of Kimberlites

L.L. Perchuk and V.I. Vaganov
Institute of Experimental Mineralogy of the USSR Ac. Sci., Chernogolovka, Moscow District, USSR

Abstract. The petrochemistry of kimberlites from Yakutia and Lesotho has been studied using a silicate melt model with the SiO_2, CO_2 and H_2O derivatives as the main anions.

A model has been developed, according to which the dissolution of H_2O in an ultramafic melt results in orthosilicates ($H_2SiO_4^{-2}$, $H_3SiO_4^-$, H_4SiO_4 etc.) rather than metasilicates, while the dissolution of CO_2 produces additional hydrocarbonate complexes. It suggests that at high $P_{CO_2}^{fl}$, and where the orthosilicic calcium salt clusters are likely to be present in the magma, the kimberlite melt can break down into carbonate and silicate liquids. Therefore, the composition of kimberlite magma will be determined by the H_2O/CO_2 ratio under the relatively constant fluid pressure. This can be seen from the distinct 'fluid' trend in the $H_2O-CO_2-SiO_2$ diagram for the Yakutia and Lesotho diamond-bearing kimberlites. The H_2O/CO_2 ratio changes with the liquidus temperature along this trend (Perchuk and Vaganov 1977) which suggests that liquid immiscibility predominates over the simple CO_2 solubility in the melts of kimberlite composition. The well-known Boyd's diagrams for the equilibrium PT-conditions in peridotites have been applied along with new experimental data to natural Cpx and Opx, and the PT-parameters were correlated for peridotite inclusions in kimberlite pipes in Yakutia and Lesotho. The liquidus temperatures for the extrapolated area of these correlations gave depths (pressures) at which kimberlite magmas are formed (200–250 km).

The hypothesis on SiO_2 partitioning between the melt and the fluid was used to calculate the composition of dry initial kimberlite which characterised the average mantle composition: SiO_2 – 45.12; TiO_2 – 2.49; Al_2O_3 – 3.58; Cr_2O_3 – 0.12; FeO – 9.32; MnO – 0.16; CoO – 0.11; MgO – 23.47; CaO – 13.44; Na_2O – 0.20; K_2O – 1.12; P_2O_5 – 0.69; S – 0.18; sum – 100 wt.%. This kimberlite is close to wehrlite in composition.

Introduction

Diamond-bearing kimberlites are closely associated with the deep horizons of the upper mantle. This has attracted many geologists to study the geology, petrography and mineralogy of kimberlites and inclusions, the absolute and relative age of kimberlites and inclusions, the composition of gas extracts from diamonds.

A number of experiments relevant to the genesis of kimberlites has been reported recently (Ito et al. 1968; Kushiro 1973; Boettcher et al. 1975; Maale and Wyllie 1975; Mysen and Boettcher 1975a, b; Wyllie and others 1977). CO_2 solubility increases with P at all pressures but becomes important at 5 kb.: at pressures above 5 kbs, the CO_2 solubility in peridotite melts increases as well as the H_2O solubility. Moreover, the H_2O/CO_2 ratio governs the differentiation path of peridotite melts: at $X_{H_2O}^V > 0.6$ and pressures 20 kbs, andesite magmas are produced; at $X_{H_2O}^V < 0.6$ ($X_{CO_2}^V > 0.4$) kimberlite-carbonatite magmas and relative olivine melilitites and nephelinites can generate as the partial melting products of the peridotite mantle (Bray and Green 1975, 1976). That is the first conclusion from experiments.

These studies have contributed a good deal to an understanding of the nature of kimberlites, and a number of interesting hypotheses have been put forward (Harris and Middlemost 1970; O'Hara and Yoder 1967; Dawson 1972; MacGregor 1970). Many petrologists agree about the mantle origin of kimberlite melts and the magmatic nature of their intrusions

into the upper horizons of the crust. For the most part, discussions are concerned with the mechanism of emplacement, migration and consolidation of kimberlite magmas, the sources of H_2O and CO_2 in crystallization products. It is as yet impossible to establish the origin of carbonatite and hydrate (hydrosilicate) mineralisation in kimberlite pipes with any degree of assurance. However, there has been growing support in recent theoretical and experimental papers for the theory that water and CO_2 are primary in kimberlites (Boettcher et al. 1975; Wyllie and Huang 1975; Perchuk 1973; Marshintsev et al. 1976; Kresten 1973; Kresten and Paul 1976; Hunt 1976). This is a crucial question, for it is fundamental for our understanding of the nature of kimberlites.
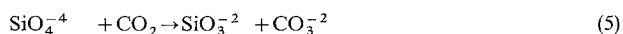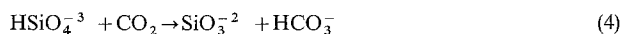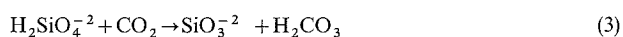
Statement of the Problem. Theory. Methods

First, a relationship between the silica-aqueous and carbonate part of kimberlites needs to be proved, for then kimberlites will give information on the composition of mantle fluid and may be regarded as a direct product of the crystallization of liquids with varying $H_2O:CO_2$. This could only happen if water and carbon dioxide enter into the minerals in almost the same proportion approximately as in the melt oversaturated in fluids (including autometamorphism in a closed chamber). We can suggest the following model.

The dissolution of water in the melt will favour the formation of orthosilicate rather than metasilicate complexes, for example:

$$SiO_3^{-2} + H_2O = H_2SiO_4^{-2};\qquad(1)$$

$$H_2SiO_3 + H_2O = H_4SiO_4.\qquad(2)$$

And the relative acidity of the melt will decrease, for metasilicic acid is stronger than orthosilicic acid (Ramberg 1952) and because the dissolution of 'neutral' water will decrease the bulk concentration of silicic anion complexes.

The reverse is likely to take place at high pressure (to 40 kbs) of carbon dioxide

$$H_2SiO_4^{-2} + CO_2 \rightarrow SiO_3^{-2} + H_2CO_3\qquad(3)$$

$$HSiO_4^{-3} + CO_2 \rightarrow SiO_3^{-2} + HCO_3^-\qquad(4)$$

$$SiO_4^{-4} + CO_2 \rightarrow SiO_3^{-2} + CO_3^{-2}\qquad(5)$$

$$H_4SiO_4 + CO_2 \rightarrow H_2SiO_3 + H_2CO_3.\qquad(6)$$

In connection with a model presented earlier (Perchuk 1971), a rise in P_{CO_2} in an equilibrium gaseous phase will result in carbonatisation of calcium salt clusters of orthosilicic acid in the melt. High CO_2 affinity for Ca and fugacity coefficient of the carbonate component might cause the melt to break down

into a carbonate-rich fluid or liquid and a silicate liquid. This model has been confirmed in experiments (Koster van Groos 1975; Koster van Groos and Wyllie 1973; Orlova and Ryabchikov 1977).

