

## DYNAMICS OF CONVERSION OF THE REDUCED GASEOUS MIXTURE WHEN INTERACTING WITH MANTLE ROCK MINERALS

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Physical and physicochemical modeling of the condensation process for carbone from the gas phase separating from basic melt have been carried out to understand the character of graphite bubble formations dragged at three various points of the Mid-Atlantic ridge. The dynamics of the conversion mixture for reduced gases under interaction with ore and non-ore minerals of mantle rocks have been studied. For these experiments we used the equipment developed at the "Zeosit" branch of the Institute of Catalysis SB RAS and aimed to study catalytic conversion of syngas flow [2]. In our case we used as catalyst unpromoted samples of garnet and spinel lherzolite, dunite, hornblendite, chromite, and magnetite. The experiments have been carried out under temperature 250-550 °C and pressure 30-40 bar, with gas mixture of composition  $H_2 = 65$  vol. %,  $CO = 34.8$  vol. %,  $N_2 = 0.2$  vol. % under time interaction from 4 to 40 hours.

Physicochemical numerical modeling has been carried out using SelectorWin [3], for temperature interval 200-1200°C and pressure from 40 to 45 kb. Two schemes have been used in this work. The first one is "fixed", that is modeling of hetero-phase equilibrium under fixed temperature and pressure for the above-mentioned intervals and mole qualities C (0.1 – 10), H (1.5 – 15), Cl (0.05 – 0.5), F (0.01 – 1), S (0.01 – 0.1), N (0.02 – 0.1) and 1 kg of lherzolite. The second scheme was of "step-by-step" type, where gas flow of the above-mentioned composition passed through magmatic reservoir consisting of 38 reactor stages of the "rock massif – fracture – rock massif" type, or through a permeable massif of ultra-basic rocks under the pressure interval from 45-10 kb to 30-100 bar and temperature from 1200 to 200°C. The quantity for time steps varied from 5 to 50.

The studied samples of natural carbon are pumiceous black-silver rock mass, where quantity of pores and bubbles exceeds 80%. A great variety of textural forms and aggregate appearances have been noticed. In general they are mono-mineral masses. The quantity of impurities and silicate particles is not more then few percent. Aggregates of hexagonal plates packed in rows and loops of sizes form tens fractions of micron to millimeter are predominant. They form a frame with numerous expansions and "throats". Near the "throats" the carbonaceous mass is grown by crystals of calcite, halite, chlorite, and sometimes by numerous skeleton microorganisms. Some particles of native iron and sulfides have been found. The second variety is represented by aggregates of tightly packed microspheres forming crusts over basalt. Their surface is irregular, with numerous incrustations and new generations of calcite and sodium, potassium magnesium and calcium chlorides. The third variety is tight accumulations of homogenous carbon with conchoidal surface and a rare net of micro-fractures incrustated with unit plates of graphite, micro-crystals of halite and calcite.

The samples used for physical modeling contained all the mineral variety of lherzolite and picrobasalt. That gave us a possibility to trace surface changes and inter-grain boundaries of the whole association under various experimental conditions and to estimate the conditions of free carbon synthesis. It has been found that during the experiments there proceeds catalytic synthesis hydrocarbon from syngas, namely methane, n-paraffins, naphthenes  $C_6 - C_8$  and aromatic compounds,  $CH_3OH$ ,  $CH_3OCH_3$ . Highly condensed carbon phase covers the surface of natural minerals.

Catalytic activity of the studied media greatly differs under lower temperature. Under the temperature of 350°C partial reduction of iron in inter-grained films is taking place, the surface of unit parts of ortho- and clinopyroxene grains, as well as basaltic glass is corroded, and unit particles of free carbon of fraction compared to micron sizes appear. Under the temperature of 400°C flat dendrites of nickel-containing iron are formed on orthopyroxene, quantity of carbon enlarges not only near inter-grained films, but on fresh fracture of silicates. Particles of carbon are concentrated in pores of bubble basaltic glass, in irregularities of inter-grain space.

Under the temperature of 450°C well crystallized particles of carbon are absorbed on the surface of all minerals, among them is spinel, which was "smooth" in all previous cases. Biomorphic aggregates of carbon with thin 'branches' of native iron are localized on grains of orthopyroxene and olivine and on numerous negative vicinal forms (etching shapes).

In the samples influenced by gases under 500°C temperature all the minerals are covered with a layer of carbon, thin needle-shaped and foliated particles of secondary minerals are found at some localities. According to data of phase X-ray analysis, together with poorly packed graphite (porous carbon) crystals of magnesian chlorite, serpentine, magnetite, spinel, pyroxenes, feldspar, phlogopite, dolomite, calcite and amphiboles are also present. This means that under these conditions the structure decay of primary minerals of lherzolites and basalts is taking place, while secondary minerals are forming.

When particles of soot forming at the reactor walls were studied using the scanning electronic microscope LEO 1430VP, equipped with EDX- spectrometer OXFORD, we found together with porous carbon nano-particles of silicates and iron oxide, and native ore chromium iron (cohenite). Impurities of zinc, sulfur, vanadium, titanium, are found in EDX- spectra of these particles; this is due to joint removal of these elements together with iron from the reaction zones of interaction between minerals and syngas.

Thus physical modeling in solid phase allowed us to obtain compounds analogous to those contained in natural samples of carbon. They are also similar in textural peculiarities, sized and shapes of mineral particles and aggregates, mineral associations being similar too.

Numerical experiments of the problem stated allowed us to detail and verify the results of thermodynamic modeling of possible compositions for mantle fluids in the lithosphere [5 et al]. A probable explanation of the observed correlation between carbon composition in peridotites of ophiolites and in mantle xenoliths, as well as in basalts and gabbroids has been found [6]. For upper mantle and oceanic crust the scheme of conversion for magmatic gas separating from basic melt is qualitatively analogous for any point of the lithosphere (for pressure interval from tens of kb to tens of bar), when filtration of the reduced fluids is taking place in both unchanged, and metasomatic ultra-basic and basic rocks. According to data of physical experiments in this case compositions of hydrocarbons do not change very much. When condensation is taking place the mineralization associated with carbon depositing greatly depends on concentration of C, H, Cl, F, and S in the separating magmatic fluid.

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