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GEOCHEMISTRY

Redox Facies of Hydrocarbons and the Formation of Oil

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The endogenic nature of hydrocarbons (HC) and their heterogeneity has been substantially refined by their findings in hydrothermal fields in the global system of ocean ridges. The methane composition (CO_2 + CH_4 + H_2O) was initially found in hydrothermal solutions and fluid inclusions captured by rock-forming minerals and apatite of olivine gabbro and norite [1]. Association of methane with many other HCs was revealed afterward. Heavy saturated HCs ($CH_{2.125}$–$CH_{2.069}$) were described from the Rainbow methane hydrothermal field (Mid-Atlantic Ridge) [2, 3] characterized by massive sulfide mineralization. According to [4], HCs in association with methane are represented by gaseous alkanes, such as ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and pentane (C_5H_{12}), as well as benzene (C_6H_6) and toluene (C_7H_8), in the Juan de Fuca hydrothermal field of the northeastern Pacific. These hydrocarbons are clearly distinguished by enrichment in the heavy carbon isotope ($\delta^{13}C$ = –20.0 to –25.3‰) relative to methane ($\delta^{13}C$ = –50.8 to –54.3‰). The high reactivity of heavy HCs is also a distinct feature compared to inert methane. In the Juan de Fuca hydrothermal field, only these HCs, rather than methane, react with water to form CO_2, which is close to heavy HCs in carbon isotopic composition, according to the following reaction: C_7H_8 ($\delta^{13}C$ = –20.2‰) + $14H_2O$ = $7CO_2$ ($\delta^{13}C$ = –20.7‰) + $18H_2$. Such reactions produce carbonates with significantly heavier carbon than methane. However, carbon from these carbonates is anomalously lighter than that from common marine carbonates with $\delta^{13}C$ ~ 0‰.

The association of methane with heavy HCs, including those of the oil series (alkanes and others), indicates that the methane related to deep sources belongs to the so-called oil type that differs from methane related to organic matter destruction and the vital activity of methanogenic microorganisms in peat bogs and other surface sources. The inert behavior of methane in hydrocarbon occurrences is accounted for by the strong bonds between carbon and hydrogen (binding energy is 425.0 kJ mol^{-1}) in comparison with other HCs. As a result, methane behaves in natural processes like molecular hydrogen (binding energy is 431.9 kJ mol^{-1}). Therefore, methane (CH_4) differs principally from other, more reactive HCs (CH_3–CH). The drastic difference of methane from other HCs in carbon isotopic composition ($\delta^{13}C$ = –50‰ in methane compared to –20‰ in other HCs) virtually rules out transformation of methane into other HCs. In relation to oxidized carbon compounds, methane correlates with CO, whereas other HCs correlate with CO_2. Therefore, we can distinguish two systems (the CO–CH_4 system based on light carbon and the CO_2–(CH_3–CH) system based on heavy carbon), which represent apparently independent chemical elements.

In terms of redox conditions, these systems are characterized by $T-\mu_{O_2} = RT\ln P_{O_2}$ diagrams (Figs. 1, 2). Equilibria between HCs in these diagrams are represented by reactions of ideal gases calculated on the basis of constants [5, 6] applied to low and moderate pressures (<1 kbar). The values are extrapolated tentatively over a region of higher pressure (Table 1). Comparison of isobars shown in the diagrams clearly demonstrates the influence of pressure that efficiently expands stability fields (facies) of methane and ethane, which are formed at the boundary of hydrogen and aqueous facies as a result of reactions with the participation of light carbon ($3H_2 + CO = CH_4 + H_2O$) and heavy carbon ($7H_2 + 2CO_2 = C_2H_6 + 4H_2O$). These four-phase reactions in the two-component systems correspond to the nonvariant points. With increasing pressure, the points shift to the region of higher temperature

