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Redox state of Earth's upper mantle peridotites under the ancient cratons and its connection with diamond genesis

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Abstract—P-T- f_{O_2} conditions and fluid compositions were estimated from mineral paragenesis from inclusions in diamonds, diamond-bearing, and diamond-free xenoliths using garnet-orthopyroxene barometers and olivine-orthopyroxene-garnet oxygen barometer. The data indicate that upper mantle is zoned, with relatively oxidized lithosphere and reduced asthenosphere. The upper mantle becomes increasingly reduced with increasing depth. Inclusions within diamonds could have formed in equilibrium with the methane-nitrogen-rich fluids which corresponded to the existence of metal-silicate melts. Diamond-bearing and diamond-free peridotite xenoliths equilibrated with CO_2 - H_2O and CO_2 -rich fluids correspondingly. Copyright © 1998 Elsevier Science Ltd

1. INTRODUCTION

Modern petrologic studies of diamond genesis have been mostly concerned with the temperature and pressure at which diamonds were formed in the subcontinental lithosphere. Comparatively little attention has been paid on the role of oxygen fugacity, which determines whether carbon exists as elemental carbon or as a carbon gas species. Diamond and graphite stabilities in equilibrium with the C-O-H system as a function of P-T- f_{O_2} have been studied by Marakushev and Perchuk (1975), Ryabchikov (1980), Saxena (1989), and Woermann and Rosenhauer (1985). In modern experimental research, diamond formation and destruction processes were investigated as a part of the peridotite-O-H-C system at high P and T. Experimental and theoretical investigations indicate that the solidus surface of this system (dependent on the H_2O/CO_2 ratio and the solubilities of these components) increases with P (Wyllie, 1977; Woermann and Rosenhauer, 1985). Wylie (1987) suggests that the upper region of asthenosphere and lower part of the lithosphere may be partially molten. The zone of the melt is variable by the depth, depending on geodynamic conditions. This implies that a free C-H-O dominated fluid phase cannot generally be stable on the depths 200–300 km, because the presence of such a fluid would promote the degree of melting, thereby dissolving the main part of fluid in the melt (Ballhaus and Frost, 1994). An exception of this may be unusually cool asthenosphere beneath old cratons where the ambient temperature is below the fluid-saturated solidus (Wylie, 1987).

The oxidation state of the mantle has been a source of recent controversy, and it can be estimated by reactions involving the solution of Fe^{+3} into spinel and garnets. Thermodynamic calculations of oxygen fugacity based on olivine-orthopyroxene-spinel (O'Neill and Wall, 1987) and olivine-orthopyroxene-garnet (Luth et al., 1990) equilibrium and measurement of Fe^{+3}/Fe^{+2} in basaltic glasses (Christie et al., 1986) support a relatively oxidized mantle, characterized by values of oxygen fugacity between FMQ (fayalite-magnetite-quartz oxygen) buffer and WM (wustite-magnetite) buffer. In contrast, intrinsic oxygen fugacity (IOF) measurement indicate more reduced values of f_{O_2} , near IW (iron-wustite buffer; Ulmer et al., 1987,

Wood et al., 1990). It has been suggested (Haggerty and Tompkins, 1983) that the upper mantle is zoned with depleted lithosphere being more reduced than deeper, fertile portions of the asthenosphere. Taylor and Green (1989) and Ballhaus and Frost (1994) suggested the opposite view that the mantle consists of relatively oxidized lithosphere and reduced asthenosphere. From the composition of phases in spinel peridotites it follows that f_{O_2} may vary by 5 log units in the lithosphere under the ancient cratons (Ballhaus, 1993). The oxidation state of garnet lherzolites has not been extensively studied as has that of spinel lherzolites.

Simakov (1983a) and Chepurov et al. (1994) supposed that initially natural diamonds are crystallized under low- f_{O_2} conditions from silicate-metal melts, traces of which were noted in natural diamonds (Bulanova and Zayakina, 1991). By the Ballhaus (1993) calculations it follows that spinel diamond-bearing parageneses were formed in the equilibrium with water-rich fluid.

2. LIST OF ABBREVIATIONS

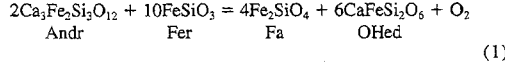
Alm	= almandine
Andr	= andradite
Enst	= enstatite
Fa	= fayalite
Fer	= ferrosilite
Fo	= forsterite
Gross	= grossular
Knor	= knoringite
Fe-Knor	= Fe knoringite
OHed	= orthohedenbergite
Pyr	= pyrope
Ski	= skiaigite
Uvar	= uvarovite
f_{O_2}	= oxygen fugacity, bar
T	= temperature, ° K
P	= pressure, kbar
G	= Gibbs free energy, J
X_i	= mole fraction of component i
a_i	= activity of component i

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3. METHODS OF COMPUTATION

3.1. Model Of Garnet-Orthopyroxene-Olivine Oxygen Barometer

As is well known, the oxidation state of the mantle assemblage can be estimated by reactions between oxygen and iron-bearing minerals. Luth et al. (1990) proposed to use the reactions of the garnet-orthopyroxene-olivine equilibrium. Another reaction (Simakov, 1994):



is also useful for calculations of f_{O_2} by using the equation

$$\log f_{\text{O}_2} = (2\Delta G_{\text{Andr}} + 10\Delta G_{\text{Fer}} - 6\Delta G_{\text{OHed}} - 4\Delta G_{\text{O}_2})/2.303RT + 2 \log \alpha_{\text{Andr}} + 10 \log \alpha_{\text{Fer}} - 6 \log \alpha_{\text{OHed}} - 4 \log \alpha_{\text{O}_2}$$

Thermochemical data on ΔG_f° were taken from papers by Moecher et al. (1988) and Lindsley (1981). The activity models for orthohedenbergite (α_{OHed}), ferrosilite (α_{Fer}), and fayalite (α_{Fa}) are taken from Wood and Banno (1973) and O'Neill and Wall (1987), respectively.