On the other hand, a partial melting of peridotite mantle at constant high H_2O and CO_2 pressure, i.e., at $P_{H_2O+CO_2} \geqq 30$ kbs, may produce basalts and kimberlites. Fractional crystallization of these magmas gives a residual carbonatite liquid with a relatively low crystallization temperature (Wyllie and Huang 1975; Huang and Wyllie 1974). This should be kept in mind in considering natural kimberlite emplacement. The miscibility of SiO_2, CO_2, and H_2O that behave as anions in melts, influences markedly the mode of fractional crystallization of deep-seated magmas. Kadic et al. (1972) showed that at constant T and P_{fl} the H_2O solubility in the melt decreased with increasing CO_2 mole fraction in an equilibrium gas phase. This is the second important conclusion from experimental data. The third conclusion from experiments (Kadic et al. 1973) is that the H_2O solubility in an equilibrium melt increases with the overall pressure, at constant T and $X_{H_2O}^{fl}$ in a gas phase, containing CO_2 too.

Consequently, the carbonate to silicate ratio in the given kimberlite pipe may indicate a degree of fractional differentiation of the primary, deep-seated magma, which is a function of a temperature at $P=$ const. The H_2O/SiO_2 in kimberlite magma depends mainly on pressure of carbonate-silicate magma differentiates at a certain depth; the H_2O/SiO_2 ratio will be constant at $P=$const., while the $CO_2/(H_2O + SiO_2)$ ratio decreases inversely with the temperature.

It should be noted that all experimental studies have been based on the peridotite model of the upper mantle, and kimberlites are regarded as products of a partial melting of the mantle. However, kimberlites may reflect the composition of the mantle more accurately than peridotites or pyrolite do. This is also a purpose of our study.

The above effects may be used in deciphering thermodynamic conditions under which kimberlite magmas are generated. Both theory and experiment imply that the differentiation of aqueous carbonate – silicate magma reflects the temperature trend. Therefore, we have attempted to find the liquidus temperature of kimberlites by a thermometric method allowing for the bulk chemical compositions of the rocks with olivine on the liquidus (Perchuk 1976; Perchuk and Vaganov 1977). The temperature of each rock-sample is found from the equation[1]:

---

[1]   We do not discuss it here because the question was treated in much detail in Perchuk and Vaganov (1977, in English)

$$t° = 1039.62 + 43.736\, X_{Mg}^{Ol} + 353.86\, y + 0.001182(100\, X_{Mg}^{Ol})^2$$
$$+ 0.125186\, y(100\, X_{Mg}^{Ol})^2 - 0.000031\, y(100\, X_{Mg}^{Ol})^3, \tag{7}$$

where $X_{Mg}^{Ol} = $ Mg: (Mg + Fe^2 + Mn) in olivine, and $y = $ (Mg + Fe + Mn): 0.5 O_2 are in atomic ratios. Where the composition of the olivine is not known, the Mg mole fraction will be given by $X_{Mg}^{Ol} = 3.15\, X_{Mg}^{r}/(1 + 2.15\, X_{Mg}^{r})$, where X_{Mg}^{r} is the Mg/Fe + Mg + Mn ratio of the rock. This method was within experimental accuracy for dry silicate systems at $P = 1$ atm. After allowing for H_2O (and CO_2), the T was found to decrease with the P_{fl}. However, this method is only valid in quite specific conditions. First, it has been worked out for 1 atm. experiments, and then there is no accurate quantitative evidence on the relationship between H_2O and CO_2 concentration in a rock and a temperature drop although some good agreement with experimental data have been found (Perchuk and Vaganov 1977). Therefore, this pattern of $t°$ C calculation provides a qualitative rather than quantitative temperature indicator.

Pressures at which kimberlite magmas were formed are not yet accessible to direct measurement. However, assuming that the volatile to SiO_2 ratios in kimberlites are essentially similar to those in parent magma, Kadic's effect (1973) – the higher the total pressure $P_{fl} = P_{H_2O} + P_{CO_2}$ the greater the H_2O solubility in a melt, – may apply. Mysen (1975) reported on this effect to $P_{fl} = 30$ kbs. The H_2O/SiO_2 ratio in kimberlite is used as an index for each given T:

$$\left(\frac{RT\,d\ln X_{H_2O}^{Lig}}{dP_{fl}} \right)_T \approx V_{H_2O}^{Lig} \tag{8}$$

$$\ln X_{H_2O}^{Lig} \approx (\ln X_{H_2O}^{Lig})_{P_{fl}^0} + \frac{1}{RT} \int_{P_{fl}^0}^{P_{fl}} V_{H_2O}^{Lig}\, dP_{fl} \tag{9}$$

where $X_{H_2O}^{Lig}$ is the water mole fraction in a silicate melt, $V_{H_2O}^{Lig}$ is the H_2O molal volume in the melt, R is the gas constant, T is the absolute temperature.

The presence of diamonds implies that kimberlites were formed at extremely high pressures ($P_{fl} > 40$ kbs). Diamonds may also contain a long-term record of the fluid regime via the reactions:

$$2CO = C + CO_2 \tag{10}$$

$$CH_4 + CO_2 = 2C + 2H_2O \tag{11}$$

$$C + 1/2\,O_2 = CO \tag{12}$$

$$C + O_2 = CO_2. \tag{13}$$

Increase in the CO_2 fugacity might as easily result in diamond dissolution (reaction (10)), as in the stabilization (reaction (11) and (13)). Analyses of a kimberlite diamond by Melton and Giardini (1975) gave the following gas composition: H_2O (42.3%), CO_2 (14.4%) and H_2, CH_4, CO, and N_2 accounting for the remaining 43.3%.

It seems that at depths of greater than 120 km, diamond forms predominantly by reaction (11). If a diamond is carried upward, the kimberlite magma would move faster than the reaction in the leftward shift, and the diamond will be preserved upon rapid crystallization of the melt. Otherwise, the diamond will dissolve and this will be reflected in the H_2O: CO_2 ratio in kimberlites. Finally, reactions (12), (13) will predominate during metasomatism: the greater the metasomatic changes, the lower the diamond content in kimberlite pipes.

The above theory and methods of evaluating thermodynamic regime of kimberlite emplacement were used to study the petrography of diamond-bearing kimberlites in Yakutia. The study was based on complete silicate analysis for 150 pipes. Average analyses were calculated for each pipe or for the most important kimberlite variations in each pipe. More than 1,000 complete chemical analyses of kimberlites and more than 100 analyses of the peridotite inclusions, using kimberlites from Lesotho are given for comparison (Gurney and Embrahim 1973).

Results

Studies bearing on mineralogy and petrology of kimberlites show that these ultramafic rocks crystallize at great depths in zones of magma generation (Bobrievich et al. 1959; Francesson 1968). Therefore, the liquidus temperature of kimberlite is an important parameter at every given pressure. These temperatures (and the H_2O/SiO_2 values as the indices of relative pressure) were calculated by Eq. (7) from petrochemical data for seven kimberlite fields in Yakutia: three diamond-bearing Palaeozoic Provinces (Daldyn, Alakit, Muna), and four Mesozoic provinces (Prilensk, Luchakansk, Kuoisk, and Kuonapsk).

According to the above theory, both the composition and the PT-conditions at which kimberlite magma is formed are determined by the water and CO_2 regime, and reaction (10) where diamonds are present. Therefore, it seems useful to consider kimberlites in relation to SiO_2 CO_2 and H_2O. If there is a regular relationship between these three components and TP of the liquidi, the said kimberlites must have been produced by the crystallization of a single aqueous-carbonate-silicate magma with subsequent spontaneous automorphism. Here, $(H_2O + CO_2)/SiO_2 \approx$ const., for magmatic and autometamorphic processes in a closed chamber.

