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Crust-mantle branch of the global carbon cycle and origin of deep-seated hydrocarbons

The processes of multi-stage and polycyclic transformation and transfer of carbon in the crust and mantle have been described. The sediments drawn in the plate underthrust zones break down, become transformed and altered by metamorphic events, and part of the newly formed carbon compounds is transferred by the mantle convective currents to rift zones of the mid-oceanic ridges and carried up to the surface as hydrocarbons of various composition and carbon dioxide. This material becomes re-deposited on the sea floor as sediments forming carbonaceous and carbon-bearing units. As a result of multi-stage mechanism of physical and chemical transformations in the crust-mantle areas of the Earth hydrocarbon compounds acquire features of abiogenic origin remaining, in fact, exogenic. The revealed crust-mantle carbon cycle represents part of a global process for the cyclic carbon transfer from the atmosphere to the mantle and back. The scale of its manifestation is likely not so wide, and numerous small (mm and portions of millimeters) particles of exogenic substance and dispersed carbon drawn in the plate underthrust zones form a stable geochemical tail of the crustal direction in the mantle propagating in the plane of convective currents motion. The scale of this process may be indirectly suggested by the volumes of hydrocarbon and carbon dioxide de-gassing and hydrogen in the rift systems of the Earth crust. The amount of generated hydrocarbon gases with deep-seated origin cannot form large gas and oil-and-gas fields since their significant part is transferred to the atmosphere. Just some portion of compounds may be deposited in oceanic sediments and generate gas-hydrate pools.

Key words: carbon cycle, subduction zones, rift zones, abiogenic hydrocarbons, crust-mantle transfer, carbon geochemistry.

Introduction

The evolution of oceans is closely related to the processes of conveyor enrichment of the Earth crust with many chemical elements and compounds, which are accumulated on its surface in the convergent and divergent zones. The investigations of the carbon geochemical cycle between various reservoirs traditionally describe events of its transformation in the crust, hydrosphere, and atmosphere, where living organisms play an important part [1–4]. As well, issues of carbon isotopes behavior in the geochemical cycle are detailed in [5]. Some researches [6–8] proposed an interesting and ambiguous option of the carbon geochemical cycle nature with the involvement of empirical data about possible mantle currents and carbon reservoirs that suggests significant replenishment from the core contact zones and lower mantle of the Earth due to its removal by ascending plumes in the presence of water and oxygen.

These studies of the crust-mantle interaction mechanisms composing the geospheres of the rock units allowed justifying the presence of a deep-seated branch in the carbon geochemical cycle without the involvement of mechanisms for its generation in the outer core and lower mantle, and without significant amount of water and oxygen in the latter. Sedimentary units deposited on the seabed are the main source of carbon that forms its crust-mantle branch in the global cycle. These contain a large number of carbon compounds and are represented by carbonaceous sediments of biogenic and chemogenic origin, and by organic substance from pelagic and terrigenous deposits and carbonaceous shales drawn down from the continental margins. These units being drawn in the plate underthrust zones undergo some changes and submerge into the under-lithosphere mantle to almost completely break down, re-melt and mainly rise as magmas and fluid solutions. Part of carbon compounds and its monomineral fraction are encapsulated, reach the level of the under-lithosphere mantle, and are transferred by the upper-mantle convective currents in the area of relief under the rift zones of the lithospheric plates to reenter the Earth's hydrosphere as new compounds (Fig. 1).

Materials and methods

This paper examines a mechanism of multi-stage carbon compounds transformation and transfer of organic carbon to inorganic form and back. This allows considering the crust-mantle branch of the global carbon cycle as motion and transformation of exogenic carbon in the nature without adding a mantle component.

The authors emphasize that writing of corresponding chemical reactions has been based on published theoretical and experimental data. Where such data are unavailable, discussions on the possible chemical reactions proceeding in metamophically loaded conditions shall be deemed as probable. In connection with this, the present work can to some extent be considered as a survey based on a large-volume published material and summarized by the authors, on the basis of which they made original conclusions.
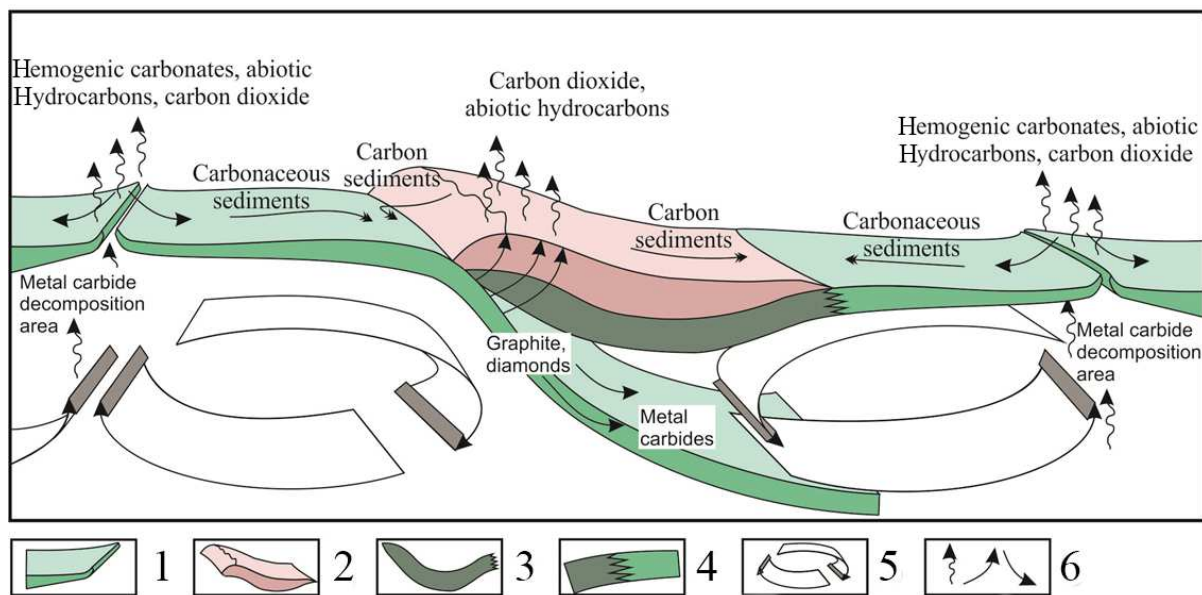
Fig. 1. Crust-mantle carbon cycle in the ocean: 1: oceanic lithosphere; 2: continental crust; 3: undercrustal continental lithosphere; 4: transition zone of the undercrustal continental lithosphere to the oceanic-type lithosphere; 5: trend of convective currents in the upper mantle; 6: trend of the carbon compounds migration

Рис. 1. Коромантийный цикл углерода в океане: 1 – океаническая литосфера; 2 – континентальная кора; 3 – подкоровая литосфера континента; 4 – зона перехода подкоровой литосферы континента к литосфере океанического типа; 5 – направление конвективных течений в верхней мантии; 6 – направление миграции соединений углерода

Results and discussion

Thermodynamic setting in the plate underthrust zones

The oceanic crust dehydration and anatexis processes taking place in the plate underthrust zones develop in accordance with quite a complicated multi-stage scenario under the conditions of reducing environment. All transformation stages are still debatable; however, it is possible to see the common trend of these processes. The spatial-temporal variability of metamorphic transformations lies in the fact that rock assemblages of the subducting oceanic lithospheric plate undergo progressive metamorphism in the contact zone with the overthrusting continent. These rocks gradually pass transformation stages from lower to higher steps. The mineralized and gas-saturated fluid formed under these conditions rises up through cracks and becoming cooled causes retrograde contact-metasomatic alterations of surrounding rocks. Numerous ultramafic protrusions and ophiolites having passed the peak of changes also undergo retrograde processes. Alongside, sedimentary rocks of the continental margins drift to the ocean become mixed with pelagic sediments and drawn together in the plate underthrust zone. Terrigenous sediments significantly increase the inflow of carbon to the total balance and undergo progressive metamorphism, being washed by saturated hydrothermal solutions. In the course of metamorphic oceanic crust rock transformations, olivine, enstatite, magnetite, and other high-melt minerals, as well as garnets formed at the depths of eclogite transition are mainly removed from the system together with the lithospheric plate submerging to the mantle. Aqueous fluids, silica and lithophile compounds are assimilated by silicate melts generated in the plate underthrust zones and predominantly pressed out upwards.

Melting of sediments and sedimentary rocks in the subduction zones mainly takes place due to the energy dissipation of viscous friction inside the strata and friction at the contact of lithospheric plates. This is added by the value of deep thermal flow permeating the continental lithospheric plates and water saturation of strata that reduces the melting temperature. This all allows suggesting that the temperature in the gap between the plates approximately corresponds to the continental plate geotherm or slightly above. Therefore, substance fallen down to the subduction zone begin to melt only at those depths, where the continental plate geotherm intersects with the sediments melting temperature (Fig. 2). The melting temperature for the majority of silicates in the presence of water and pressure increased up to 5–10 kbar abruptly falls down to 600–700 °C [9]. Water-saturated carbonates [10] and many other compounds behave similarly. The indicated laws allow concluding that aluminosilicate water-saturated sediments start melting at depths of ca. 50–70 km, while carbonate ones at a depth of ca. 80 km.

