Pokhilenko L.N., Tomilenko A.A. Composition of fluids in upper mantle rocks

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Introduction. Recently a number of papers have reported that volatile components, along with temperature and pressure, play an important role in the formation of mantle minerals [e.g. 1-6]. The paper presents the results of compositional studies of volatiles in mantle xenoliths from the kimberlites of Yakutia (Udachnaya, Mir, and Zagadochnaya pipes) and South Africa (Roberts Victor) and P-T-fO2 estimations of fluid regimes during the formation of rocks.

Samples. All 103 samples studied are mantle xenoliths from the kimberlite pipes of Yakutia and South Africa. They are 12 harzburgite-dunites, 13 spinel lherzolites, 10 garnet-spinel lherzolites, 19 garnet lherzolites, 30 sheared lherzolites, four pyroxenites, and 5 eclogites from the Udachnaya Pipe; one garnet lherzolite, one pyroxenite and 2 eclogites from the Mir Pipe; five eclogites from the Roberts Victor Pipe, and one grospidite from the Zagadochnaya Pipe.

Analytical and Research Techniques. Analysis of volatiles from deep-seated xenolith minerals was made with three series-connected LXM chromatographs [7]. The setup was equipped with original devices for thermal and mechanical gas liberation. The first device was used for the study of powder materials and consisted of a U-shaped quartz dish and a system of thermal degassing. Each device was connected with a working channel of the chromatographic unit. The gas line connecting the devices and chromatographic columns was maintained at 70°C. Before the analysis the U-shaped dish was blown with He at 90°C. This setup permits to determine simultaneously all the gases of interest, such as CO_2, H_2O, CH_4, H_2, N_2, CO, O_2, C_2-C_n, in one powder sample. The chromatographic setup was calibrated through the introduction of certain amounts of pure gas components allowing a determination of the accuracy of analysis: CO_2, C_2-C_n, N_2, CO, CH_4- 2 rel.%, H_2, and H_2O – 10 rel.%.
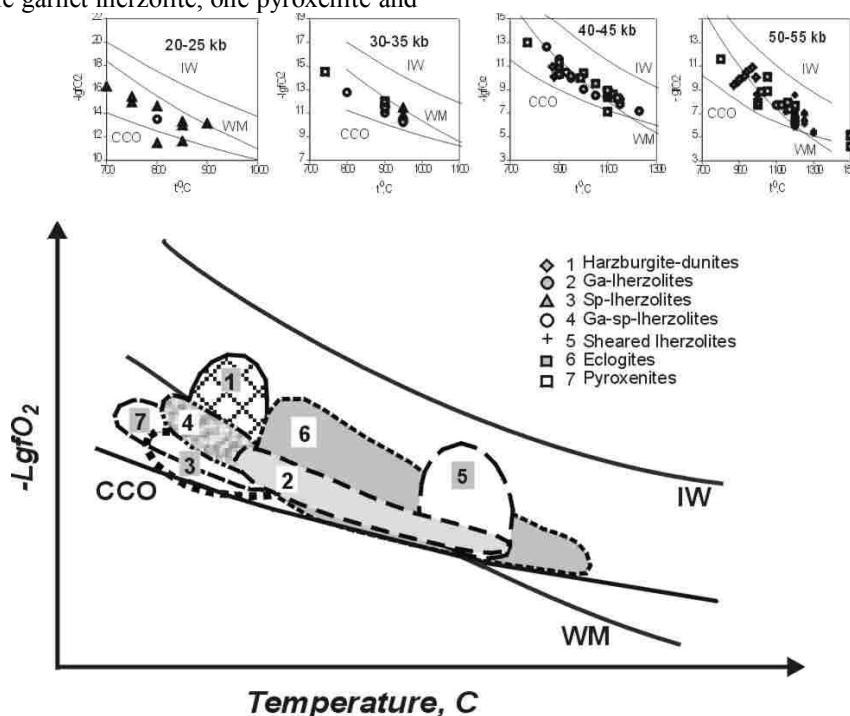

Fig. 1. Temperature vs oxygen fugacity plot at 20 to 55 kbar.

The reconstruction of the fluid regime of upper mantle mineral formation implied the calculations for the C-O-H system. The mixture of H_2O, CO_2, CH_4, H_2, and CO was taken as a perfect mix of real gases in equilibrium with solid carbon, i.e. diamond or graphite. The calculations also included O_2 for the determination of oxygen fugacity, which is indicative for oxidation-redox conditions. The other components, such as C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_5H_{12}, which existed in small proportion in the fluid (less than 10^{-4} – 10^{-5} %), were neglected.