Figure 1 shows that diamond-bearing kimberlites have been formed during crystallization of a water-
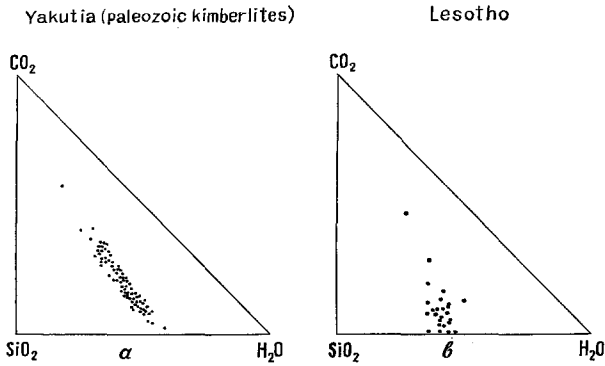
Yakutia (paleozoic kimberlites)   Lesotho

Fig. 1a and b. The mole ratios H_2O, CO_2, and SiO_2 in the diamond-bearing kimberlites from Lesotho (the data by Gurney and Ebrahim 1973) (b) and Yakutia (a)

saturated carbonate-silicate magma with varying CO_2 (carbonatite) content and slightly varying SiO_2/H_2O ratio. If these rocks reflect crystallization differentiation of the magma (Wyllie and Huang 1975; Brey and Green 1975, 1976), a certain relationship will show up in the diagram $X^*_{CO_2} = CO_2 : (H_2O + SiO_2 + CO_2)$ vs temperature [from Eq. (7)]. In other words, the shift of figurative points towards the CO_2 vertex of the triangle will represent the temperature through during differentiation of the carbonate-silicate magma. The $X^*_{CO_2}$-T diagrams for every Palaeozoic kimberlite area (Fig. 2) show the relationship between these parameters.

The patterns shown in Figs. 1 and 2 could only have developed after the bulk fluid composition had set up over a relatively limited volume of rocks in the mantle, and after the fluid-charged kimberlite magma had ascended quickly into the upper levels of the crust and crystallized as described. It is only where these conditions have been met, that the system will provide information on the very distinct relations between the major anion groups in a carbonate-silicate melt. We discussed just one oportunity to explain the geneses of kimberlitic magma – its carbonate and silicate parts. However, there is another way – liquid immiscibility, – the problem is discussed briefly in several papers (Willey and others 1977).

The melting systems at very high values of $P_{fl}T$ parameters in the liquidus area have not been investigated as yet. The hypothesis on carbonatization of basaltoid melts at high P_{CO_2} involving the breakdown of liquid into carbonate and silicate parts (Perchuk 1971, 1973) accounts for the nature of the assemblage ijolite-carbonatite.

A high chemical affinity of CO_2 for CaO is responsible for the liquid-high volatile liquid esxolution of kimberlite melts. This can be shown schematically
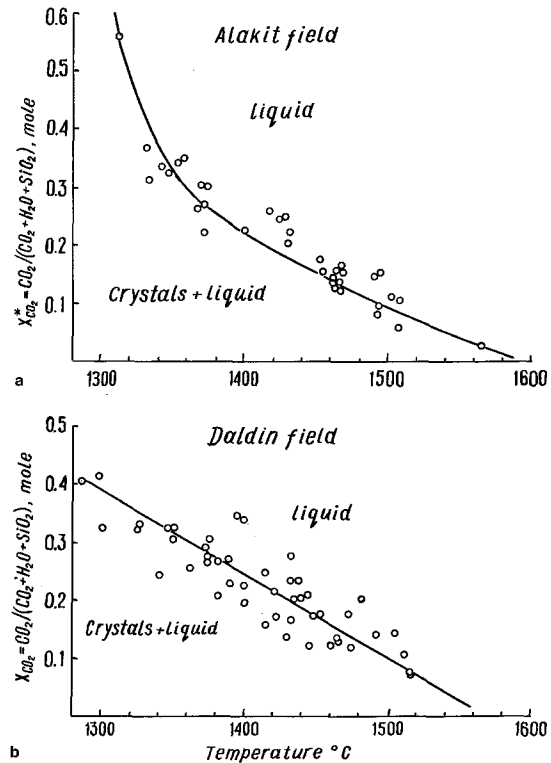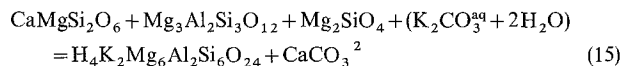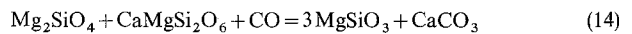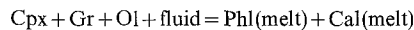

Fig. 2a and b. Drop in the liquidus temperatures of the Alakite and the Daldyn kimberlite fields in Yakutia with increasing CO_2 content in the melting rock systems (liquid+fluid)

as a rightward shift of reactions between ortho- and metasilicate clusters under the effect of CO_2:

$$Mg_2SiO_4 + CaMgSi_2O_6 + CO = 3MgSiO_3 + CaCO_3 \qquad (14)$$

$$CaMgSi_2O_6 + Mg_3Al_2Si_3O_{12} + Mg_2SiO_4 + (K_2CO_3^{aq} + 2H_2O)$$
$$= H_4K_2Mg_6Al_2Si_6O_{24} + CaCO_3 \text{ }^2 \qquad (15)$$

or

$$Cpx + Gr + Ol + fluid = Phl(melt) + Cal(melt)$$

Liquid immiscibility and carbonatization of these melts were studied on the diamond-bearing (Palaeozoic) kimberlites from Yakutia. It is evident that the intensity of the magma carbonatization is directly related to μ_{CO_2}. In other words, the rightward shift of reactions (14) and (15) cannot be confirmed unless the linear relation between the CO_2 mole fraction and CaO content in the melt has been established. This relationship is readily obtained from chemical analyses through the equation:

$$CaO = 67.69 \, X^*_{CO_2} \text{ wt. } \%$$

at least to 20% CaO. However, a number of pipes show a positive deviation from this relationship. This
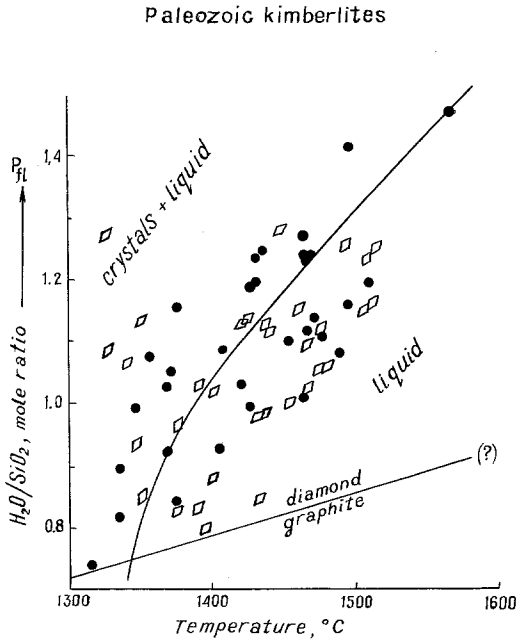
Paleozoic kimberlites

Fig. 3. The position of the liquidus of Palaeozoic kimberlites from Yakutia in the diagram (H_2O/SiO_2)–temperature

means that at very high $X^*_{CO_2}$, magnesite-siderite liquid can be formed to enrich the calcite liquid. Reactions (14) and (15) may reflect metasomatic carbonatization of kimberlites, though this process is not typical of any of the ultrabasic complexes close to kimberlites in composition. Alternatively, carbonatites re-

lated to the formation of ultramafic alkali rocks are commonly referred to as the primary rocks; moreover, the kimberlites, being more enriched in diamond, suggest that they have not undergone the usual metasomatic transformations.