The melting degree of sedimentary rocks abruptly increases below the critical level of continental geotherm intersection with a curve of sedimentary substance melting start. That is why the differentiation of formed melts and gravity segregation shall take place at deeper depths. Heavy iron and sulphide fractions sink and ultimately settle down to the depth of convecting mantle to be gradually assimilated by its substance. Light fractions composed of separated fluids, carbonate, and silicate melts cannot rise up and are accumulated (preserved) in the lower horizons of continental plates (Fig. 3, 4), gradually forming hearths of alkaline-ultramafic, carbonatite, and lamproite-kimberlite magmas.
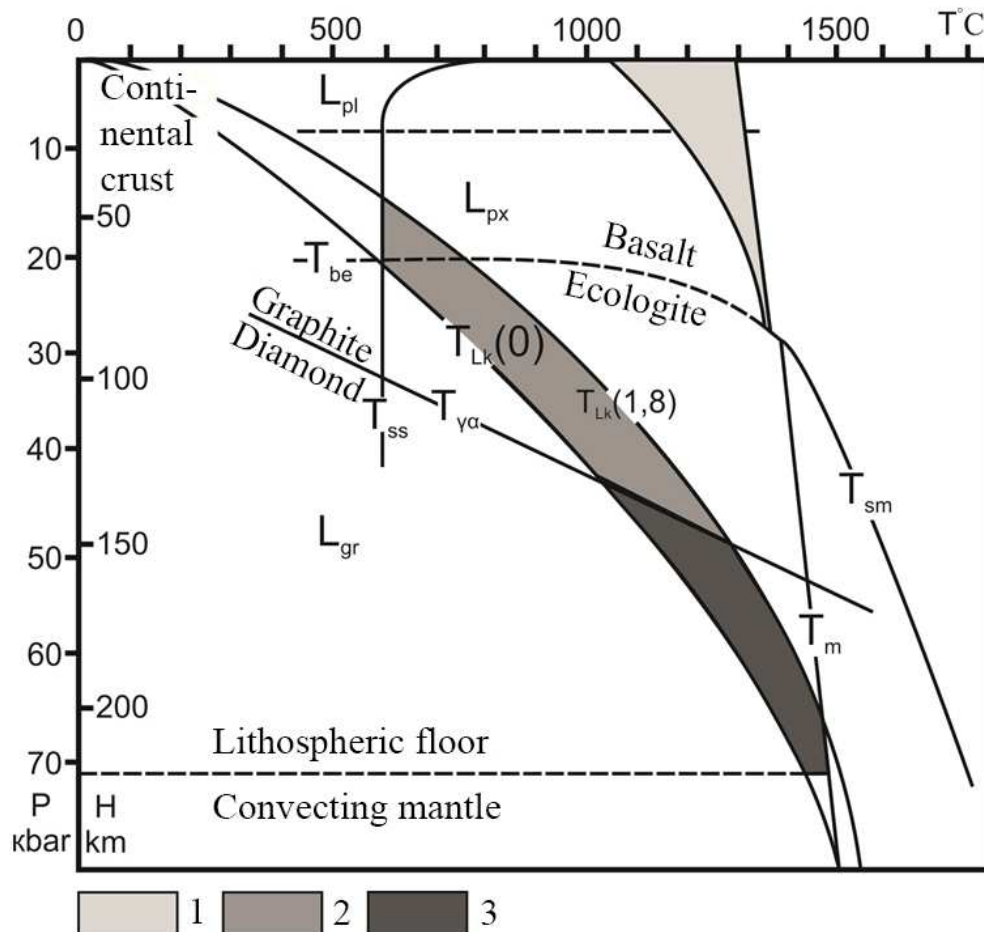

Fig. 2. Thermodynamic conditions of the alkaline-ultramafic and kimberlite magma melting [11]:
1: juvenile mantle (basalt) melts area of existence; 2: alkaline-ultramafic and alkaline-carbonatite melts area of existence; 3: area of existence for diamond-bearing deep-seated lamproite, kimberlite, and calcareous carbonatite melt; T_m: mantle temperature; T_{sm}: mantle substance solidus temperature; T_{be}: basalt to eclogite transition temperature; $T_{\gamma\alpha}$: graphite to diamond transition temperature; $T_{Lk}(0)$: modern continental geotherm; $T_{Lk}(1.8)$: ancient continental geotherm at 1.8 Ga; L_{pl}, L_{px}, and L_{gr}: area of stable existence for plagioclase, pyroxene, and garnet lherzolite; T_{ss}: water-saturated sediments melting temperature

Рис. 2. Термодинамические условия выплавления щелочно-ультраосновных и кимберлитовых магм [11]:
1 – область существования ювенильных мантийных (базальтовых) расплавов; 2 – область существования щелочно-ультраосновных и щелочно-карбонатитовых расплавов; 3 – область существования алмазоносных глубинных расплавов лампроитов, кимберлитов и кальциевых карбонатитов; T_m – температура мантии; T_{sm} – температура солидуса мантийного вещества; T_{be} – температура перехода базальт – эклогит; $T_{\gamma\alpha}$ – температура перехода графит – алмаз; $T_{Lk}(0)$ – современная континентальная геотерма; $T_{Lk}(1,8)$ – древняя континентальная геотерма на момент времени 1,8 млрд лет назад; L_{pl}, L_{px} и L_{gr} – области устойчивого существования плагиоклазовых, пироксеновых и гранатовых лерцолитов; T_{ss} – температура плавления водонасыщенных осадков

In the transition zone from the continental lithosphere bottom to the convecting mantle at similar chemical medium parameters, no significant jumps of temperature and density are observed. This border rather marks the phase transition of the mantle substance from hard to plastic state. It shall be expected that the

dehydration processes of oceanic crust and fragments of sedimentary rocks not completely proceed in this zone. Remaining water, carbon, carbon dioxide, and other volatiles may submerge to the convecting mantle.

The pulling of carbon-bearing compounds to the subduction zone results in their multi-stage decomposition and transformation with the release of monomineral carbon. At depths of ca. 120–150 km, a phase transition from graphite to diamond is observed, below which there is a diamond stability field. Diamonds crystallize exactly at such depths with distinctive mineral assemblages in eclogites and garnet peridotites of the diamond-pyrope depth facies [12]. On the other hand, it is known [13] that at depths of ca. 350 km orthorhombic olivine shall evolve into the denser cubic modification (spinel phase), or ringwoodite. However, this mineral has not yet been found in kimberlites or diamond inclusions, apparently limiting the maximum depth of diamond-bearing rock generation at 300 km [14] (Fig. 2). Summarizing these data allowed outlining the area of balanced existence of diamond-bearing eclogites and garnet lherzolites in the mantle with some high level of confidence [12; 14; 15]. It turned out quite wide. At a pressure (P) of ca. 50 kbar, the temperature range is 1120–1380 °C, and 1300–1500 °C at 70 kbar. This area is also wide for garnet lherzolites with a temperature range of 900–1400 °C (Fig. 2).

The demonstrated data allow suggesting that at depths exceeding 250–300 km carbon transforms to the graphite phase and forms various compounds fallen to the area of metal carbide stability. There are a few carbide minerals known in the nature, which occur in meteorites, kimberlites, metamorphosed ultramafic rocks and shungites. The most common are cohenite $(Fe,Ni,Co)_3C$, moissanite (SiC), tantalum carbide $(Ta,Nb)C$, niobium carbide $(Nb,Ta)C$, khamrabaevite $(Ti,V,Fe)C$, and vanadium $(V_8C_7$ and $V_2C)$ and chromium (Cr_2C_3) compounds. Such a limited amount of metal carbide minerals is accounted for by their deep origin and tendency towards decomposition under low thermobaric conditions and in the presence of water. We suppose that metal carbide minerals are more common in the upper mantle and do not rule out that calcium, aluminum, manganese, iron, etc carbides may exist there.
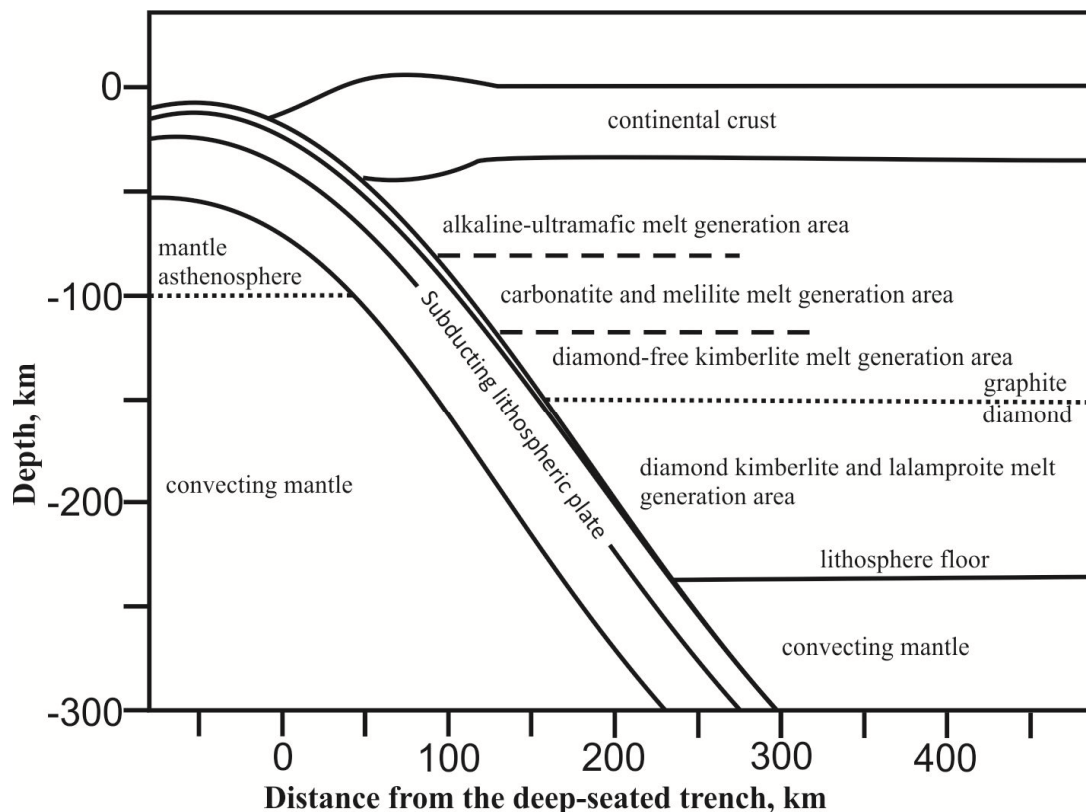
Fig. 3. Drawing of oceanic crust sedimentary units into the plate subduction area at larger depths
(down to 250 km) and position of the deep-seated rock melts areas of existence
Рис. 3. Затягивание осадочных комплексов океанической коры в зону поддвига плит
на большие глубины (до 250 км) и положение областей формирования расплавов глубинных пород