The andradite activity is calculated by using the multicomponent solid solution model:

$$\log \alpha_{\text{Andr}} = (G_{\text{Andr}}^{\text{ref}} + 3G_{\text{Andr}}^{\text{int}} + 2G_{\text{Andr}}^{\text{ext}})/RT + \log X_{\text{Ca}}^3 X_{\text{Fe}^{+3}}^2$$

Non-ideal mixing on the dodecahedral sites was treated with an asymmetric subregular solution model with the formulation given by Aranovich (1991):

for garnets with $X_{\text{Ca}} < 0.9$ f.u.:

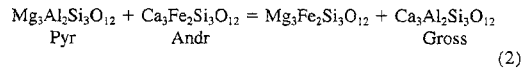
$$G_{\text{Andr}}^{\text{int}} = ((2404 + 0.26T)X_{\text{Ca}}(2 - X_{\text{Ca}}) + (5704 - 1.24T)X_{\text{Mg}}(1 - X_{\text{Ca}}) - (234 + 0.75T) + (0.75 - 4.566(0.2 - X_{\text{Ca}})^2)P) \times 4.18$$

for garnets with $X_{\text{Ca}} > 0.9$ f.u.:

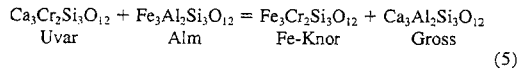
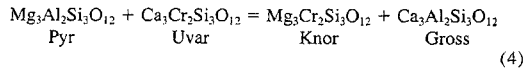
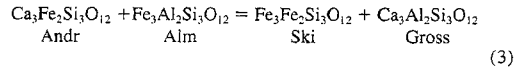
$$G_{\text{Andr}}^{\text{int}} = ((2404 + 0.26T)X_{\text{Ca}}(2 - X_{\text{Ca}}) + (5704 - 1.24T)X_{\text{Mg}}(1 - X_{\text{Ca}}) - (234 + 0.75T)) \times 4.18$$

(K, bar, J/mole)

Nonideal mixing on the octahedral sites ($G_{\text{Andr}}^{\text{ext}}$) was treated with a symmetric regular solution model with the $W_{\text{Al-Cr}} = 2508$, $W_{\text{Al-Fe}} = 3700$, $W_{\text{Cr-Fe}} = 1267$ (all in J/mole) (Luth et al., 1990). Reciprocal solid solution effects in the garnets (Wood and Nicols, 1978; Aranovich, 1991) were accounted for, with the Gibbs free energy of the exchange reactions:



taken to be 25.08 kJ/mole (Luth et al., 1990). The Gibbs free energy of three another reciprocal reactions in garnet:



are taken from Woodland and O'Neill (1993) and Aranovich (1991), respectively:

Table 1. Calculated data (f_{O_2}) for garnet-orthopyroxene-olivine paragenesis synthesized in the systems of the peridotite-granite-H₂O at 30 kbar nearly MH (magnetite-hematite) buffer (Sekine and Wyllie 1982) and of the carbonatized peridotite with graphite at 50 kbar and EMOD buffer.

N	T(°C)	P(kb)	log f_{O_2}	MH	NNO	EMOD
P-2	1000	30	-4.8	-4.9		
455	1450	50	-5.5			-4.4
450	1400	50	-4.9			-4.8
454	1450	50	-5.9			-4.4
448	1400	50	-4.2			-4.8
404	1400	50	-4.8			-4.8

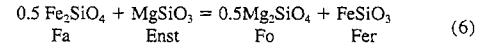
$$G_{\text{III}} = 40200 - 7P$$

$$G_{\text{IV}} = (29229 - 11.88T)*4.18$$

$$G_{\text{V}} = (25575 - 10.395T)*4.18$$

(K, kbar, J/mole)

This model can be also applied to the garnet-orthopyroxene paragenesis. We can calculate composition of fictive olivine in accordance with the thermodynamic model of olivine-orthopyroxene equilibrium in the upper mantle (Seckendorff and O'Neill, 1993) by the reaction:



Uncertainties of the calculated oxygen fugacity result from uncertainties in the activity model of minerals involved and the calculated pressure and temperature. Temperature and pressure uncertainties of $\pm 75^\circ\text{C}$ and ± 5 kbar concurrently yield an uncertainty of about ± 0.2 log f_{O_2} (Luth et al., 1990). The 4 kJ/mole error in the free energy of formation of andradite yields an uncertainty of about ± 0.1 log f_{O_2} . The largest contribution to the uncertainty of the method is the determination of the Fe^{+3} content of garnet. Since most analyses are performed by electron microprobe, which cannot distinguish Fe^{+2} and Fe^{+3} , the latter must be calculated from assumed ideal stoichiometry in accordance with the model of Schumacher (1991). An accuracy of stoichiometric estimation was tested by comparing the calculated $\text{Fe}^{+3}/(\text{Fe}^{+3} + \text{Fe}^{+2})$ values for Yakutian pyropes (samples U-5, -18 and -92, Sobolev, 1977) with those determined from chemical analyses and the calculated values for South African garnets (Luth et al., 1990) and with those determined by Mossbauer techniques. Average differences between calculated and experimentally obtained values of $\text{Fe}^{+3}/\Sigma\text{Fe}$ in the garnets is nearly ± 0.13 , which corresponds to an average error of ± 1.26 log f_{O_2} . Uncertainty for garnet-orthopyroxene model estimation (with calculation of fictive olivine composition by the reaction VI) corresponds to an average error ± 0.83 log f_{O_2} . Assuming normal distribution of these errors implies total uncertainty of ± 1.28 and ± 1.53 and log units in f_{O_2} for the garnet-orthopyroxene-olivine and garnet-orthopyroxene-(fictive olivine) models, respectively.