All the points in Fig. 3 for the Palaeozoic Yakutian kimberlites are within relatively narrow temperature $(\Delta T \approx 200°)$ and $H_2O/SiO_2(0.8-1.2)$ limits. This means that the kimberlite magma originated within a relatively narrow depth interval. Since all the pipes are diamond-bearing, it may be that the hearths originated at $P \geq 42$ kbs. They could have originated after the more abyssal fluids had intruded this particular area of the upper mantle, heated if through H_2, CH_4, CO oxidation and saturated the melt with water and carbonatic acid. This in turn would have produced gravitational instability and caused speedy magma ascent to the surface. 'The gas drill' model may describe the mechanism of this ascent (Perchuk 1973).

If Ca content in the primary melt specifies the quantity of a carbonatite melt in a heterogenic kimberlite magma, the N_{H_2O} in kimberlites will not exceed the known H_2O solubility limits in silicate melts. The H_2O content of the Palaeozoic kimberlites is normally 6–14 wt.% (Table 2) with rare exceptions which, however, are also within the experimental water solubilities in ultrabasic silicate melts. Hodges (1974) reported 21.5 wt.% H_2O in diopside and 27% H_2O in forsterite melts. Analyses of Palaeozoic kimberlites are even more striking when compared with similar
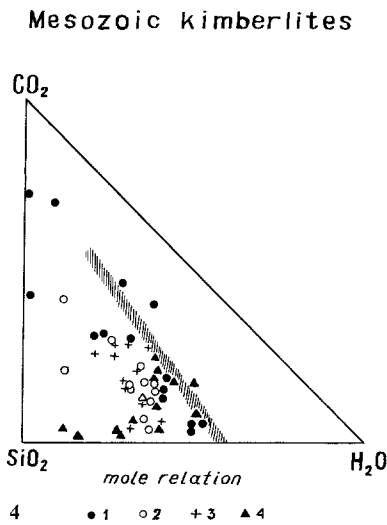

Fig. 4. The SiO_2, CO_2, and H_2O ratios of Mesozoic kimberlites in Yakutia. Kimberlite fields: (1) Prilenskoe; (2) Luchakanskoe; (3) Kuoiskoe; (4) Kuonapskoe. The hatched area is for the Palaeozoic kimberlite points ('a fluid trend')
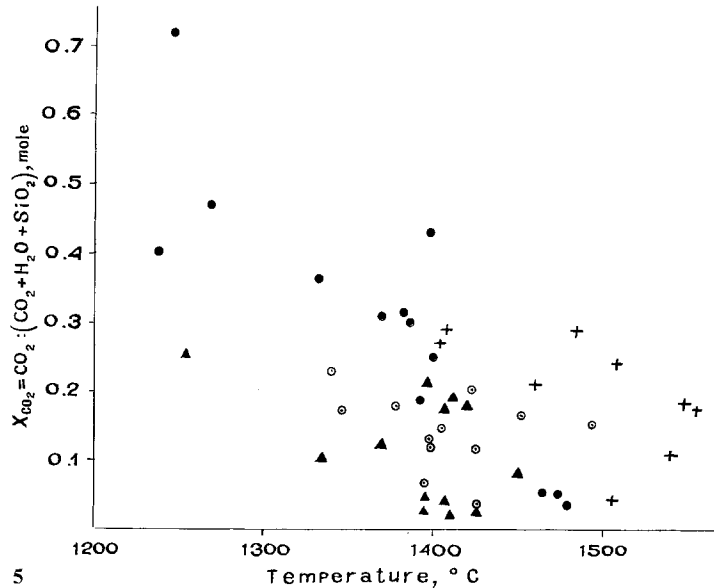
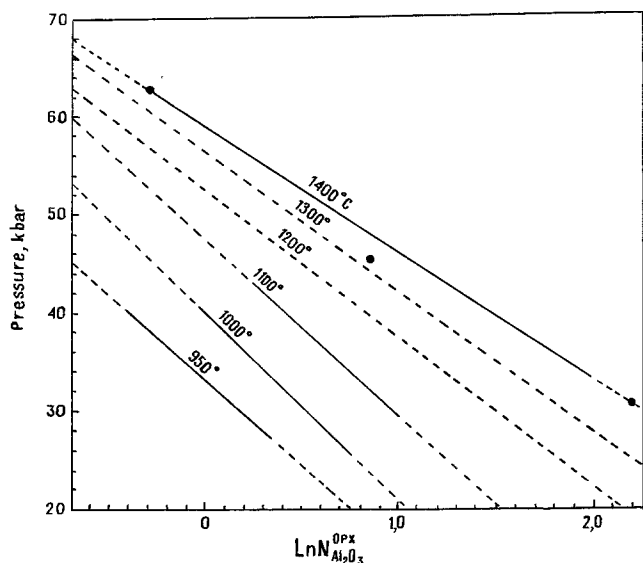**Fig. 5.** The $TX^*_{CO_2}$ diagram for Mesozoic kimberlites from Yakutia. Symbols as in Fig. 4

Fig. 6. Isothermal relationship between the logarithm of Al_2O_3 concentration in Opx and pressure. *Solid lines* from experimental data (see the text); *dash lines* from extrapolation and interpolation

Mesozoic Yakutian kimberlites. These pipes are virtually devoid of diamonds, none having any particular economic value. For these pipes, the H_2O : SiO_2 : CO_2 relationship is highly inconsistent, and diagram in Fig. 4 is a clear example, especially when comparison with the 'fluid trough' of Palaeozoic kimberlites is made. This suggests that the $X^*_{CO_2}$ correlation with temperature would either disappear or become negligible. This is confirmed in Fig. 5.

The above relationships show that the regime under which the Mesozoic kimberlites were formed differs sharply from the Palaeozoic. There are two possible explanations: differing geotectonic conditions of magma crystallization following the explosion – very often the cavity was not tight and some of the fluid escaped at the point of explosion. This mechanism is supported by the multiphase Kuoisk pipe field which is close to harzburgites in composition and contains very little carbonates and hydrosilicates.

On the other hand, the multiphase Prilensky kimberlites show a very different variance H_2O : CO_2 : SiO_2 which might indicate secondary hydrothermal

transformations in Mesozoic pipes. The absence of diamonds would seem to support this.