Carbon in the subduction zones

All chemical reactions in the plate underthrust zones are irreversible and proceed with thermal absorption or release, and under various reducing-oxidizing settings. Geological time plays an important part in the implementation of all the above processes since it ultimately brings the physical and chemical features of the fold system evolution to the equilibrium state. Modern sedimentary strata on the seabed contain up to 20–40 % of water

while the water content in the diagenized varieties drops to 10–15 %. Such hydromicas as illite, smektite, montmorillonite, kaolin, and diaspora form in argillaceous rocks with a large amount of organic matter (0.5 to 1.0 %).

Fig. 4. Abiotic-genesis hydrocarbon generation mechanisms in convergent and divergent settings:
1: mantle asthenosphere; 2: oceanic-type crust; 3: oceanic lithosphere; 4: island-arc-type structural and compositional units; 5: caldera-type volcano-sedimentary units; 6: deep-seated hearths of carbonatite and kimberlite magma melting;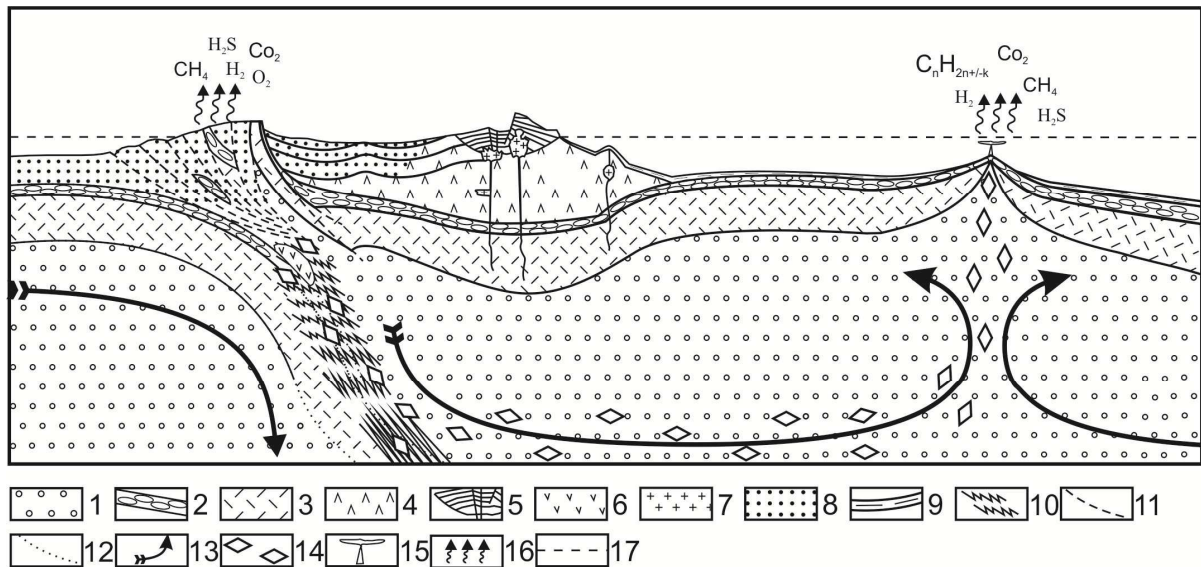 7: granitoid intrusions; 8, 9: sedimentary units: 8: poorly defined units of oceanic and island-arc-type sediments; 9: oceanic sediments; 10: area of maximum manifestation of stress metamorphism; 11: generalized tectonic dislocations; 12: area of partial subducting lithospheric plate disintegration; 13: trend of convective currents in the mantle; 14: encapsulated solid and gas-liquid inclusions of disintegrated crustal rocks; 15: hydrothermal structures at the sea bottom; 16: trend of chemical compound degassing; 17: ocean level
Рис. 4. Механизмы генерации углеводородов абиогенного происхождения в конвергентных и дивергентных обстановках:
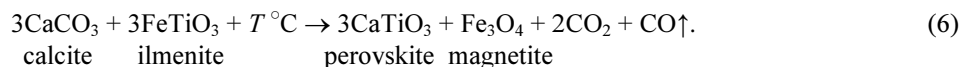1 – астеносфера мантии; 2 – кора океанического типа; 3 – океаническая литосфера; 4 – структурно-вещественные комплексы островодужного типа; 5 – осадочно-вулканогенные комплексы кольдерного типа; 6 – глубинные очаги плавления карбонатитовых и кимберлитовых магм; 7 – гранитоидные интрузии; 8, 9 – осадочные комплексы: 8 – нерасчлененные комплексы осадков океанического и островодужного типов; 9 – океанические осадки; 10 – зона максимального проявления стресс-метаморфизма; 11 – генерализованные тектонические нарушения; 12 – зона частичной дезинтеграции субдуцирующей литосферной плиты; 13 – направление конвективных течений в мантии; 14 – закапсулированные твердые и газово-жидкие включения дезинтегрированных пород корового состава; 15 – гидротермальные постройки на морском дне; 16 – направление дегазации химических соединений; 17 – уровень океана

At an early stage of metamorphic transformations sediments and sedimentary rocks drawn in the subduction zone undergo intense dehydration. Firstly, they lose porous (free), and then crystallization water with subsequent development of a complex series of endothermic (heat-absorption-related) metamorphic transformations accompanied by the release of water, CO_2, silica, alkalis (especially potassium), and lithophile elements. In the maximum compression zones, the rocks become consolidated and partially seal generated solutions creating high fluid pressure and expanding the water-bearing minerals stability field.

The majority of such fluid flows move from the bottom up and laterally, or perpendicular to the long axis of folding from the area of high pressure to the zones of tectonic shadow. In case of existing tangential pressure gradient in the permeable medium, the movement of these flows and their transition from one metamorphic facies to another shall always be observed (Fig. 5). The given sketch successfully reflects the specific nature of metamorphic facies field correlation, where the separating zones represent the transition areas from one facies to another. Exactly in these areas at the borders of stability fields, processes of mineral phase recrystallization begin and rigorously proceed. Analyzing the sketch, it is possible to come to another very important geodynamic conclusion. At larger depths, in the subduction zones, the contact edge for the lithospheric plates fades away, mineral assemblages stay under the physical and chemical equilibrium state, and fluid phase acquires features of a supercritical liquid. This effect above all, arises due to the affinity of chemical composition for the substance of the third oceanic and undercrust continental lithosphere layer. As a result, the degrading

oceanic crust submerged to the mantle together with the residues of the sedimentary cover becomes sandwiched in between the homogenous units with the mantle composition.

This process unavoidably causes the separation and isolation of large and small volumes of substance, encapsulation of crustal melts, metamorphized crustal rocks, dispersed matter, fluid solutions, and gas-liquid inclusions. In the under-lithosphere mantle, gas-liquid inclusions become a supercritical fluid with the absent differences between these two phases. Under the conditions of viscous flow, capsules are transferred to the convecting mantle and spread for long distances, being detached from the lithospheric plate submerging towards the core, or jointly moving to the area of ascending convective current in case of its flattening (Fig. 4).