The accuracy of this oxygen barometer was tested on the experimental data of garnet-orthopyroxene-olivine assemblages synthesized in the systems of granite-peridotite-H₂O at 30 kbar near the MH (magnetite-hematite) buffer (Sekine and Wyllie, 1982) and in the

Table 2. Calculated data (f_{O_2}) for garnet-orthopyroxene assemblages synthesized at 1300°C and 25–35 kbar in the Fe-Pt alloy and graphite (CCO buffer) capsules (Gudmundson and Wood, 1995).

N	T(°C)	P(kb)	log f_{O_2}	Fe-Pt alloy	CCO
GR1	1300	25	-8.3	-6.51	
GR13	1300	35	-6.8	-7.94	
GR16	1300	35	-7.8		-5.73;-6.46
GR25	1300	30	-7.7	-7.33	
GR31	1300	35	-10.8	-5.86	

Table 3. Garnet-spinel-orthopyroxene-olivine parageneses separated for P-T- f_{O_2} calculations. NG85—barometer of Nickel and Green (1985) (in kbar), H84, NW79 and B91—thermometers of Harley (1984), O'Neill and Wood (1979) and Ballhaus et al. (1991) correspondingly (in $^{\circ}\text{C}$). $\lg(f_{O_2})_1$ —calculated values by garnet-spinel-orthopyroxene-olivine barometer $\lg(f_{O_2})_2$ —values obtained by spinel-orthopyroxene-olivine barometer of Ballhaus et al. (1991) at the same pressures and temperatures.

Sample	NG85	H84	NW79	B91	$\lg(f_{O_2})_1$	$\lg(f_{O_2})_2$
Yakutian inclusions in diamonds AB-75 (Sobolev et al., 1976)	75.25	1045	1172	1110	-11.1	-10.40
Yakutian diamond-bearing xenoliths Uv-216 (Pokhilenko et al., 1991)	49.64	957	917	856	-7.91	-8.40
South African graphite-bearing xenoliths FRB 888 (Pearson et al., 1994)	50.18	1035	953	959	-5.60	-7.00
PHN 2826B (Pearson et al., 1994)	30.78	867	989	949	-10.22	-12.00
Lesotho xenoliths 209 (MacGregor, 1979)	43.92	1005	994	985	-8.20	-7.00

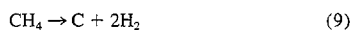
carbonatised peridotite system with graphite (Ryabchikov et al., 1993) at 50 kbar and EMOD (enstatite-magnesite-olivine-diamond) buffer (Table 1) and on the experimental data of the garnet-orthopyroxene assemblages synthesized at 1300 $^{\circ}\text{C}$ and 25–35 kbar in the Fe-Pt alloy and graphite (CCO buffer) capsules (Gudmundson and Wood, 1995) (Table 2). Garnet-orthopyroxene-olivine-spinel parageneses were treated for oxygen fugacity calculations. Ballhaus et al. (1991) have demonstrated that stoichiometric Fe^{+3} in spinel agrees well with ones measured by Mossbauer spectroscopy. The accuracy of the barometer was tested on the garnet-spinel lherzolites by comparing the results from the garnet-orthopyroxene-olivine equilibrium with those from the olivine-orthopyroxene-spinel equilibrium. In these results the difference between garnet-orthopyroxene, spinel-olivine and garnet-olivine thermometers did not exceed 130 $^{\circ}$ (Table 3). Inclusion within diamond, diamond-bearing, and -free xenoliths from Yakutian and South African pipes were treated and calculated. The values of oxygen fugacity were compared with those obtained by olivine-orthopyroxene-spinel equilibrium of Ballhaus et al. (1991; Table 3).

3.2. Upper Mantle Fluid Calculation

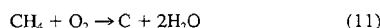
Before calculating mantle fluid compositions, it is instructive to study the behavior of a fluid in equilibrium with carbon. For a C-O-H system the upper limit of carbon stability in terms of oxygen fugacity corresponds to the reactions of CCO buffer:



The following gas-solid reactions can be proposed for diamond formation in a mantle fluid:



The composition of the fluid that coexists with graphite at a given temperature and pressure can be specified through the equilibrium 7–8. The assumed presence of diamond imposes an upper limit to f_{O_2} given by redox equilibrium 7 and 8 (CCO in Fig. 1). In the mantle, however, this limit is only of theoretical importance. In a C-O-H system diamond does not impose a lower f_{O_2} limit. One may be included to place a common lower limit near an f_{O_2} defined by the equilibrium:



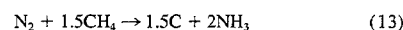
below which partial pressures of $[\text{CH}_4 + \text{H}_2]$ exceed the partial pressures of $[\text{CO}_2 + \text{CO}]$ and main part of the free carbon transfers to the methane (Frost, 1979).

N_2 was noted as one of the main gaseous components in the kimberlite breccias (Gogineni et al., 1978 and Kravtsov et al., 1979) and in

the olivine glasses from lamproite (Sobolev et al., 1989) and the ocean floor basalts (Shnikov et al., 1987). Nitrogen is the main structural admixture in natural diamonds, with concentrations up to 4×10^{20} at/cm 3 (Kaiser and Bond, 1959). N_2 can reach 87.1% in gaseous inclusions of diamond (Giardini and Melton, 1975). Sobolev (1966) proposed that nitrogen was included into the diamond structure at a deep-seated stage of degassing of the mantle, e.g., included by the reaction:



I considered the reaction of the interaction of nitrogen with methane as another possible reaction responsible for the diamond formation process (Simakov, 1983b):



Hirsch et al. (1986) proved the existence of a cubic phase of size 10–100 \AA with a high nitrogen content included in diamond. They hypothetically inferred this phase to be solid NH_3 stable at high pressures. This is further, although indirect, evidence for reaction 13.