There are other hypotheses on the nature of Mesozoic kimberlites. Davidson (1967) concludes that the kimberlite diatremes were emplaced initially as a massive magmatic rock, which was later brecciated and fluidized and carried upwards to a higher level by a flow of gases at a relatively low temperature. However, Fig. 6 shows that Mesozoic kimberlites contain much less H_2O and CO_2 than the Palaeozoic. This implies a 'defluidization' rather than a 'fluidization' of the Palaeozoic diatremes in Mesozoic time.

The depths at which kimberlite magma may be formed have not been discussed as yet. As it was stated above, the pressure of magma formation cannot be directly measured for the lack of relevant experimental data, so the PT estimates of mineral equilibria in inclusions (xenoliths) in kimberlite pipes were used.

These estimates were based on the improved variant (Perchuk 1977a) of an earlier bi-pyroxene thermometer (Perchuk 1972), according to which the temperature is obtained from:

$$t(°C) = 10^3/(0.4305 - 0.1651 \ln K_{FeO} + 1.1072 X_{Mg}$$
$$- 1.0525 X^2_{Mg} - 0.0304 (\ln K_{FeO}) X^2_{Mg} - 273, \qquad (16)$$

where

$$K_{FeO} = \frac{wt.\% \ FeO \ in \ Cpx}{wt.\% \ FeO \ in \ Opx} \qquad (17)$$

$$X_{Mg} = 0.5(X^{Opx}_{Mg} + X^{Cpx}_{Mg}) \qquad (18)$$

$$X_{Mg} = Mg/(Mg + Fe + Mn). \qquad (19)$$

Equation (16) is valid for the high-temperature area at $P > 10$ kb.

Equilibrium pressure is usually assessed by Al_2O_3 content in orthopyroxene from garnet lherzolites (Boyd 1973; MacGregor 1974; MacGregor and Basu 1974; and others). However, we decided to use as a geobarometer experimental data on natural equilibria, though these data are limited (Akella and Boyd 1974; Green and Ringwood 1967; Hensen 1973) and inconsistent. Thermodynamic treatment showed that Akella and Boyd's results (1973, 1974) were the most accurate, but they were valid only to 44 kb and

Table 1. Preliminary results of high-pressure experiments for 1,400° C

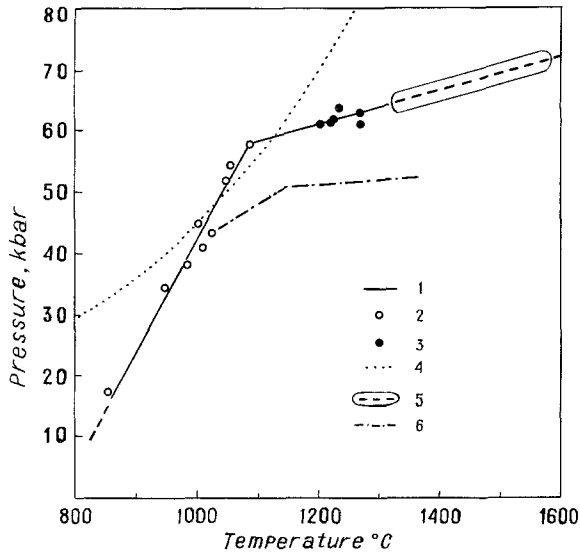| P (kbar)	Starting material	Products	$N^{Opx}_{Al_2O_3}$ (wt.%)	Number of analysis (the runs)
30	Gr + Opx + Cpx + Al	Gr + Opx + Cpx + Al	9.22	13
45	Gr + Opx + Cpx + Al	Gr + Opx + Cpx + Al	2.22	11
62	Gr + Opx + Cpx + Al	Gr + Opx + Cpx + Al	0.81	5

Fig. 7. The *PT* correlation for the upper mantle beneath the East-Siberian platform in Palaeozoic: (1) from the geothermobarometery data on mineral equilibria in granular (2) and sheared (3) lherzolite inclusions in kimberlite pipes of Yakutia; (4) the modern continental geotherm (Clark and Ringwood 1964); (5) the supposed region of kimberlite melting; (6) the geotherm calculated from the data on Matsoku pipe

Fig. 8. Pressure correlations for the H_2O/SiO_2 and CO_2/SiO_2 ratios in Alakite kimberlites

1,200° C. Using their technique we experimented with the mixtures of natural minerals from garnet lherzolites at 1,400° C and 30, 45, and 62 kb. The tests were carried out in 'anvil with-a-hole' apparatus (NL and NLT). The NLT apparatus was calibrated against the fayalite-ringwoodite equilibrium at 45 and 62 kb. The temperature accuracy was ± 5° C, pressure ± 1 kb. The minerals were placed into graphitic capsules and kept for 26 h at the given conditions. After runs the Al content in Opx was determined by microprobe analysis (Table 1).

These results together with Akella and Boyd's data (1973, 1974) were taken to derive the diagram in Fig. 6. The 1,200° C and 1,300° C isotherms were inferred from the ln $N_{Al_2O}^{Opx}$ − $1/t°$ K graph.

With the temperature obtained from (16) and the known Al_2O_3 (wt.%) content in Opx, the equilibrium pressure for garnet peridotites (lherzolites) from xenoliths in kimberlites can be found from Fig. 6. Several dozen such rocks from Southern African pipes (Nixon 1973) and 15 parageneses from xenoliths of Palaeozoic Yakutian kimberlites ('Deep-seated' xenoliths, 1975; Vladimirov et al. 1976; Sobolev 1974; Boyd et al. 1976) were chosen for the purpose. Figure 7 gives the *PT* correlations for these provinces. The Yakutian xenolith geotherm is steeper than the South African, perhaps partly because the Yakutian kimberlite pipes are farther from the oceanic crust, so that their dP/dT would be higher.
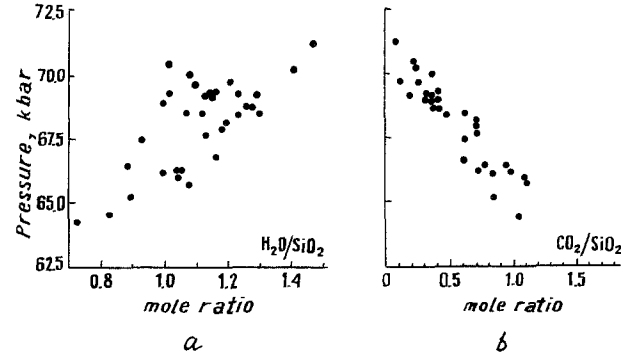
The extension of geotherm 1 is a likely area of kimberlite magma generation in the Palaeozoic under the East Siberian platform. A positive correlation between the H_2O/SiO_3 ratio and pressure in kimberlites may be verified with this geotherm. This relationship can be easily traced down for Alakite kimberlites in Fig. 8a.

A negative correlation between pressure and CO_2/SiO_2 shows up in Fig. 8b. An analysis of Figs. 2, 3, and 7 leeds to similar correlations. These correlations mean that an increase in pressure and temperature prevents ultrabasic magmas from being carbonatized and liquated into carbonate and silicate melts. The increase of temperature with depth implies that the zone of generation of carbonate magmas will disappear with depth, the most favourable range being 200 to 220 km. However, it should be remembered that the temperature estimates are only provisional and valid for one atmosphere, so that the depth estimates of kimberlite magma generation also remain provisional. Nevertheless we believe that they are not likely to differ greatly from the real values, for all liquidus curves within the TP_{fl} coordinates show minimal temperature within 20–30 kb. It can be assumed that the temperature curve rise with fluid pressure will send the kimberlite liquidus curve through the calculated $T°$ C at 70 kb.