Fig. 5. Distribution diagram for metamorphic facies in the PT coordinates, after [16]
Рис. 5. Схема распределения метаморфических фаций в координатах PT, по [16]

The formation of hydrothermal solutions is tightly related to the processes of progressive stress-metamorphism and overheating of the water-saturated rock system. Carbonates entering the plate underthrust area become transformed and decomposed with the release of CO_2. This results in the binding of some bases in silicate phases, and other in carbonates. Thus, the siderite heat of formation from oxide components is equal to 22.3 kcal/mol, magnesite – 23 kcal/mol, and calcite – 42.6 kcal/mol [11]. Hence it appears that the direct carbonate dissociation could only take place in hot areas of the plate underthrust zones: for siderite and magnesite at depths of ca. 80–100 km, and for calcite deeper than 150 km. This means that it only occurs in the melting areas of water-saturated sediments entered the subduction zones. All the below reactions are endothermic:

$$CaCO_3 + SiO_2 + T\,^{\circ}C \rightarrow CaSiO_3 + CO_2\uparrow, \qquad (1)$$
$$\text{calcite} \qquad\qquad\qquad \text{wollastonite}$$

$$MgCO_3 + SiO_2 + T\,^{\circ}C \rightarrow MgSiO_3 + CO_2\uparrow, \qquad (2)$$
$$\text{magnesite} \qquad\qquad\qquad \text{enstatite}$$

$$2MgCO_3 + SiO_2 + T\,^{\circ}C \rightarrow Mg_2SiO_4 + 2CO_2\uparrow, \qquad (3)$$
$$\text{magnesite} \qquad\qquad\qquad \text{forsterite}$$

$$2FeCO_3 + SiO_2 + T\,^{\circ}C \rightarrow Fe_2SiO_4 + 2CO_2\uparrow, \qquad (4)$$
$$\text{siderite} \qquad\qquad\qquad \text{fayalite}$$

$$CaCO_3 + MgCO_3 + 2SiO_2 + T\,^{\circ}C \rightarrow CaMg[Si_2O_6] + 2CO_2\uparrow. \qquad (5)$$
$$\text{calcite} \quad \text{magnesite} \qquad\qquad \text{diopside}$$

Carbon dioxide released as a result of reactions (1–5) is dissolved in the originating melts and contained in a water-carbon dioxide fluid.
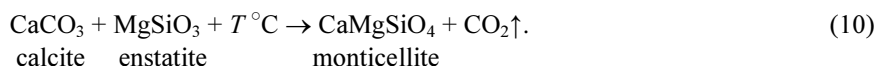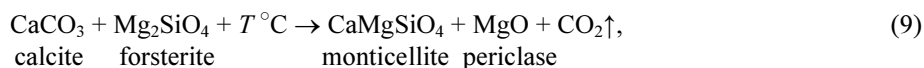
Under the high-pressure conditions (40–50 kbar) typical of the lower continental plate parts, the decomposition of carbonatites shall apparently be accompanied by the reduction of ferrous iron with the formation of compacted crystalline magnetite structures and reduction of CO_2 to carbon oxide, see the reaction below (6):

$$3CaCO_3 + 3FeTiO_3 + T\,^\circ C \rightarrow 3CaTiO_3 + Fe_3O_4 + 2CO_2 + CO\uparrow. \qquad (6)$$
calcite   ilmenite   perovskite   magnetite

At larger depths, garnet, corundum, and calcite form with the release of carbon dioxide:

$$3Ca[Al_2Si_2O_8] + 6MgCO_3 + T\,^\circ C \rightarrow 2Mg_3Al_2[SiO_4] + 3CaCO_3 + Al_2O_3 + 3CO_2\uparrow, \qquad (7)$$
anorthite   magnesite   pyrope   calcite   corundum

$$3Ca[Al_2Si_2O_8] + 6FeCO_3 + T\,^\circ C \rightarrow 2Fe_3Al_2[SiO_4] + 3CaCO_3 + Al_2O_3 + 3CO_2\uparrow. \qquad (8)$$
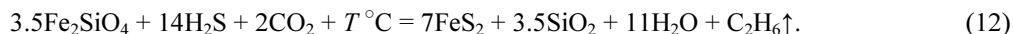anorthite   siderite   almandine   calcite   corundum
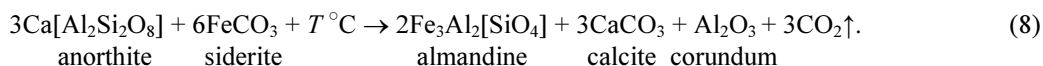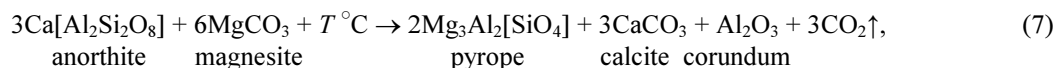
In addition to exchange reactions (6–8), at higher temperatures and pressure, decomposition of carbonates possibly takes place in the presence of olivine and pyroxene with the release of free carbon dioxide, generation of monticellite and periclase:

$$CaCO_3 + Mg_2SiO_4 + T\,^\circ C \rightarrow CaMgSiO_4 + MgO + CO_2\uparrow, \qquad (9)$$
calcite   forsterite   monticellite   periclase

$$CaCO_3 + MgSiO_3 + T\,^\circ C \rightarrow CaMgSiO_4 + CO_2\uparrow. \qquad (10)$$
calcite   enstatite   monticellite

As per [17] in the presence of carbon dioxide (CO_2) and hydrogen sulphide (H_2S), olivine (fayalite) forms marcasite (FeS_2), magnetite (Fe_3O_4), quartz, water, and abiogenic methane:

$$4Fe_2SiO4 + 4H_2S + CO_2 + T\,^\circ C = 2FeS_2 + 2Fe_3O_4 + 4SiO_2 + 2H_2O + CH_4\uparrow, \qquad (11)$$
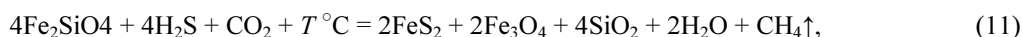
and even heavier hydrocarbons (ethane):

$$3.5Fe_2SiO_4 + 14H_2S + 2CO_2 + T\,^\circ C = 7FeS_2 + 3.5SiO_2 + 11H_2O + C_2H_6\uparrow. \qquad (12)$$
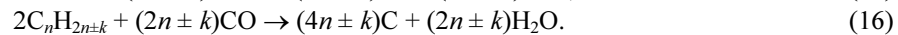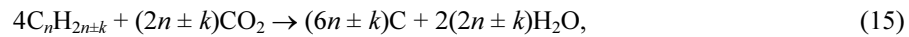
At depths below 120–150 km, diamonds are generated through the reduction of carbon by reactions between carbon oxide and carbon dioxide with methane or other organic and abiogenic hydrocarbons drawn in through the subduction zones together with sediments at larger depths. It is known that oceanic sediments and sedimentary rocks and those taken away from the continental margins often contain increased concentrations of organic matter, which, when entered to the plate underthrust zones, is subject to the thermolysis and hydrolysis, and promptly passes all stages of transformation to hydrocarbons, nitrates, and ammonium compounds. Part of these movable compounds together with porous waters is squeezed from the plate underthrust zones at the uppermost horizons. However, some portion together with the terrigenous rocks continues moving to the mantle depths. In modern subduction zones, where water-saturated silicate melts are easily removed from the plate friction zones, the magma-generation temperature quickly rises to a basalt melting level. That is why hydrocarbons cannot enter deeply into the mantle through such zones since far before this, they have to almost completely dissociate with the generation of disseminated graphite.

It is known [18] that the stability of all the hydrocarbons significantly decreases with the increase of temperature and pressure. It occurs due to the rupture of carbon bonds in long chains of composite hydrocarbon molecules. As a result of this cracking process, the content of composite hydrocarbons becomes gradually reduced in the system with the increase of simple hydrocarbon concentration. The highest stability is shown by methane sustaining heating (at normal pressure) up to 1200 °C. At a quite long reaction under the conditions of high temperature and pressure, all the organic matter may ultimately transform into methane, hydrogen, and free carbon. However, the thermal decomposition of hydrocarbons, or an endothermic process, cannot lead to the formation of crystalline carbon phases. The releasing carbon remains dispersed.

To form crystalline phases of carbon, it has to be released due to the exothermal reaction resulting in the reduction of the system's internal energy. Such conditions are met by the reactions that bind hydrocarbons with carbon oxide and carbon dioxide and proceed with the release of energy, for example [19]:

$$CH_4 + CO_2 \rightarrow 2C + 2H_2O + T\,^\circ C, \qquad (13)$$
$$CH_4 + 2CO \rightarrow 3C + 2H_2O + T\,^\circ C. \qquad (14)$$

In general, the diamond formation may be accounted for by reactions between common hydrocarbons and carbon oxides [19; 20]

$$4C_nH_{2n\pm k} + (2n \pm k)CO_2 \rightarrow (6n \pm k)C + 2(2n \pm k)H_2O, \tag{15}$$

$$2C_nH_{2n\pm k} + (2n \pm k)CO \rightarrow (4n \pm k)C + (2n \pm k)H_2O. \tag{16}$$

Carbon dioxide shall be released due to the thermal dissociation of carbonates in hot parts of the plate underthrust zones by endothermic reactions (1–5). Carbon oxide is possibly also generated by an exothermal reaction during reduction, for example, of wustite to the magnetite stoichiometry

$$3FeO + CO_2 + T\,^\circ C \rightarrow Fe_3O_4 + CO + T\,^\circ C. \tag{17}$$
$$\quad\text{wustite} \qquad\qquad \text{magnetite}$$
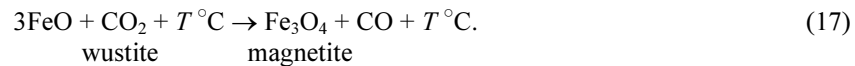
In addition to hydrocarbons of purely organic origin, abiogenic methane generated by, for example, reactions No.No. 43 and 45 below may take part in the diamond formation. These reactions become possible due to the multi-stage process of dehydration and hydration in the subduction zone. The ultramafic rock hydration processes are more typical of the rift genesis conditions, and the listed chemical reactions are detailed below.