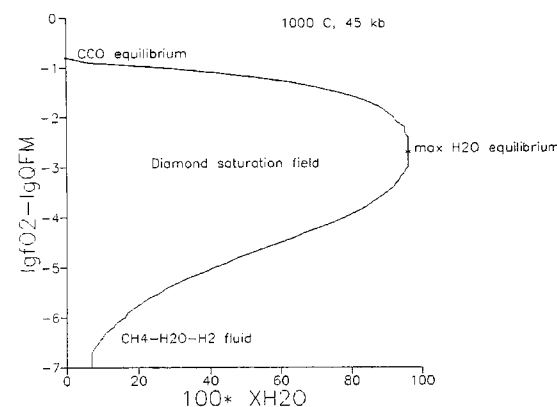


Fig. 1. The diamond saturation field as a function of and water content in a coexisting fluid. CCO corresponds to equilibria (7) and (8), and max H_2O to equilibrium (XI) in the text. Along the oxidized side of the graphite saturation field fluids are $\text{H}_2\text{O}-\text{CO}_2$, at the max H_2O equilibrium fluids are water with equal molar proportions of CO_2 and CH_4 , and along the reduced side fluids are $\text{H}_2\text{O}-\text{CH}_4-\text{H}_2$. Thermochemical data for calculations were taken from Cox et al. (1989) and Glushko (1979); γ_i of the gases were performed by the methods of Belonoshko and Saxena (1992).

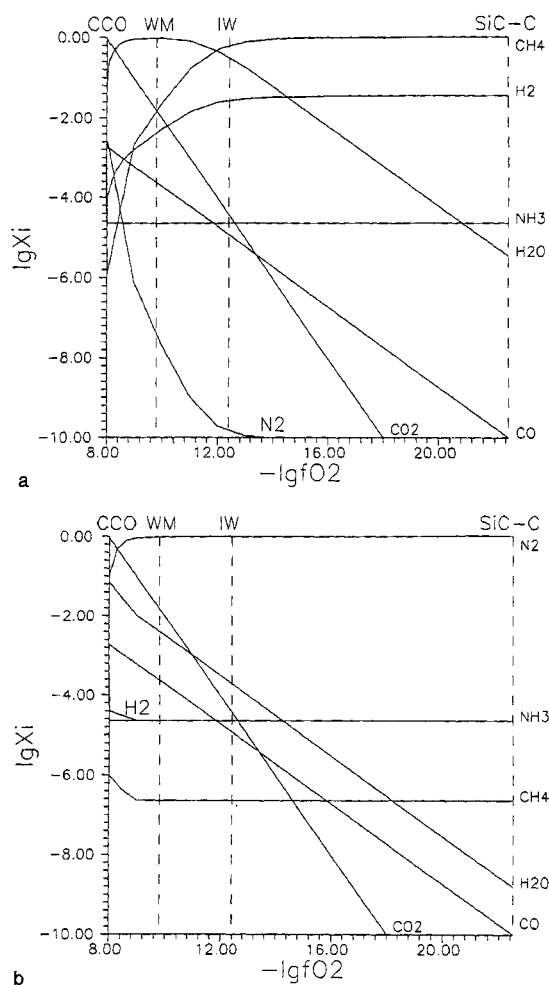


Fig. 2. Result of calculation of O-H-N-C system up to SiC-C boundary (equilibrium XV, by the data of Woerman and Rosenhauer, 1985) at $P = 45$ kbar and $T = 1000^\circ\text{C}$ and $P_{\text{NH}_3} = 1$ bar. a - "methane mixture", b - "nitrogen mixture."

On the basis of all these data, the model of C-H-O-N gaseous system has been used for considering the processes of diamond formation in the upper mantle. Previous calculations for the fluid system C-H-O-N (Holloway and Reese, 1974) showed that only seven (H_2 , H_2O , CH_4 , CO , CO_2 , N_2 and NH_3) out of the forty-six gaseous species of this system are of vital importance. Therefore, only the mole fractions of these main gaseous species were calculated in equilibrium with free carbon in this system using equilibria 7-13. Calculations of γ_i at high P and T were performed by the methods of Belonoshko and Saxena (1992), who fit their expressions to experimental data for molar volume of these components up to 6090°K and 80 GPA.

For the calculation of the gaseous mixture composition it is necessary to solve one equation with three unknowns: P_{H_2} , P_{O_2} and P_{NH_3} . If P_{O_2} and P_{NH_3} are given, the unknown value is P_{H_2} , and may be two types of fluid in this case (Fig. 2): (1) a C-H-dominated mixture, which varies from CH_4 (at low f_{O_2}) to water, then to carbon dioxide at increasing oxygen pressure. (2) a C-N-dominated mixture, which varies from N_2 (at low f_{O_2}) to carbon dioxide at increasing oxygen pressure. Estimations of the mixture compositions in the C-H-O system, which correspond to the C-H-dominated mixture (at high pressures and tem-

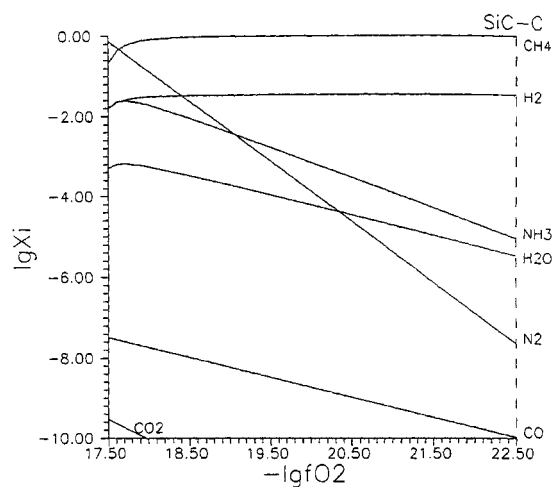
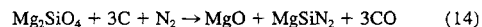


Fig. 3. Result of calculation of O-H-N-C system at $P = 45$ kbar and $T = 1000^\circ\text{C}$, nitrogen fugacity is controlled by equilibrium (XIV). Thermochemical data for calculations of the equilibrium were taken from Barin and Knacke (1973), David et al. (1970), Kaufman et al. (1982), and Robie et al. (1978).

peratures by this method), agrees with experimental data (Matveev et al., 1995).