Table 2 gives average analyses for 16 kimberlite areas, No. 17 is an average composition of monticellite-melilite picrite from Kuonap kimberlite pipes; No. 18 is the average Yakutian kimberlite. Its composition is unusual even when recalculated for a degassed sample. However, such recalculation does not apply to kimberlites. Kimberlite magma was shown to be an aqueous-carbonate-silicate melt, so that H_2O and CO_2, introduced into magma, will replace SiO_2 – the only component which forms anion groups (see Fig. 1). Consequently, the bulk composition of the upper mantle will differ from kimberlites only for silica by $H_2O + CO_2$, No. 19 in Table 2.

Table 2. Average chemical compositions of kimberlite fields in Yakutia

N	n	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Gr$_2$O$_3$	Fe$_2$O$_3$	FeO	MnO	NiO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	S	CO$_2$	H$_2$O$^+$	H$_2$O$^-$	t°C	Total
1	198	33.55	1.29	2.94	0.11	4.69	2.97	0.10	0.16	25.40	9.18	0.13	0.47	0.29	0.34	8.50	17.75	1.61	1,436	99.80
2	61	25.51	1.17	3.00	0.11	3.90	2.39	0.12	0.10	17.00	21.37	0.19	0.47	0.56	0.14	16.21	13.69	1.49	1,329	99.83
3	229	27.03	1.47	2.46	0.15	5.53	1.71	0.10	0.10	25.43	13.56	0.12	0.34	0.46	0.09	11.12	19.35	0.95	1,429	99.92
4	117	27.76	1.90	3.18	0.15	6.18	1.84	0.13	0.11	25.90	12.33	0.11	0.41	0.55	0.04	9.48	18.93	1.21	1,439	99.94
5	72	30.38	1.37	2.50	0.18	5.84	1.96	0.14	0.16	31.19	8.04	0.14	0.50	0.58	0.12	6.18	20.31	1.07	1,508	99.97
6	42	26.58	1.89	3.06	0.11	5.61	3.00	0.12	0.12	25.45	13.45	0.14	0.78	0.77	0.23	10.91	15.00	0.72	1,441	100.08
7	8	28.06	4.02	4.58	0.09	7.41	5.18	0.22	0.07	22.01	10.83	0.16	1.86	0.77	0.31	9.21	9.77	0.45	1,440	99.89
8	36	25.19	3.51	3.69	0.09	7.98	3.66	0.20	0.08	21.50	13.86	0.10	1.57	1.06	0.09	9.77	14.92	–	1,376	99.81
9	23	27.78	4.42	3.80	0.09	8.44	4.17	0.19	0.09	21.77	11.28	0.17	1.79	0.88	0.19	6.97	15.36	–	1,405	99.71
10	53	22.27	1.76	3.10	0.12	5.12	2.40	0.14	0.10	19.18	19.30	0.16	1.16	0.66	0.62	15.00	16.37	0.47	1,349	99.51
11	28	25.55	2.55	3.51	0.08	5.24	3.81	0.15	0.08	19.34	16.68	0.22	1.49	0.59	0.19	12.39	14.60	1.20	1,360	99.77
12	48	30.02	1.91	3.53	0.19	5.58	4.14	0.18	0.07	24.88	10.62	0.14	1.30	0.93	0.10	6.78	18.76	–	1,435	99.75
13	29	32.15	2.82	4.37	0.15	5.99	3.98	0.16	0.10	22.54	10.87	0.28	1.73	0.67	0.06	6.38	14.72	0.80	1,411	100.01
14	22	28.26	2.90	3.56	0.09	7.09	5.05	0.21	0.05	20.00	15.16	0.23	1.26	1.13	0.10	7.78	12.39	0.63	1,405	99.88
15	38	28.79	2.94	3.84	0.12	7.48	3.81	0.16	0.18	21.40	12.61	0.21	1.07	0.51	0.08	7.96	16.66	1.12	1,395	100.05
16	5	32.89	3.95	6.06	0.14	5.15	8.61	0.26	0.08	19.76	14.62	0.91	2.00	0.85	0.12	1.22	3.22	–	1,405	99.84
17	11	28.90	1.75	2.70	0.10	5.03	4.85	0.11	0.16	29.18	10.95	0.19	0.50	0.56	0.25	8.15	5.55	–	1,518	99.18
18	1,020	28.27	2.45	3.52	0.12	6.02	3.77	0.16	0.11	23.06	13.22	0.20	1.10	0.68	0.18	9.06	14.89	–		99.80
19	–	34.20	2.96	4.26	0.14	7.28	4.56	0.19	0.13	27.89	16.00	0.24	1.33	0.82	–	–	–	–		100.00
20	–	45.12	2.49	3.58	0.12	–	9.32	0.16	0.11	23.47	13.44	0.20	1.12	0.69	0.18	–	–	–		100.00

1 = 'Mir' pipe
2 = Malo-Botuobinski field (except the 'Mir' pipe)
3 = Alakitski field
4 = Daldinski field
5 = Verkhne-Munski field
6 = Chomurdakhski field – kimberlites
7 = Chomurdakhski field – picritic porphyrites
8 = Ulukitski field – kimberlites
9 = Ulukitski field – picritic porphyrites
10 = Merchimdenski field
11 = Prilenski field

12 = Malo-Kuonapski field
13 = Luchakanski field – kimberlites
14 = Luchakanski field – picritic porphyrites
15 = Kuonapski region
16 = Average montichellite-melilitic picrite
17 = Kuoiski field
18 = Average kimberlite of Yakutia
19 = The same, but without H$_2$O and CO$_2$, recalculated to 100%
20 = Possible composition of the upper mantle

All CO$_2$ and H$_2$O = SiO$_2$

The CO$_2$ and H$_2$O replacement of silica in the melt will either enrich the residue in the silica during partial melting or, upon complete melting of the mantle, will precipitate in the subliquidus the phases with higher silica content than kimberlite magma. Indeed, inclusions in kimberlites have always more SiO$_2$ than the host rock N 21 in Table 2. Therefore, some of the silica must dissolve in an equilibrium fluid, as has been in enstatite melting experiments under water pressure (Kushiro and Yoder 1969). The fluid will take up about 16.85 wt.% SiO$_2$, taking into consideration the equilibrium fluid – melt. The silica will be replaced isomorphously by H$_2$O and CO$_2$, the rest of H$_2$O and CO$_2$ will enter the melt, i.e., it will dissolve without remarkable changing the ratios of other components. All these figures are within the gas solubility range in the melt and silicate solubilities in the fluid.