In the course of hydrogen release and its binding with carbon dioxide, the reaction of monomineral carbon generation may be given as follows:

$$2H_2 + CO_2 \rightarrow C + 2H_2O + T\,^\circ C. \tag{18}$$

Reactions like (13–16) and (18) proceed with the energy release, and thus may result in carbon crystallization (to graphite at a moderate pressure, to diamond at a high pressure, and to dispersed graphite at above-critical conditions).

For the sake of visualization, it is easy to calculate based on the enthalpy of chemical compounds formation [21] that under normal PT conditions, the reaction (13) of methane combination with carbon dioxide releases energy at 24.6 kcal/mol while the reaction (14) of CH_4 and CO combination produces more energy, at 65.9 kcal/mol. At higher pressure and temperatures, this ratio may be somewhat different, but always formation enthalpy ΔH_t^0 for the reaction products in accordance with the first scheme is lower than that of the second one (since $\Delta H_t^0 < 0$). It follows that, from the gaseous $CO + CO_2$ mixture, the carbon crystallization reaction shall initially be fed by CO and only after by CO_2.

Sulphide, especially pyrrhotite inclusions may often be found in diamonds. This makes the following endothermic carbon release reaction possible:

$$2FeS + CO_2 + T\,^\circ C \rightarrow 2FeO + S_2 + C, \tag{19}$$

or

$$2FeS + CH_4 + T\,^\circ C \rightarrow 2H_2S + 2Fe + C. \tag{20}$$
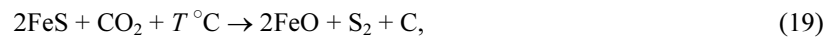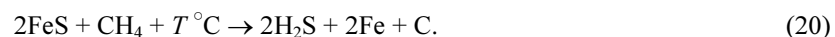
An important part in this process is played by nitrogen, which in excess occurs in hydrothermal and pneumatolytic solutions:

$$3CH_4 + 2N_2 + T\,^\circ C \rightarrow 3C + 4NH_3. \tag{21}$$

However, reactions (19–21) are endothermic and may only result in the generation of dispersed carbon. Moreover, at high temperatures, ammonium is instable and most likely falls into nitrogen and hydrogen, which further enter a fluid. Some nitrogen is absorbed by growing diamond crystals and enters it crystalline grid, but its major part probably remains in the fluid.

In addition to hydrocarbons of purely organic origin, simplest abiogenic hydrocarbons, and especially methane may arise in kimberlites, eclogites, and garnet peridotites formed from the rocks of the oceanic crust. Being formed from biogenic matter and undergone a series of physical and chemical transformations, these, in the essence of formation and certain acquired features, are abiogenic. Thus, the border between the biogenic and abiogenic nature of hydrocarbons that form under such geodynamic settings vanishes.

For the methane generation, significant amount of hydrogen, which may be obtained during the water dissociation in the presence of iron, is necessary. This reaction results in heat absorption and in the presence of water fluid:

$$4H_2O + 3Fe + T\,^\circ C \rightarrow Fe_3O_4 + 4H_2. \tag{22}$$
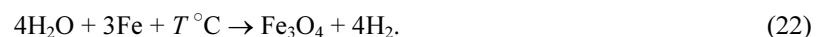
Due to reduction of ferrous (silicate) iron to the magnetite stoichiometry, in contrast, the exothermic reaction proceeds

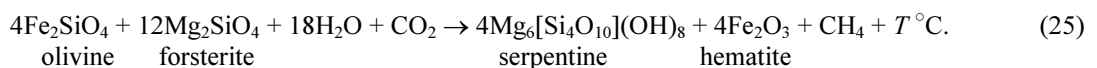$$H_2O + 3FeO \rightarrow Fe_3O_4 + H_2 + T\,^\circ C. \tag{23}$$

Since the latter reaction releases heat, it is thus more preferable, and free hydrogen in the diamond-formation areas most likely is generated by reaction (23). It shall be remembered that magnetite is the spinel phase of iron oxides, and thus more stable under the conditions of increased pressure. It is thus improbable that part of magnetite coronas around olivine crystals and other ferro-silicates forms exactly in this way.

The methane synthesis takes place through exothermic reactions of simple binding of CO and CO_2 with hydrogen or water. In the presence of catalysts, for example, nickel, nickel carbonate, or native iron, these reactions significantly accelerate and begin to proceed from 250–400 °C (though at normal pressure). All these reactions are accompanied by heat release, and there are reasons to expect that under higher PT conditions typical of plate underthrust zones, these may proceed with no catalyst added

$$CO + 3H_2 \rightarrow CH_4 + H_2O + T\,^{\circ}C,$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O + T\,^{\circ}C. \tag{24}$$
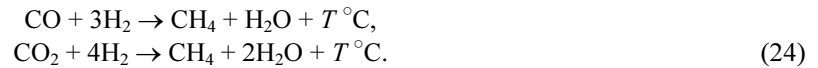
At comparably low temperatures of green-schist and epidote-amphibolite metamorphic facies (up to 400–500 °C), abiogenic synthesis of methane may take place through serpentinization reaction for iron-containing olivines in the presence of carbon dioxide:

$$4Fe_2SiO_4 + 12Mg_2SiO_4 + 18H_2O + CO_2 \rightarrow 4Mg_6[Si_4O_{10}](OH)_8 + 4Fe_2O_3 + CH_4 + T\,^{\circ}C. \tag{25}$$
$$\text{olivine} \quad \text{forsterite} \qquad\qquad\qquad \text{serpentine} \qquad \text{hematite}$$

At higher temperatures (over 660–700 °C), this reaction apparently proceeds as a side one at the formation of metasomatic pyroxene (clinoenstatite) crystalls

$$4Fe_2SiO_4 + 4Mg_2SiO_4 + 2H_2O + CO_2 \rightarrow 8MgSiO_3 + 4Fe_2O_3 + CH_4 + T\,^{\circ}C. \tag{26}$$

Moreover, abiogenic methane may be generated at direct reduction of native iron in the presence of carbon dioxide:

$$4Fe + 2H_2O + CO_2 \rightarrow 4FeO + CH_4 + T\,^{\circ}C. \tag{27}$$
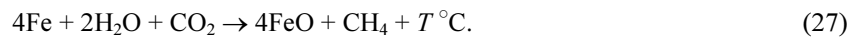
Studying the shown methane release reactions, it shall be remembered that carbon isotopes easily fractionate between CH_4 and CO_2. Abiogenic methane like organic one always predominantly concentrate light carbon isotope, ^{12}C.

In addition to the above, it may be added that in [22; 23], possible formation of complex hydrocarbons up to $C_{10}H_{22}$ with the use of solid iron oxide, marble, and water was experimentally proven. This reaction becomes possible at a temperature of 1500 °C and a pressure of above 30 kbar that corresponds to the depths of over 100 km.

These and some other exchange reactions between carbon and hydrogen-containing compounds shall lead to the formation of composite kimberlite fluid phase. Gas-liquid inclusions in diamonds preserved sealed compositions of those sulphides, from which they had crystallized, are of special interest. The executed [24] studies of the inclusion compositions have shown the following concentrations: H_2O, 10 to 60 %; H_2, 2 to 50 %; CH_4, 1 to 12 %; CO_2, 2 to 20 %; CO, 0 to 45 %; N_2, 2 to 38 %; Ar, ca. 0.5–1.2 %. Moreover, it turned out that these inclusions contain ca. 0.5 % of ethylene (C_2H_4) and 0.05 to 3 % of ethyl alcohol (C_2H_5OH). Free oxygen in such inclusions was not found witnessing the reducing conditions of the diamond formation. This specific set of gases, in our opinion, almost unambiguously indicates predominantly exogenous origin of fluid phase, from which diamonds in kimberlites crystallized.

Thus, hydrocarbons necessary for the formation of diamonds could enter kimberlites both due to the thermolysis of organic matter drawn together with carbonate sediments and terrigenous rocks into the plate underthrust zones and reduction of carbon dioxide at oxidation of iron and iron-containing silicates. It follows that all carbon in diamonds is of exogenic origin. For many diamond grains, noticeable (up to 0.25 %) nitrogen (up to 0.25 %) entered directly into the crystal lattice of this mineral [14; 25] is typical. As carbon, this element falls within diamonds from the fluid phase of deep subduction zone segments formed due to the melting of drawn-in pelagic sediments.

In addition to gas-liquid inclusions, diamond crystals often contain solid inclusions of deep mineral assemblages, among which sulphides predominate, but also olivine, serpentine, phlogopite, omphacite, pyrope, almandine, magnetite, wustite, native iron, chromite, and some other minerals. Almost all the solid inclusions in diamonds represent high-pressure mineral phases of eclogite or peridotite paragenesis.

Examining the diamond generation conditions, a consistent question arises, why this uniquely rare accessory mineral does not become a rock-forming one under the conditions of excess of initial carbon-containing compounds (CO_2 and CH_4)? The explanation may be ambivalent. Firstly, in the overheated and apparently exclusively liquid kimberlite melt, diamonds as a heavier fraction (with a density of ca. 3.51 g/cm^3) shall sink in the hearth of kimberlite magma and enter the under-lithosphere mantle levels. In these areas, diamonds again transforms into graphite, becomes bound with metals by endothermic reactions, and forms a series of metal carbide compounds, which further spread by convective currents through the whole mantle.