As shown in the experimental work of Strehletov et al. (1990), nitrogen can be dissolved in mafic and ultramafic magmas in the presence of carbon at reduced conditions by the reaction:



The traces of such phases were found in the olivines of the lamproites (Ryabchikov et al., 1986). Calculations show that nitrogen could be dissolved at very reduced conditions below the IW buffer, where ammonia is a more stable fluid phase (Fig. 3). From it follows that nitrogen could be important in the fluid phase of the asthenosphere on the great depths at oxygen fugacities at which a fluid rich in methane would be stable; meanwhile CO_2 , H_2O , and probably CH_4 (Taylor and Green, 1987) are dissolved in the melts. The lithosphere oxidation begins on the upper levels with extraction of H_2O vapor from melt, methane destruction, and free carbon formation by the reaction 11. At the highest levels CO_2 and carbonates are formed. On the above-mentioned, we can assume that the mantle could be fluid-saturated.

3.3. Model Of Diamond Growth From Mantle Fluid

Studies of diamond genesis have been mostly connected with investigations on inclusions occurring in diamond itself. The presence of syngenetic inclusions such as iron, taenite, chromium, periclase-wustite, and moissanite in diamonds indicate that the diamonds grew in a reduced environment (Bulanova et al., 1979; Gorshkov et al., 1995; Harris and Gurney, 1979; Otter and Gurney, 1989; Sobolev et al., 1981; Wilding et al., 1991). On the other hand, the presence of carbonate inclusions in diamonds would indicate an oxidizing environment (Bulanova and Pavlova, 1987). On the basis of mineral inclusions in diamonds, Garanin and Kudryavtseva (1990) concluded that Yakutian diamonds may have formed in four environments: (1) Nucleation and growth of diamond under extremely reducing high pressure conditions; (2) Diamond formation associated with eclogitic type of paragenesis; (3) Diamond formation associated with peridotitic type of paragenesis; (4) Diamond crystallization directly from the kimberlite magma itself at relatively oxidized conditions. Detailed investigation of physical properties of diamonds confirmed this conclusion. It shows that there are three main zones in the crystals: central, periphery, and intermediate (Beskrovanov, 1986).

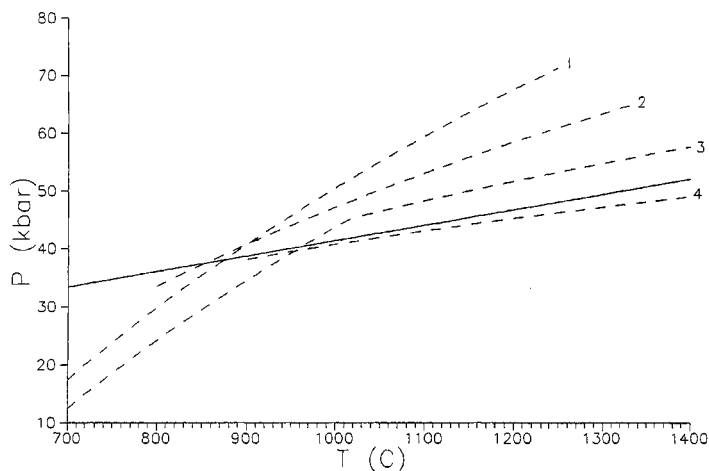


Fig. 4. Paleogeotherms (reconstructed as logarithmic fit lines) of Yakutian (1), South African (2), Lesotho (3), and Namibian (4) kimberlites. P-T calculations performed on the basis of Harley (1984) and Nickel and Green (1985) geothermobarometers, solid lines-diamond-graphite boundary. Data for the calculations were taken from the papers listed in Appendix and from (Daniels and Gurney 1989; Gurney et al., 1979; Gurney et al., 1984; Rickard et al., 1989; and Tsai et al., 1979).

The lowest oxygen fugacity at which diamonds may occur corresponds to formation of solid carbon after reaction (Harris and Gurney, 1979):



The primordial mantle fluid from which initial diamonds began to grow appears to consist of H_2 , CH_4 , and N_2 . The degree to which diamond dissolves in the upper mantle depends upon the quantities of nitrogen and hydrogen in the initial fluid. It is inversely proportional to the concentration of nitrogen and indirectly proportional to the concentration of hydrogen. Haggerty (1986) already proposed that diamond formation from fluid is controlled by the reaction of methane destruction (lower limit of diamond stability by f_{O_2}). This conclusion was based on calculations for the C-H-O system, in which diamond could be dissolved in hydrogen at low f_{O_2} . Optimum conditions for diamond growth and preservation here correspond to water-rich fluids. For the C-H-O-N system this conclusion could not be corroborated, since in the case of a nitrogen mixture presence diamond does not react with hydrogen and is stable at lower f_{O_2} . In natural diamonds the contents of nitrogen and hydrogen decrease from the core to the rim (Blinova, 1989; Griffin et al., 1995), which corresponds to decreasing decomposition of NH_3 to H^- and N^{+3} (reaction 12) at decreasing temperature. The field of diamond stability, according to the mineralogical data, is limited by the carbonate stability (upper limit) and by the moissanite stability (lower limit - reaction 15); in other words: it corresponds to a wider range of f_{O_2} .