Now that kimberlites have been defined as products of water-silicate-carbonate magma crystallization, there remains to establish not only the nature of this magma, but the primary mantle composition as well. It was shown (Perchuk and Vaganov 1977)

that basalt series originate from the partial melting of mantle rocks at $N_{SiO_2}^m \approx 43$ wt.% and $N_{Na_2O}^m + N_{K_2O}^m = 1.2$ wt.% or, allowing for water, at $N_{H_2O}^m + N_{SiO_2}^m \approx 44.5$ wt.%, $N_{Na_2O}^m + N_{K_2O}^m = 1.3$ wt.%. The average mantle composition in Table 2 gives $N_{SiO_2} = 45.12$ wt.% and $N_{Na_2O} + N_{K_2O} = 1.3$ wt.% – the most striking coincidence which has only become possible owing to extensive, statistically reliable evidence on the petrochemistry of basalts and kimberlites.

Equations (10)–(13) relate the oxidation degree of fluids and free carbon in kimberlites. Although it has been shown that diamond-bearing in kimberlites depends on a number of conflicting factors, the relationship is fairly distinct in certain kimberlite areas. Taking a very rough approximation, the occurrence of diamonds in the Daldyn pipes will be proportional to the degree of reduction of fluid and to the depth of kimberlite magma generation. The reduction-oxidation degree of the magma is found from the Fe$_2$O$_3$/FeO ratio, the depth (pressure) – from the H$_2$O/SiO$_2$ ratio. Denoting Fe$_2$O$_3$/FeO and H$_2$O/SiO$_2$ as (Fe) and (H), respectively, we shall have
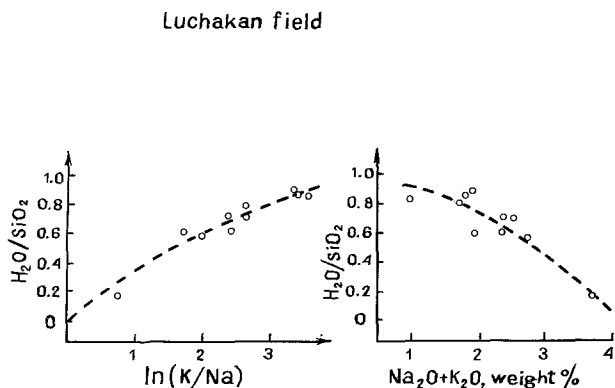
Luchakan field

Fig. 9. Change in Luchakan kimberlite alkalinity with H_2O/SiO_2

for the Daldyn area that the logarithm of a provisional coefficient of diamond occurrence (D) relates to these parameters by the following equations:

$$\ln D = 5 - 0.75\, Fe \tag{21}$$

$$\ln D = 15 - 11.67\, H \tag{22}$$

$$Fe = (11.67\, H - 10)/0.75. \tag{23}$$

Very important is a direct relationship between [H] and ln(K/Na) and an inverse relationship between [H] and the sum of alkalis, which is seen clearly in certain Mesozoic kimberlites (Luchakanskoe, Kuonapskoe, and other fields), originated within very wide depth limits. Figure 9 is an example of a correlation between these petrochemical parameters. The first diagram is the most important because it shows the well-established direct relationship between the K/Na of magmatic rocks and their depth of generation (Perchuk 1973; Marakushev and Perchuk 1975), which has been confirmed in experimental study (Markov et al. 1968). Since Eq. (22) suggests a direct relationship between diamond-bearing in kimberlites and H_2O/SiO_2, it is only reasonable to suggest similar relationship between the occurrence of diamonds in kimberlites and depth of magma generation. Needles to say, this relationship is empirical.

Conclusion

Theoretical analysis of kimberlite systems, based on numerous experimental and empirical data, has contributed a good deal to an understanding of the nature of kimberlites. It has been established that kimberlite magma is the product of complete mantle melting under the action of alkalic (K_2O) water-carbon dioxide fluids and formation of a water-carbonate-silicate fluid, supersaturated with volatiles having low density and a high-migration ability. Carbonate magma re-

sults from kimberlite magma immiscibility at the extremely high CO_2 fugacity and $t=1,300°\,C$, $P=60$–70 kbs. Increase in the temperature with the depth of this process prevents the magma from being broken down. Palaeozoic kimberlites which are products of magma crystallization in the vicinity of the earth's surface, give information on the gas composition of magmatic fluid.

Diamond bearing in kimberlites relates to the depth of magma formation, the speed at which the magma ascends to the surface, the oxidation degree of fluids and their postmagmatic transformations. Where these factors combine favourably, the highest diamond-bearing may be expected.

References

Akella, J., Boyd, F.R.: Effect of pressure on the composition of coexisting pyroxenes and garnet in the system $CaSiO_3$–$FeSiO_3$–$CaSiTi_2O_6$. Annu. Rep. Carnegie Inst. Washington, Yearb. **72**, 523–526 (1973)

Akella, J., Boyd, F.R.: Petrogenetic grit for garnet peridotites. Annu. Rep. Carnegie Inst. Washington, Yearb. **73**, 269–273 (1974)

Bobrievich, A.P., Gnevushev, M.A., Krasov, L.M.: Diamond deposits in Yakutia. Moscow: Gosgeoltekhisdat 1959

Boettcher, A.L., Mysen, B.O., Modreski, P.J.: Melting in the mantle: phase relationships in natural and synthetic peridotite-H_2O and peridotite-H_2O-CO_2, C–H–O–S with application to kimberlite. In: Phys. Chem. Earth (L.H. Ahrens et al., eds.). pp. 857–867. Cambridge: Pergamon Press 1975

Boyd, F.R.: A pyroxene geotherm. Geochim. Cosmochim. Acta **37**, 2533–2546 (1973)

Boyd, F.R.: Ultramatic nodules from the Frank Smith kimberlite pipe, South Africa. Annu. Rep. Carnegie Inst. Washington, Yearb. **73**, 285–294 (1974)

Boyd, F.R., Fujii, T., Danchin, R.V.: Noninflected goetherm from the Udachnaya kimberlite pipe, USSR. Annu. Rep. Carnegie Inst. Washington, Yearb. **75**, 523–531 (1976)

Brey, G., Green, D.H.: The role of CO_2 in the genesis of olivine melilitite. Contrib. Mineral. Petrol. **49**, 93–103 (1975)

Brey, G.P., Green, D.H.: Solubility of CO_2 in olivine melilitite at high pressures and role of CO_2 in the Earth's upper mantle. Contrib. Mineral. Petrol. **55**, 217–230 (1976)

Clark, S.P., Ringwood, A.E.: Density distribution and constitution of the mantle. Rev. Geoph. **2**, (1) (1964)

Davidson, C.F.: The kimberlites of the USSR. In: Ultramafic and related rocks (P.J. Wyllie, ed.). pp. 251–261. New York-London-Sydney: John Wiley & sons 1967

Dawson, J.B.: Kimberlites and their relation to the mantle. Phil. Trans. R. Soc. London A **271**, 297–311 (1972)

Francesson, E.V.: The petrology of kimberlites. Moscow: 'Nedra' 1968

Green, D.H., Ringwood, A.E.: The stability fields of aluminous pyroxene peridotite and garnet peridotite and their relevance in upper mantle structure. Earth Planet. Sci. Lett. **3**, 151–160 (1967)

Gurney, J.J., Ebrahim, S.: Chemical composition of Lesotho kimberlites. In: Lesotho kimberlites (P.H. Nixon, ed.). pp. 280–285. Lesotho National Development Corporation 1973

Harris, P.G., Middlemost, E.A.K.: The Evolution of kimberlites. Lithos **3**, 77–88 (1970)