Secondly, it is not improbable that diamonds mainly crystallize by the reaction (12), and the amount of carbon oxide in the system is limited. This may possibly explain the extreme slowness of the diamond-generation process that during the lifetime of kimberlite magmas (i. e. over 1–2 Ga), only small crystals could form.

Submerging to the convecting mantle, carbon and some encapsulated solid mineral compounds and gas-liquid inclusions of degraded sedimentary units do not form large accumulations. More likely, these are numerous, but small (mm and fractions of mm) dispersed particles of substance forming a stable crust-trending geochemical tail in the mantle spreading in the plane of convective currents motion.

At depths of ca. 200–300 km, carbon may contact with hydrogen (see reactions of hydrogen generation 22, 23) by the reaction [26]:

$$2n\text{C} + m\text{H}_2 \rightarrow 2\text{C}n\text{H}m, \tag{28}$$

where n and m are factors.

Possibly due to this reaction, liquid inclusions of composite hydrocarbons up to alcohol may be found in diamonds. The resultant compounds further react with oxides of various metals with the yield of carbides:

$$(\text{Me})\text{O} + \text{C}n\text{H}m + T\,^\circ\text{C} \rightarrow (\text{Me})\text{C} + \text{H}_2 + \text{H}_2\text{O}, \tag{29}$$
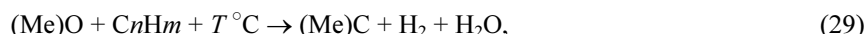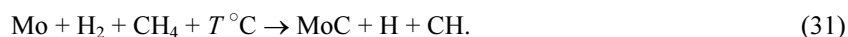
where (Me) means metal.

The reduction of metal oxides with carbon with the formation of carbides under the conditions of oxygen deficiency may proceed with the absorption of heat by the reaction [27]:

$$(\text{Me})\text{O} + \text{C} + T\,^\circ\text{C} \rightarrow (\text{Me})\text{C} + \text{CO}. \tag{30}$$
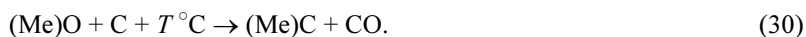
For example, at temperatures of 700–800 °C, molybdenum carbide forms in the presence of methane and hydrogen by the reaction [28]:

$$\text{Mo} + \text{H}_2 + \text{CH}_4 + T\,^\circ\text{C} \rightarrow \text{MoC} + \text{H} + \text{CH}. \tag{31}$$

In a close temperature range, lithium carbide may form due to the melting with calcite, which is in excess present in the plate underthrust zone (calcite-generation reactions 7 and 8) [29]:

$$\text{Li}_2\text{CO}_3 + 4\text{C} + T\,^\circ\text{C} \rightarrow \text{Li}_2\text{C}_2 + 3\text{C}. \tag{32}$$

At temperatures exceeding 900 °C, carbon forms a solid solution with iron with the iron carbide generation (Fe_3C and Fe_2C).

$$3\text{Fe} + \text{C} + T\,^\circ\text{C} = \text{Fe}_3\text{C}. \tag{33}$$

In the rocks of mantle composition, in the presence of carbon, iron reduces, and its telluric phase forms. Cohenite also forms under similar conditions ($(\text{FeNiCo})_3\text{C}$).

Carbon in rift zones

During the spreading of lithospheric plates in oceanic rift systems, open cracks occur, through which basalt melts rise to the surface from the mantle. The oceanic lithosphere overlain by a water bed hydrates, and a serpentinite layer forms in its lower horizons due to the re-crystallization of olivine-bearing ultramafic rocks. The depth of oceanic water penetration is limited by the lithostatic pressure of ca. 2.3 kbar. Below this level, serpentine becomes so plastic to seal all the cracks arising in the lithosphere and prevent water from penetrating deeper [30]. Higher, all the rock units of the oceanic lithosphere become significantly hydrated and contain at least 5 % of bound water of the total weight in hydrosilicates. Serpentinites is composed of bound water for at least 10–11 %.

Hydrothermal systems of rift zones, which are common on the sea bottom, remove a large amount of endogenous matter to the hydrosphere [31; 32], which is generated in the oceanic lithosphere and upper mantle. As a result, silica, calcium, magnesium, manganese, metal sulphides, methane, carbonates, sulphates, and many other compounds are removed. In depressive structures, in the north of the Juan de Fuca ridge in the Pacific Ocean, manifestations of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), benzene (C_6H_6), and toluene (C_7H_8), which associate with H_2O and CO_2 [17], are described. In hydrothermal fields in the Mid-Atlantic ridge, escapes of hydrocarbons are found, which are represented by methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), and butane (C_4H_{10}) [33]. It is natural to expect that such a variety of hydrocarbons cannot generate in the mantle, and all these are the products of crustal (exogenic) matter decomposition or form due to the processes of near-surface modification of mantle rocks.

The generation of carbon compounds in the rift zones may take place by two major methods. The first one lies in the transfer of encapsulated and dispersed fragments of compounds and monomineral phases of crustal substance from the subduction zones by convective mantle currents. The second one is implemented due to the hydration of mantle rocks in the oceanic lithosphere and their serpentinization.

Moving to the under-rift zones above the ascending convective mantle currents, metal carbides, solid particles of the crustal substance, and gas-liquid inclusions come up to the levels of oceanic lithosphere hydration (Fig. 6). Entering the stability field of mineralized water fluids, carbides are easily decomposed with the release of various hydrocarbons and metal hydroxides. It shall therefore be noted that the melting temperature for many carbon compounds with metals significantly exceeds the temperature of the upper mantle ($\approx$1300–1600 $^{\circ}$C) and fall within the range of 1000–4000 $^{\circ}$C. This fact seems extremely important and indicates that metal carbides in the almost dry mantle may occur in a stable balanced state and preserve geochemical markers of exogenic origin. For example, entering the near-surface zones of rifts and undergoing hydrolysis, calcium and sodium carbides decompose with the release of acetylene [29]:
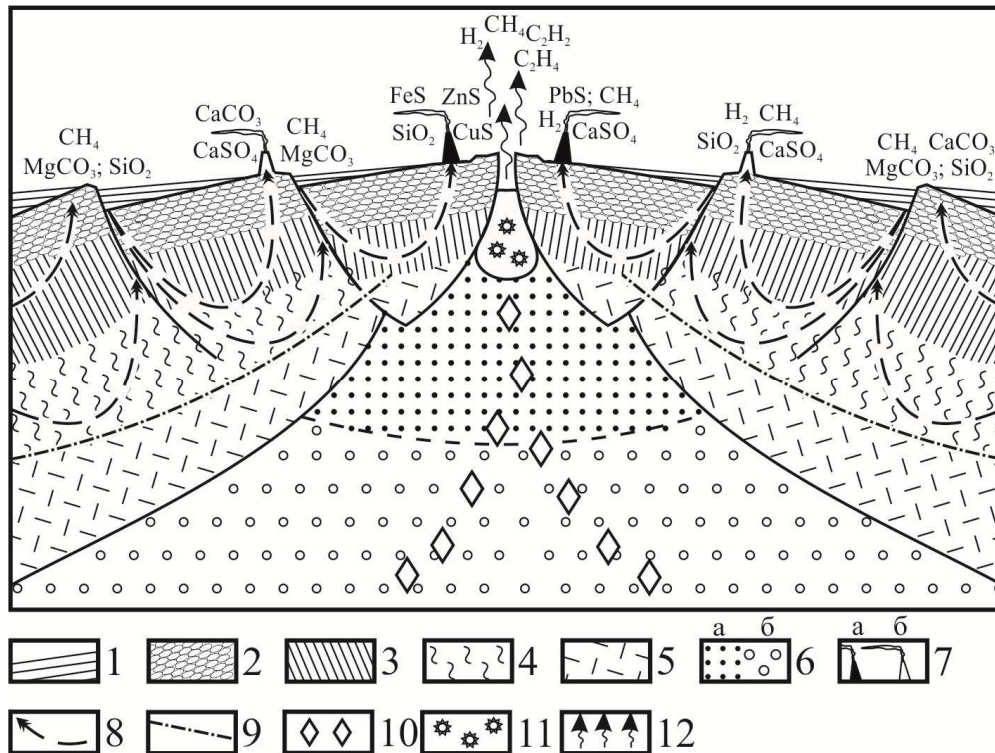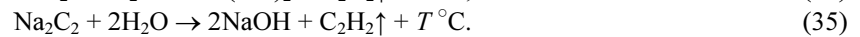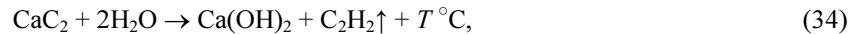
$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow + T\,^{\circ}C, \tag{34}$$

$$Na_2C_2 + 2H_2O \rightarrow 2NaOH + C_2H_2\uparrow + T\,^{\circ}C. \tag{35}$$

Fig. 6. Geochemistry of hydrothermal process and mechanisms of carbon compounds generation in rift zones of the mid-oceanic ridge:
1: sediments; 2: basalts (pillow lavas); 3: dolerite dikes (dike-in-dike unit); 4: serpentinite layer; 5: undercrustal lithospheric layer; 6: mantle: *a* for igneous hearth under the mid-oceanic ridge crest, *б* for asthenosphere; 7: structures in black (*a*) and white (*б*) smokers; 8: trend of the oceanic waters in the oceanic crustal mass; 9: critical level of water stability; 10: metal carbides and encapsulated solid mineral compounds and gas-liquid inclusions of degraded sedimentary units moved from the subduction zone; 11: metal carbide decomposition area; 12: metal carbide decomposition product degassing
Рис. 6. Геохимия гидротермальных процессов и механизмы генерации соединений углерода в рифтовых зонах срединно-океанического хребта:
1 – осадки; 2 – базальты (подушечные лавы); 3 – долеритовые дайки (комплекс дайка в дайке); 4 – серпентинитовый слой; 5 – подкоровый слой литосферы; 6 – мантия: *a* – магматический очаг под гребнем срединно-океанического хребта, *б* – астеносфера; 7 – постройки черных (*a*) и белых (*б*) "курильщиков"; 8 – направление движения океанических вод в толще океанической коры; 9 – критический уровень устойчивости воды; 10 – карбиды металлов и закапсулированные твердые минеральные соединения и газово-жидкие включения деградированных осадочных комплексов, перенесенных из зоны субдукции; 11 – область разложения карбидов металлов; 12 – дегазация продуктов распада карбидов металлов