4. RESULTS AND DISCUSSION

Fluid compositions for garnet-orthopyroxene-olivine mineral paragenesis were estimated as a function of P, T and f_{O_2} . For temperature and pressure calculations we used models of Harley (1984) and Nickel and Green (1985) as the most accurate sensors for garnet-orthopyroxene association (Taylor and Green, 1991). P-T parameters were calculated on the basis of these equilibria for inclusions within diamonds, diamond-bearing, diamond-free, and graphite-bearing xenoliths of Yakutiya and South Africa (see Appendix and Fig. 4). Fluid composition of C-O-H system in equilibrium with diamond

was calculated using the P and T obtained from the above calculations (Fig. 5). These calculations show that the boundaries of the aqueous fluid and CCO buffer (dashed lines on Fig. 5) fall in the zones of WM and IW buffers with increasing of depth and temperature. It corresponds to theoretical and experimental data for the C-O-H system (Saxena, 1989; Fei et al., 1990). Calculations of oxygen fugacity of garnet-orthopyroxene-olivine paragenesis are possible if these minerals are in the mutual equilibrium. We can check it to compare results of garnet-orthopyroxene and garnet-olivine thermometers at calculated pressure. The experiments of Brey and Kohler (1990) show that the maximum difference between temperatures obtained from the Harley (1984) and O'Neill and Wood (1979) thermometers can reach 140° . Garnet-orthopyroxene-olivine paragenesis were distinguished from diamond-bearing and diamond-free xenoliths and from inclusions within diamonds for oxygen fugacity estimations by means of the temperature calculations (see Appendix).

According to the calculations all the inclusions within diamonds correspond to more reduced mantle ($f_{\text{O}_2} < \text{WM}$), meanwhile diamond-free xenoliths mainly correspond to more oxidized mantle ($f_{\text{O}_2} > \text{WM}$) (Fig. 5). Diamond- and graphite-bearing xenoliths correspond to the field lower CCO buffer mainly and to the field of water-contained fluid (Fig. 5). Andradite contents in the mantle garnets, and consequently the calculated f_{O_2} decrease with increasing pressure and temperature (Fig. 6). These results indicate that upper mantle is zoned and the degree of reduction increases with depth. Figure 6 indicates that the gradient of oxidation changes in the range $1100\text{--}1200^\circ\text{C}$ and $40\text{--}45$ kbar at oxygen fugacities in the range from the QFM up to 2 log units below the QFM buffer. These parameters correspond to CO_2 and water-rich fluids (Fig. 1) and to the solidus curve of peridotite- $\text{H}_2\text{O-CO}_2$ system

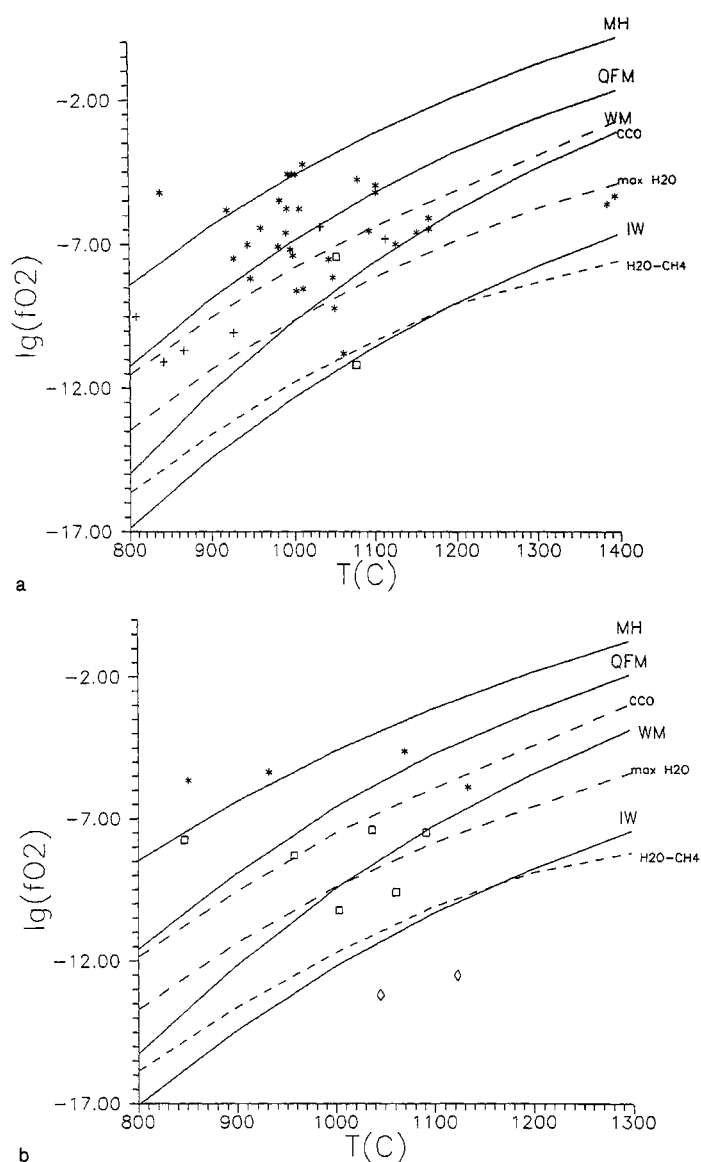


Fig. 5. Results of oxygen fugacity calculations for South African and Lesotho (a) and Yakutian (b) objects (see Appendix). Solid lines: MH - magnetite-hematite, QFM - quartz-fayalite-magnetite, WM - wustite-magnetite, IW - iron-wustite oxygen buffers. Dashed lines: CCO buffer - correspond to upper limit of diamond stability in C-H-O system, max H₂O - correspond to the reaction XI, H₂O-CH₄ - correspond to the lower boundary of water-rich ($X_{\text{H}_2\text{O}} > 0.5$) fluids. Calculations of the lines were performed on the basis of obtained kimberlitic paleogeotherms (see Fig. 4). Symbols: ◇ - inclusions within diamonds, □ - diamond-bearing xenoliths, + - graphite-bearing xenoliths, * - diamond-free xenoliths.