Hensen, B.J.: Pyroxenes and garnet as geothermometers and barometers. Annu. Rep. Carnegie Inst. Washington, Yearb. **72**, 527–534 (1973)

Huang, W.L., Wyllie, P.J.: Eutectic between wollastonite II and calcite contrasted with thermal barrier in MgO–SiO$_2$–CO$_2$ at 30 kbs, with applications to kimberlite-carbonatite petrogenesis. Earth Planet. Sci. Lett. **24**, 305–310 (1974)

Hunt, G.: Carbonatitic material of ultramafic rocks of Kentucky. Trans. Am. Geophys. Union **57**, 761 (1976)

Ito, K., Matsumoto, T., Kawai, N.: Experimental study of a kimberlite at pressures between 42 and 88 kbars. J. Geosci., Osaka City Univ. **11**, 1–12 (1968)

Kadik, A.A., Lukanin, O.A.: Water and carbon dioxide behaviour in magmatic processes as determined by their solubility. Geokhimiya **2**, 163–179 (1973)

Koster van Groos, A.E., Wyllie, P.J.: Liquid imiscibility in the join NaAlSi$_3$O$_8$–CaAlSi$_2$O$_8$–Na$_2$CO$_3$–H$_2$O. Am. J. Sci. **273**, 405 (1973)

Koster van Groos, A.F.: The effect of high CO$_2$ pressures on alkalic rocks and the associated carbonatites. Am. J. Sci. **275**, 163–185 (1975)

Kresten, P.: Differential thermal analysis of kimberlites. In: Lesotho kimberlites (P.H. Nixoni, ed.). pp. 269–280. Lesotho National Development corporation 1973

Kresten, P., Paul, D.K.: Mineralogy of Indian kimberlites – a thermal and X-ray study. Can. Mineral. **14**, 487–491 (1976)

Kushiro, I.: Partial melting of garnet lherzolites from kimberlite at high pressures. In: Lesotho kimberlites (P.H. Nixon, ed.). pp. 294–299. Lesotho National Development corporation (1973)

Maaløe, S., Wyllie, P.J.: The join grossularite-calcite through the system CaO–Al$_2$O$_3$–SiO$_2$–CO$_2$ at 30 kbars: Crystallization range of silicate and carbonates on the liquidus. Earth Planet. Sci. Lett. **28**, 205–208 (1975)

MacGregor, I.D.: A hypothesis for the origin of kimberlite. Mineral. Soc. Am. Spec. Paper **3**, 51–62 (1970)

MacGregor, J.D., Basu, A.R.: Thermal structure of the lithosphere: a petrologic model. Science **185**, 1007–1011 (1974)

Marakushev, A.A., Perchuk, L.L.: The main trends of evolution of magmatism in the Earth's crust. In: The crust and upper mantle of the Earth, pp. 18–34. Moscow: Moscow State University 1975

Marshintsev, V.V., Migalkin, K.N., Nikolaev, N.S., Barashkov, Yu.P.: Unaltered kimberlite from the Udachnaya-Vostochnaya pipe. Akad. Nauk USSR, Doklady **231**, 961–964 (1976)

Markov, V.K., Ryabinin, Yu.N., Delitsin, I.S., Petrov, V.P.: On the possible causes responsible for potassium uplifting from the Earth's Interior and its bearing on geothermycs. Phys. Earth **2**, 3–7 (1968)

Melton, C.E., Giardini, A.A.: Experimental result and a theoretical interpretation of gaseous inclusions. Am. Mineral. **60**, 413–418 (1975)

Mysen, B.O., Arculus, R.J., Eggler, D.H.: Solubility of carbon dioxide in melts of andesite, tholeiite and olivine nephelinite composition to 30 kbar pressure.

Mysen, B.O., Boettcher, A.L.: Melting of a hydrous mantle. I. Phase relations of natural peridotite at high pressures and temperatures with controled activities of H$_2$O,CO$_2$ and H$_2$. J. Petrol. **16**, 520–548 (1975)

Mysen, B.O., Boettcher, A.L.: Melting of a hydrous mantle. II. Geochemistry of crystals and liquids formed by anatexis of mantle peridotite at high pressures and high temperatures as a function of controlled activities of water, hydrogen, and carbon dioxide. J. Petrol. **16**, 549–593 (1976)

O'Hara, M.J., Yoder, H.S.: Formation and fractionation of basic magmas at high pressures. Scott. J. Geol. **3**, 67–118 (1967)

Orlova, G.P., Ryabchikov, I.D.: CO$_2$ dissolution in the aluminosilicate melts of elivated alkalinity and problems of carbonatite magmas origin. Izv. Acad. Sci., USSR, Phys. Solid Earth (Geol. issue) **12**, 5–17 (1977)

Perchuk, L.L.: Equilibria of rock-forming minerals. Moscow: 'Nauka' 1970

Perchuk, L.L.: Carbonatites as possible products of carbonatization of basaltoid magmas. In: Geochemistry, petrology and mineralogy of alkali rocks, pp. 72–77. Moscow: 'Nauka' 1971

Perchuk, L.L.: Ca-pyroxene and orthopyroxene equilibrium in deep-seated rocks. Contrib. Phys.-chem. Petrol. **3**, 3–11 (1972)

Perchuk, L.L.: Thermodynamic regime of deep petrogenesis. Moscow: 'Nauka' 1973

Perchuk, L.L.: Thermodynamik regime of magmatism and metamorphism at the early stages of the evolution of islandsarcs. In: Geochemistry, Mineralogy, Petrology. The reports of Soviet geologists on the 25th Session of IGC, pp. 363–373. Moscow: 'Nauka' 1976

Perchuk, L.L.: The modification of bi-pyroxene geothermometer for deep-seated peridotites. Akad. Nauk USSR, Doklady **233**, 456–460 (1977a)

Perchuk, L.L.: Pyroxene barometer and 'pyroxene geotherms'. Akad. Nauk USSR, Doklady **233**, 1196–1199 (1977b)

Perchuk, L.L., Vaganov, V.I.: The temperature regime of formation of continental volcanic series. Akad. Sci. USSR. Inst. Chem. Physics. Inst. Experimental Mineralogy. Chernogolovka: 1977 (In English)

Ramberg, H.: Chemical bonds and distribution of cations in silicates. J. Geol. **60**, 331–355 (1952)

Sobolev, N.V.: Deep-seated inclusions in kimberlites and the problems of the upper mantle structure. Novosibirsk: 'Nauka' 1974

Sobolev, V.S., Dobretsov, N.L., Sobolev, N.V. (ed.): Deep-seated xenolithes and the upper mantle. Novosibirsk: 'Nauka' 1975

Vladimirov, B.M., Volyanyuk, N.Yu., Ponomarenko, A.I.: Deep-seated inclusions in kimberlites, basalts and kimberlite rocks. Moscow: 'Nauka' 1976

Wyllie, P.J., Huang, W.: Influence of mantle CO$_2$ in the generation of carbonatites and kimberlites. Nature **257**, 297–299 (1975)

Wyllie, P.J.: Mantle fluid compositions buffered by carbonates in peridotite CO$_2$-H$_2$O. J. Geol. **85**, 187–209 (1977)