Similar exothermic reactions proceed at the decomposition of potassium (K_2C_2), sodium, and other metal carbide. In the presence of metals, acetylene hydrates and may be transformed to ethane in two stages:

$$C_2H_2 + H_2 \rightarrow C_2H_4 + H_2 \rightarrow C_2H_6\uparrow. \tag{36}$$

It shall be noted that under normal conditions, hydrolysis of alkaline metal carbides proceeds exclusively violently and results in explosion in case of its fast contact with a large amount of water. In the geological system, these processes proceed exclusively slow (hundreds of thousands and million years) in a sub-solidus medium at a relatively high pressure (a few kbar) and in the presence of minor amounts of free water that allows being sure in the possibility of normal proceeding of such chemical reactions.

Aluminum and manganese carbide hydration proceeds with the release of methane:

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4\uparrow + T\,^\circ C, \tag{37}$$
$$Mn_3C + 3H_2O \rightarrow 3Mn(OH)_2 + CH_4 + H_2\uparrow + T\,^\circ C. \tag{38}$$

Beryllium (BeC_2) and lithium (Li_2C_2) carbide reactions proceed similarly. The manganese hydroxide resulting from the reaction (38) easily oxidizes in the presence of oxygen, which is abundant in water. The reaction proceeds with the release of heat and yield of pyrolusite in two stages:

$$2Mn(OH)_2 + O_2 + H_2O \rightarrow MnO(OH)_2 \rightarrow MnO_2. \tag{39}$$

The iron carbide decomposition is accompanied by the release of ethylene. However, this reaction is most likely not widely common in nature due to the fact that the main iron mass tends to sink to the lower mantle levels and forms no appreciable amount of carbides, which then enter the rift zones of the ocean:

$$2FeC + 3H_2O \rightarrow Fe_2O_3 + C_2H_4\uparrow + T\,^\circ C. \tag{40}$$

Hydration of near-surface mantle layers in the rift systems may cause chemical reactions of rock re-crystallization and formation of carbonaceous and siliceous compounds, which are brought from the depths of the oceanic crust and deposited on the seabed. All reactions are irreversible and proceed with the release of energy. Hydration reactions of olivine-bearing rocks in the oceanic crust binding carbon dioxide (CO_2) and forming chemogenic carbonates are the main ones:

$$4Mg_2SiO_4 + 4H_2O + 2CO_2 \rightarrow Mg_6[Si_4O_{10}](OH)_8 + 2MgCO_3 + T\,^\circ C, \tag{41}$$
$$\text{forsterite} \qquad\qquad\qquad \text{serpentine} \qquad\quad \text{magnesite}$$

$$2CaAl_2Si_2O_8 + 4H_2O + 2CO_2 \rightarrow Al_4[Si_4O_{10}](OH)_8 + 2CaCO_3 + T\,^\circ C. \tag{42}$$
$$\text{anortite} \qquad\qquad\qquad\quad \text{kaoline} \qquad\quad \text{calcite}$$

Due to the processes described for these reactions, source material is continuously added to the ocean for the normal life of skeletal organisms (corals, foraminifer and cocolithofore mollusks), which transform dissolved chemogenic carbonates to the rocks of biogenic origin.

During hydration of olivines in the rift zones, the bivalent silicate iron oxidation to trivalent iron in the presence of carbon dioxide forms abiogenic methane:

$$4Fe_2SiO_4 + 12Mg_2SiO_4 + 18H_2O + CO_2 \rightarrow 4Mg_6[Si_4O_{10}](OH)_8 + 4Fe_2O_3 + CH_4 + T\,^\circ C. \tag{43}$$
$$\text{fayalite} \quad\;\; \text{forsterite} \qquad\qquad\qquad \text{serpentine} \qquad\quad \text{hematite methane}$$

A large part of formed methane is oxidized (serves as a nutritive basis) by methane-consuming bacteria, which participate in the generation of organic matter:

$$CH_4 + \text{bacteria} \rightarrow CO_2 + [OB]. \tag{44}$$

Some methane is transferred to the atmosphere, and some volatiles may be preserved in the oceanic sediments and form hydrocarbon strata of gas hydrates [34].

Ascending to the surface, mantle substance in insignificant amounts contains metallic iron (Fe), which, being oxidized by water generates abiogenic methane, and then, being bound with carbon dioxide (CO_2) forms a highly water soluble iron bicarbonate:

$$4Fe + 2H_2O + CO_2 \rightarrow 4FeO + CH_4 + T\,^\circ C, \tag{45}$$
$$FeO + 2CO_2 + 2H_2O \rightarrow Fe(HCO_3)_2. \tag{46}$$

Carbon isotope geochemistry

Considering the laws of geochemical carbon compound transformations, it is worth to recall that, as it was shown above, they initially have exogenic origin, and their isotope composition depends on the compositions of compounds participating in chemical reactions. In rifts and plate underthrust zones, the carbon isotope system has own genetic peculiarities and variability of displacements. In light of this, it is wise to describe carbon isotope geochemical transformations gradually from the convergent to the divergent borders of the oceanic lithospheric plates.

Defining carbon isotope shifts in the subduction zones formed by the reactions (13 and 14) from abiogenic methane (C_{meth}) and carbonate carbon (C_{carb}) may be made as follows:

$$\delta^{13}C_{dia} = \frac{\delta^{13}C_{meth} + \delta^{13}C_{carb}}{2},$$ (47)

$$\delta^{13}C_{dia} = \frac{\delta^{13}C_{meth} + 2 \cdot \delta^{13}C_{carb}}{3}.$$ (48)

Carbon isotope shifts in diamonds, which formed by the reactions (15) and (16) with the participation of organic carbon (C_{org}) from the wide-range hydrocarbons $C_nH_{2n\pm k}$ may be determined as follows:

$$\delta^{13}C_{dia} = \frac{4n \cdot \delta^{13}C_{org} + (2n \pm k) \cdot \delta^{13}C_{carb}}{6n \pm k}.$$ (49)

In case of diamond generation by the reaction (18), the following shall be accepted as follows:

$$\delta^{13}C_{dia} \approx \delta^{13}C_{carb}.$$ (50)

A carbon isotope shift in abiogenic methane, which formed in mid-oceanic ridges, is approximately equal to –3–14 ‰ [35]. The deviation of the organic substance isotope signature is most often $\delta^{13}C_{org} \approx -15$ to –50 ‰, being in average –25 ‰ [36]. At the age of accumulating iron-bearing sediments, ca. 2.3 to 2 Ga, carbonate carbon demonstrated a positive isotope anomaly with a shift of up to +13 ‰ [37]. Thus, using the equation (47) at an average value of $\delta^{13}C_{meth} \approx -25$ ‰, it is possible to identify that $\delta^{13}C_{dia} \approx -6$ ‰. Such distributions of isotope shifts by the expression (48) vary from +0.3 ‰ to –6.3 ‰ [30].

The theoretical estimations of isotope ratios in diamonds generally correspond to the available experimental data. Thus, the paper [38] provides results of a layer-to-layer analysis for the variations of carbon isotope ratios in individual diamond crystals and shows that, in majority cases, a regular trend of varying carbon isotope ratios is observed from the center of crystals towards the periphery. Cores of crystals are always enriched with a light isotope, ^{12}C, and outer shells are weighted by the isotope ^{13}C. The general shift of isotope compositions reaches 4 ‰ and varies in average from –11.01 ‰ in the center of diamonds to –7.32 ‰ at the surface.

The revealed changes of the carbon isotope composition in diamonds most likely indicate the initial growth of crystals due to the biogenic carbon. As the lithospheric plates sink to the subduction zone, their further growth took place with the participation of deep chemogenic carbon forming a relatively weighted shell. In light of this, we may conclude that the majority of diamond crystals form from the mixture of biogenic and abiogenic methane, and decomposition products of carbonates various in origin.