(Wyllie, 1977). In this zone H₂O and CO₂ vapors were released during the processes of decompression.

The calculations in the C-H-O system indicate that the formation of the inclusions within diamonds occurred at oxygen fugacities in the region of IW buffer. At these parameters a methane-rich fluid is stable in the C-H-O system. In contrast most diamond-bearing xenoliths occurred at oxygen fugacities

where a CO₂-H₂O fluid is stable, whereas the majority of diamond-free xenoliths have equilibrated with a CO₂-rich one.

The above calculations of the fluid compositions could be applied to the mantle objects in that case, if we assume that upper mantle would be fluid-saturated.

Calculated P-T- f_{O_2} results confirmed the conclusion of Taylor and Green (1989) that the upper mantle under the ancient

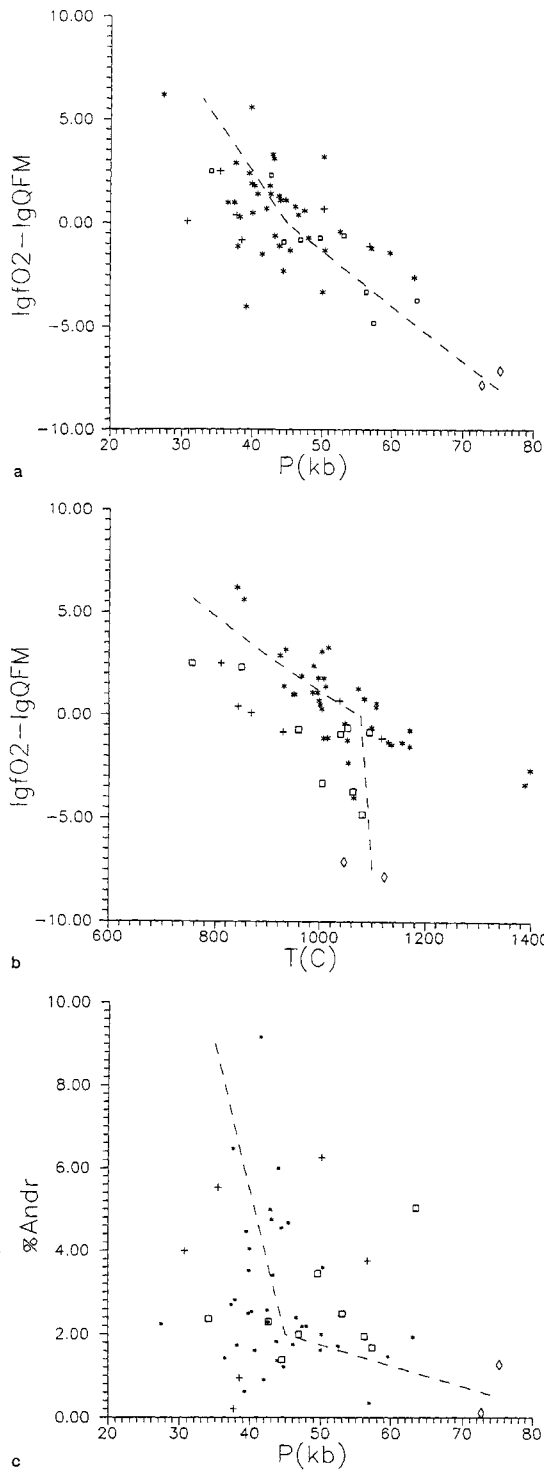


Fig. 6. Dependences of $\lg f_{O_2} - \lg QFM$ (a,b) and andradite contents (c) from the calculated pressures and temperatures (symbols: the same as from Fig. 5).

cratons is zoned and consists of relatively oxidized lithosphere and reduced asthenosphere, which have different gradient of oxygen fugacity. Reduction and the fluid H_2O/CO_2 ratio increase with increasing depth, which agrees with the experimental data in the carbonated peridotite-fluid system (Wyllie, 1977) and with thermochemical computation of oxidation state of the mantle (Saxena, 1989). Oxidized peridotite xenoliths were formed mainly on the depths less than 130 km. On the deeper levels, up to 200 km, diamond- and graphite-bearing xenoliths are situated. I, therefore, conclude on that f_{O_2} in the lithospheric upper mantle under the Archean cratons varies over a range of five to six log units (see Appendix and Fig. 5), which agrees with previously obtained results for spinel xenoliths (Ballhaus, 1993). Inclusions within diamonds which were formed on the depths greater than 200 km correspond to very reduced asthenospheric conditions, on 2–3 degree lower IW buffer (see Fig. 5a). Calculation on the basis of olivine-orthopyroxene-spinel oxygen barometer support this conclusion (see sample AB75, Table 3).

Diamond preservation in the mantle processes depends upon the oxygen conditions. The optimum conditions for diamond growth and preservation in C-H-O system correspond to those where a water-rich fluid would be stable (if upper mantle would be fluid-saturated), which agrees with previously obtained results for spinel xenoliths (Ballhaus, 1993). Meanwhile we must consider two main stages of diamond formation in the upper mantle: (1) Crystallization of initial diamonds under very low- f_{O_2} conditions. They were formed in the asthenosphere in equilibrium with the methane-nitrogen-rich fluid from metal-silicate melts, traces of which are noted in natural diamonds. (2) Diamond formation and growth near the boundary of lithosphere and asthenosphere which corresponds to the solidus curve of peridotite- H_2O-CO_2 system (Wyllie, 1977). Here the process of oxidized vapor releasing from the cooling melt took place with methane oxidation and free carbon and H_2O fluid formations. Diamond-bearing and graphite-bearing xenoliths were formed as the result of these processes.