Modal fractions of components were calculated with the HCh program by Y.V. Shvarov (Moscow University, Geological department; G values were calculated by the authors) using the chromatographic analyses of volatiles from deep-seated xenolith minerals, which were recalculated for PT-parameters of the formation of the rocks under investigation. The PT parameters were estimated using mineral microprobe analyses by TEMPEST program based on various thermometers and barometers. The program was created by A.A. Finnerti in 1978, and modified and supplemented by T.M. Blinchik in the Institute of Mineralogy and Petrography SB RAS. PT estimates for spinel lherzolites were made with a help of a new program Teral developed by I.V. Ashchepkov (Institute of geology SB RAS).

To determine the position of the rocks in the "oxidation-redox section" of the upper mantle the calculated fO_2 were compared with the fO_2 of buffer reactions, in which oxygen fugacity depends only on temperature and pressure. The values of oxygen fugacity for the iron-wustite (IW), wustite-magnetite (WM), and graphite-CO-CO_2 (CCO) buffers were defined by the following equations [8]:

IW $\log fO_2 = 6.57 - 27215/T + 0.055*((P-1)/T)$
WM $\log fO_2 = 13.12 - 32730/T + 0.083*((P-1)/T)$
CCO $\log fO_2$ (до 30 кбар) $= 2.74 - 19559/T + 0.13((P-1)/T)$

log fO_2 for the CCO buffer at 30 to 50 kbar was taken from [9]. The calculations of fluid components were based on an assumption of a closed system, and therefore, a constant H/(O+H) ratio for any reaction between the components of the system during temperature and pressure release after the rock transportation up to the surface and subsequent exhumation.

Results. The obtained results showed that the main fluid components in all samples studied are water, carbon dioxide, and to a lesser degree, methane. Several samples also contain significant amounts of nitrogen. The dominating component in the fluid is water – up to 80-90 mol.% Comparable amounts of water and carbon dioxide were determined in only a few of samples. The proportions of carbon dioxide and methane in several samples of sheared lherzolites are 48 and 25 mol.%, respectively.

Four inlets in the upper part of the figure show fO2 vs ToC plots for mantle rocks at 20-25, 30-35, 40-45, and 50-55 kbar. Position of oxygen fugacity fields in respect to buffer equilibria is shown in the lower part. This part of the figure is a juxtaposition of four f_{O2} -T^{o}C sections shown in the inlets, i.e. projection of all the data onto one plane. The most "reductive" area, far from the CCO buffer, is a harzburgite-dunitic field (Field 1) in between the IW and WM buffers (Fig. 1). The remote position of Field 1 in respect to the CCO buffers obviously evidences for the stability of solid carbon in this area. This accords well with the ideas suggesting that the majority of diamonds are captured by kimberlitic magma from the disintegrated rocks of this group. Eclogites also produce diamonds, although in a lesser degree. The field of eclogites (Field 6) is extended along the CCO buffer due to a big scattering of determined equilibria parameters. The oxygen fugacity of the eclogitic field is higher then of the dunitic field. Its major part is located in between the WM and IW buffers. The field of sheared lherzolites (Field 7) takes a position between the IW buffer and the crossing point of the WM and CCO buffers. The highest equilibria parameters were estimated for sheared lherzolites, occurring in both areas - between the WM and IW buffers and between the IW and CCO buffers - i.e. they could have formed under more "oxidized" conditions than harzburgite-dunite. The fields of garnet-spinel lherzolite (Field 4) and garnet lherzolite (Field 2) are close to the WM buffer, correspondingly, in its high- and low-temperature areas. The field of spinel lherzolite (Field 3) occupies a low-temperature area between the WM and CCO buffers, closer to the CCO. The field of pyroxenite (Field 5) lies just in between the WM and CCO buffers. Thus, the fields of oxygen fugacity of various mantle rocks overlap to a significant extent.

Conclusions.

1. The composition of the deep fluid co-existing with upper mantle rocks is dominated by H_2O followed by carbon dioxide and methane.

2. The field of oxygen fugacities of mantle rocks has an intermediate position between the CCO and IW buffers, in the vicinity to the WM buffer.

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