In [39], an equally interesting feature of isotope distribution in diamonds of various parageneses was revealed. When studying the diamond grains from eclogite and peridotite xenolyths, the authors found that the above-described distributions of $\delta^{13}C_{dia}$ values belong only to crystals formed in the kimberlite matrix and eclogites. Diamonds of peridotite paragenesis show a relatively narrow distribution of $\delta^{13}C_{dia}$ (–2 to –8 ‰) values, being –6 ‰ on the average. This feature is apparently related with the fact that diamonds could form from exogenic carbon containing organogenic carbonates and hydrocarbons in kimberlites and eclogites. Exactly this may account for the wide scatter of $\delta^{13}C_{dia}$ variations in these rock units. By contrast, carbon could enter the diamonds of peridotite paragenesis only from chemogenic carbonates formed at the hydration stage of rocks from the former oceanic crust by the reactions like (41 and 42) and from chemogenic methane generated by the reactions (43).

As it was noticed earlier, all the carbon generated in rift zones forms by two main ways. The first one suggests its transfer from the subduciton zones by convective currents in the upper mantle. The second one means hydration of mafic and ultramafic rocks of the oceanic lithosphere. During the transfer of dispersed carbon, metal carbides, and encapsulated particles of the crustal substance from the plate underthrust zones, its isotope shifts shall comply with those indicators, which formed in the parental geodynamic setting. Consequently, spectra of carbon isotope shifts typical of the subduciton zones and formed in-situ due to the hydration of the oceanic lithosphere rocks are superimposed in the rift zone.

Examining main laws of carbon isotope shifts in the black smokers system of the rift zones, it may be concluded that the negative values of $\delta^{13}C \approx -13... -14$ ‰ in methane do not correspond to the average values of the HCO_3^- and CO_2 isotope composition in the oceanic waters, $\delta^{13}C = -5.5$ ‰. This fact may be accounted for by carbon isotope fractionation at the generation of methane from carbon dioxide.

Based on the Le Chatelier's principle, it may be inferred that a chemical reaction proceeding with the release of heat always evolves on the path of highest reduction of internal energy (enthalpy). Thus, predominantly atoms of light isotope, ^{12}C, shall participate in the methane (CH_4) generation reaction from carbon dioxide with

a mix of light and heavy carbon isotopes since the thermal effect of the ^{12}C isotope fractionation reaction as compared with the ^{13}C isotope reaches 0.412 kcal/g [11]. This effect tends to the lightening of carbon in the resultant methane. Thus, the exchange isotope reaction is as follows:

$$^{12}CO_2 + {^{13}}CH_4 \rightarrow {^{13}}CO_2 + {^{12}}CH_4 + T\,^{\circ}C \tag{51}$$

and evolves from the left to the right.

The deviation of the methane isotope signature in black smokers is usually $\delta^{13}C \approx -13$ to -14 ‰ while the compositions of HCO_3^- and CO_2 dissolved in oceanic waters show values close to $\delta^{13}C = -5.5$ ‰ [35]. It is hence evident that the isotope exchange reaction between carbon dioxide and methane, as it follows from the reaction (51), proceeds towards the reduction of $\delta^{13}C$ in methane. Further, during the processing by methane-absorbing bacteria, the carbon composition becomes additionally lightened in the formed organic matter (C_{org}) of bacterial communities. The organic matter acquires extremely low shift values of $\delta^{13}C_{org}$ to -50 ‰ and even to $\delta^{13}C_{org} \approx -80$ ‰. The same phenomenon apparently may account for the origin of minimums in the distribution of $\delta^{13}C_{org}$ in marsh gases of Quaternary sediments and in shale gas deposits.

Conclusion

Studying the crust-mantle carbon cycle processes, the issue of carbon content in the Earth mantle has to be touched on. It cannot provide an unambiguous response, but the solution lies in the plane of revealing indirect features that allow some degree of confidence. Thus, in mafic eruptive rocks, dispersed carbon demonstrates negligible concentrations of 10 to 100 ppm and deficiency of heavy isotope, $\delta^{13}C = -22–27$ ‰. The carbon contained in the Earth crust is heavier, $\delta^{13}C = -3–8$ ‰ [40] while the values are typical of isotope shifts in diamonds. The tholeiite basalts of oceanic rifts contain 20 to 170 ppm of carbon with isotope shifts of ca. -5 ‰ [41]. Alongside, two factors shall be considered that significantly cut down the values of free carbon presence in the Earth mantle. On the one hand, part of it is in atomic state there and composes the crystal lattice of silicates [42]. On the other hand, some certain portion of carbon represents a product transferred by the mantle convective currents from the plate underthrust zones to the rift systems and participates in the crust-mantle exogenic carbon cycle.

The given data show that the Earth mantle may contain a negligible carbon amount, and its total concentrations may significantly differ from those accepted downwards. By the data from [43], the carbonates of the Earth crust bind ca. $3.91 \cdot 10^{23}$ g of CO_2 and ca. $1.95 \cdot 10^{22}$ g of organic carbon (C_{org}). A significant portion of this substance is deposited as sediments on the seabed and slopes of continents and participates in the conveyor process of crust-mantle carbon cycle together with a drift of lithospheric plates and generation of convergent and divergent structures at their borders.

The above-described fact that a wide spectrum of hydrocarbon gases from methane (CH_4) and ethane (C_2H_6) to propane (C_3H_8) and butane (C_4H_{10}) is present in the rift zones draws special attention. Complex hydrocarbons alone in a free state at high PT conditions become instable and tend to decompose to simpler ones down to methane (CH_4). This indicates the generation of the listed compounds in near-surface and low-temperature settings, but not due to their removal from the deep mantle. This variety of hydrocarbon compositions may apparently be accounted for by the fact that, under high temperature and pressure values of the dry mantle, metal carbides remain stable, and their decomposition starts only when the hydration levels are reached, i. e. below 400 °C.

The analysis of isotope geochemical data demonstrates that, in the rift zone, together with a wide spectrum of hydrocarbon gases, there is an effect of intense fractionation of carbon isotopes, which scatter of values may vary in a very wide range. It is related to the fact that, alongside with the in-situ process, convective currents add carbon here from the subduction zones with their own isotope features and another genetic type. For example, this may result both in the contamination of radiocarbon analysis data and meaningless age values.

The studied processes allow concluding that the crust-mantle carbon cycle is related to the formation of this element in one geodynamic setting and its transfer due to the drift of lithospheric plates to another. As a result, it undergoes multi-stage transformation from the chemogenic state to the biogenic one and vice versa, and submersion to the mantle at the levels of its convective mixing and rise to the surface through rift zones (Fig. 1). Almost all carbon has an exogenic origin. This process is tightly related to the crust-atmospheric carbon cycle since it is primarily supplied by carbon dioxide and products of transformation (carbides, carbonates, hydrocarbonates, organic substance). Together they form a global carbon cycle in the nature.

The amount of abiogenic hydrocarbon gases generated by the described methods cannot provide the formation of large gas and oil-and-gas fields since their significant part is transferred to the atmosphere. Just some hydrocarbon compounds may deposit in oceanic sediments and form gas-hydrate beds [34].

One of the main conclusions of this investigation represents a factor of no need to involve a large amount of water for the implementation of physical and chemical transformations of crustal substance in the mantle asthenosphere. The data in the paper allow inferring that the notion of the global carbon cycle, which was originally proposed by the academician A. Ye. Fersman in the 1920s has to be expanded by including processes

of the mantle carbon transfer from the subduction zones to the rift systems. Thus, a crust-mantle component shall be added to the conventional branch of the crust-mantle carbon cycle. The scale of its manifestation is most likely not so large, and numerous small (mm and fractions of mm) particles of exogenic matter and dispersed carbon may form a stable geochemical tail of the crustal trend in the mantle that extends in the plane of moving convective currents. The scale of this process may indirectly be judged by the volumes of degassing hydrocarbon and carbon dioxide gases, as well as hydrogen and its compounds in the rift systems of the Earth crust.

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Коромантийная ветвь глобального цикла углерода и происхождение глубинных углеводородов

Описаны процессы многостадийного и полициклического преобразования и переноса углерода в коре и мантии. Затянутые в зонах поддвига плит осадки разрушаются, трансформируются и преобразуются метаморфическими процессами, а часть вновь сформированных углеродистых соединений переносится конвективными течениями мантии в рифтовые зоны срединно-океанических хребтов и выносится на поверхность в виде углеводородов различного состава и углекислого газа. Далее они снова отлагаются на морском дне в виде осадков, образуя карбонатные и углеродсодержащие структурно-вещественные комплексы. В результате проявления многоступенчатого механизма физико-химических преобразований в коромантийных областях Земли углеводородные соединения приобретают черты абиогенного происхождения, по сути оставаясь экзогенными. Выявленный коромантийный цикл углерода является частью глобального процесса циклического переноса углерода из атмосферы в мантию и обратно. Масштабы его проявления, скорее всего, не столь широки, а многочисленные мелкие (мм и доли мм) частицы экзогенного вещества и рассеянного углерода, затянутые в зоны поддвига плит, образуют устойчивый геохимический шлейф коровой направленности в мантии, распространяющийся в плоскости перемещения конвективных потоков. Косвенно о масштабе проявления данного процесса можно судить по объемам дегазации углеводородных и углекислого газов, а также водорода в рифтовых системах земной коры. При этом количество генерируемых углеводородных газов глубинного происхождения не может формировать крупных газовых и нефтегазовых месторождений, так как значительная их часть переносится в атмосферу. Лишь некоторое количество соединений способно отлагаться в океанических осадках и формировать в них залежи газогидратов.

Ключевые слова: цикл углерода, зоны субдукции, рифтовые зоны, абиогенные углеводороды, коромантийный перенос, геохимия углерода.