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APPENDIX

Garnet-orthopyroxene-olivine paragenesis separated for P-T-calculations. (%Fe⁺³ - 100*Fe⁺³/(Fe⁺³ + Fe⁺²)) in the garnets; % and - percent of andradite component, NG85 - barometer of Nickel and Green (1985) (in kbar), H84 and NW79 - thermometers of Harley (1984) and O'Neill and Wood (1979) correspondingly (in C°), lg (lg - lgQFM);* in this sample pressure were calculated on the basis of Perkins et al. (1981) method).

Sample	NG85	H84	NW79	%Fe ⁺³	%And	$\Delta l g f_{O_2}$
Yakutian inclusions in diamonds						
AB-75 (Sobolev et al., 1976)	75.25	1045	1172	7	1.3	-7.1
AS-108 (Sobolev, 1977)	72.7	1123	977	1	0.1	-7.8
South African diamond-bearing xenoliths						
XM-46 (Shee et al., 1982)	57.39	1079	997	8	1.7	-4.8
XM-48 (Shee et al., 1982)	53.11	1050	1097	10	2.5	-0.6
Yakutian diamond-bearing xenoliths						
A-47 (Ponomorenko 1977)	34.20	754	663	7	2.4	2.5
U-255 (Pokhilenko et al., 1976)	46.93	1092	1078	8	2.0	-0.8
Uv-198 (Sobolev et al., 1984)	56.29	1003	970	9	2.0	-3.3
BD-2125 (Sobolev et al., 1984)	44.53	1037	1120	7	1.4	-0.9
Uv-216 (Pokhilenko et al., 1991)	49.64	957	917	14	3.5	-0.7
Uv-251 (Pokhilenko et al., 1991)	64.53	1061	979	19	5.1	-3.7
Uv-624 (Pokhilenko et al., 1991)	42.68	847	856	9	2.3	2.3
South African graphite-bearing xenoliths						
FRB 888 (Pearson et al., 1994)	50.18	1035	953	25	6.3	0.7
PHN 2492 (Pearson et al., 1994)	56.73	1116	1102	18	3.8	-1.1
PHN 2826B (Pearson et al., 1994)	30.78	867	989	19	4.0	0.1
PHN 5633 (Pearson et al., 1994)	35.45	808	762	19	5.3	2.5
PHN 1569 (Pearson et al., 1994)	38.56	928	798	5	1.0	-0.8
JAG 84-292 (Pearson et al., 1994)	37.75	841	736	1	0.2	0.4
Lesotho xenoliths						
PTH 400 (Carswell et al., 1979)	42.94	1014	924	18	5.0	3.3
PTH 207 (Carswell et al., 1979)	56.96	1050	1059	1	0.4	-1.2
PTH 403 (Carswell et al., 1979)	44.80	983	985	4	1.2	1.1
PTH 404 (Carswell et al., 1979)	40.76	929	962	7	1.6	1.4
PTH 407 (Carswell et al., 1979)	39.90	962	932	14	3.5	1.9
PTH 410 (Carswell et al., 1979)	39.55	985	975	18	4.5	2.4
209 (MacGregor, 1979)	43.92	1005	994	7	1.4	-1.1
133 (MacGregor, 1979)	44.51	1052	1064	17	4.5	-2.3
157 (MacGregor, 1979)	27.48	838	794	8	2.2	6.2
130 (MacGregor, 1979)	45.46	1129	1062	18	4.7	-1.3
125 (MacGregor, 1979)	41.49	1170	1139	32	9.2	-1.5
203 (MacGregor, 1979)	63.14	1397	1288	8	1.9	-2.6
204 (MacGregor, 1979)	48.08	1170	1180	7	2.2	-0.7
A (Lock and Dawson, 1980)	50.37	1155	1202	16	3.6	-1.3
B (Lock and Dawson, 1980)	42.64	1009	1050	11	2.3	1.4
LBM 22 (Gurney et al., 1975)	52.55	1045	975	7	1.8	-0.4
Namibian xenoliths						
1 (Mitchell, 1984)	47.46	1105	1071	9	2.2	0.6
4 (Mitchell, 1984)	37.43	949	915	11	2.7	1.0
10 (Mitchell, 1984)	42.54	1005	989	11	2.6	1.8
14 (Mitchell, 1984)	37.64	921	880	24	6.5	2.9
17 (Mitchell, 1984)	46.59	1105	1042	10	2.4	0.4
19 (Mitchell, 1984)	40.28	994	936	12	3.0	1.8
20 (Mitchell, 1984)	42.03	996	1006	4	0.9	0.7
22 (Mitchell, 1984)	39.25	1063	1081	3	0.6	-4.0
23 (Mitchell, 1984)	43.12	1001	989	18	4.8	3.1
32 (Mitchell, 1984)	40.02	998	1023	16	4.1	0.5
33a (Mitchell, 1984)	43.31	1096	1179	16	3.4	-0.6
34 (Mitchell, 1984)	38.27	1001	1021	7	1.7	0.3
37a (Mitchell, 1984)	50.07	1387	1501	7	1.6	-3.3
41 (Mitchell, 1984)	44.08	993	941	23	6.0	1.1
42 (Mitchell, 1984)	37.97	1013	909	12	2.8	-1.1
1 (Mitchell, 1984)	36.50	946	881	6	1.4	1.0
6 (Mitchell, 1984)	46.14	1082	1090	8	1.8	0.8
Yakutian xenoliths						
518/8 (Solovieva and Zavijalova, 1992)	50.15	932	824	8	2.0	3.2
Tm-47 (Lazko, 1988)	39.81	851	765	9	2.5	5.6
Tuv-48 (Lazko, 1988)	59.64	1135	1136	6	1.5	1.4
Ob-15 (Ukhanov et al., 1988)	43.86	1071	1037	7	1.8	1.3