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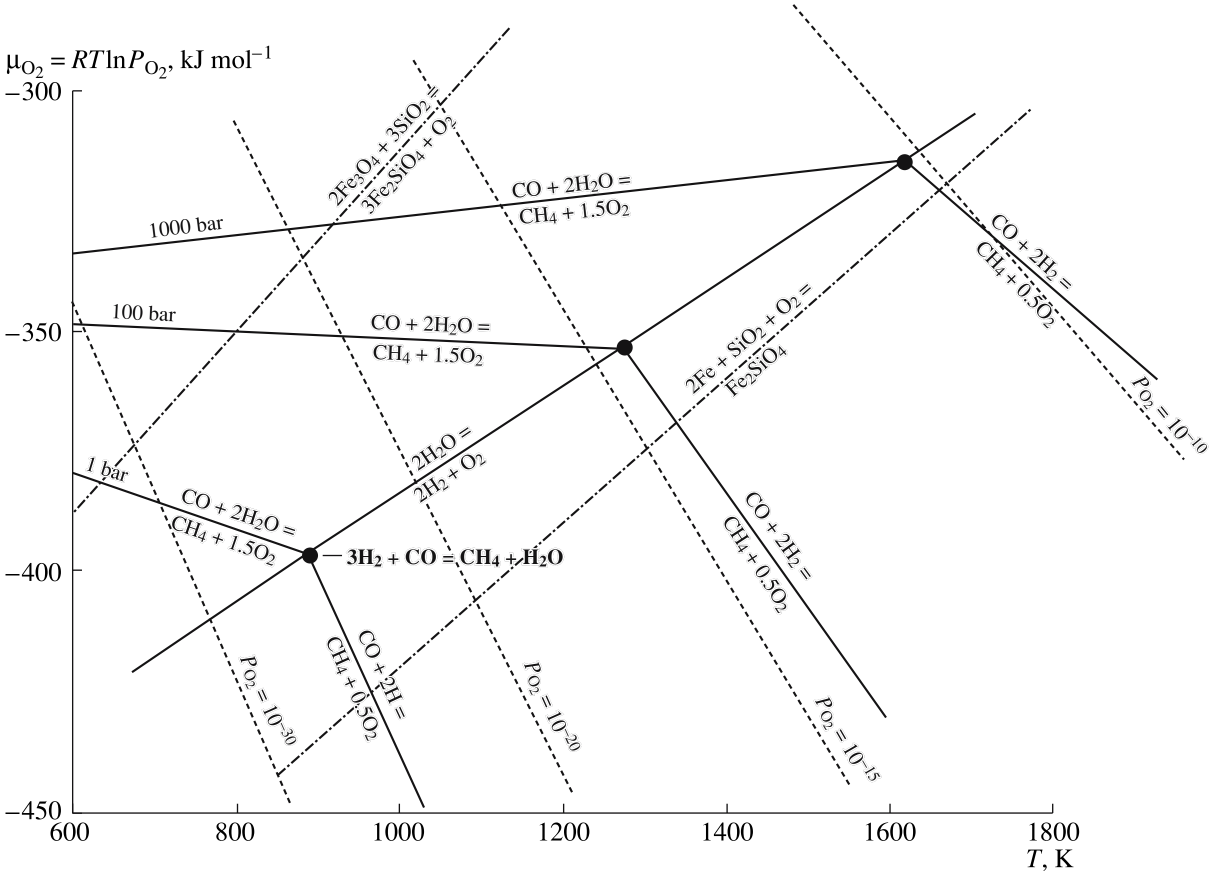

Fig. 1. Isobars that bound stability fields (redox facies) in a pressure range of 1–1000 bar (Table 1). The dashed lines indicate oxygen partial pressure in fluid; dot-and-dash line corresponds to redox mineral buffers. The arrow points to the reaction of nonvariant equilibrium.

and chemical potential of oxygen along the H_2O–H_2 equilibrium.

This shift is caused by the great negative volumetric effect of the above gas reactions that define HCs as "abyssophile" elements tending to concentrate in deep zones of the Earth's interior. The formation of methane (Fig. 1) is directly related to migration of the lightest carbon along with hydrogen flows (H_2 + CO) from the Earth's core. The production of water in these flows promotes melting of mantle material, formation of magma sources, and the further evolution of hydrocarbon generation. The development of magma sources can be accompanied by influx of hydrogen from the Earth's core and continuous generation of methane. The latter binds the light carbon and thus provides efficient fractionation of carbon isotopes toward enrichment in the heavy isotope. Instability of CO in the fluids due to oxidation ($2CO + O_2 = 2CO_2$) fosters the formation of ethane ($7H_2 + 2CO_2 = C_2H_6 + 4H_2O$), which is pivotal in the system of hydrocarbon generation at a higher evolution level (Fig. 2) and compatible nevertheless with the methane system (Fig. 1). The compatibility is related to the continuous input of light carbon into the magmatic sources by hydrogen fluids (H_2 + CO_2). However, in contrast to inert methane devoid of hydrocarbon derivatives, ethane formed in the new system produces a large family of heavy HCs (CH_3–CH), which are close to ethane in carbon isotopic composition. As has been shown in [7] and schematically illustrated by the diagram (Fig. 2), the total pressure promotes stabilization of the newly formed HCs. With increasing pressure, the equilibrium limiting the ethane facies ($2CO_2 + 3H_2O = C_2H_6 + 3.5O_2$) shifts to the region of very high temperatures and chemical potentials of oxygen. The growth of pressure also promotes formation of heavy HCs. This is shown in the diagram in a simplified form using only butane (C_4H_{10}) and hexane (C_6H_{14}) among numerous hydrocarbons (CH_3–CH). The oxygen potential plays a dual role in transformation of ethane in accordance with two assemblages of ethane and other hydrocarbons: ($C_2H_6 + CO_2$) and ($C_2H_6 + H_2O$). In the first case, the isotopic composition of HCs becomes heavier with a decrease in oxygen potential. This model corresponds to transfer of carbon from CO_2 to HCs: $3.5C_4H_{10} + CO_2 = 2.5C_6H_{14} + O_2$, etc. In the second case, the concentration of the heavy carbon isotope is related to an increase in the oxygen potential with transfer of hydrogen from HCs to the water component: $6C_4H_{10} + O_2 = 4C_6H_{14} + 2H_2O$, etc.

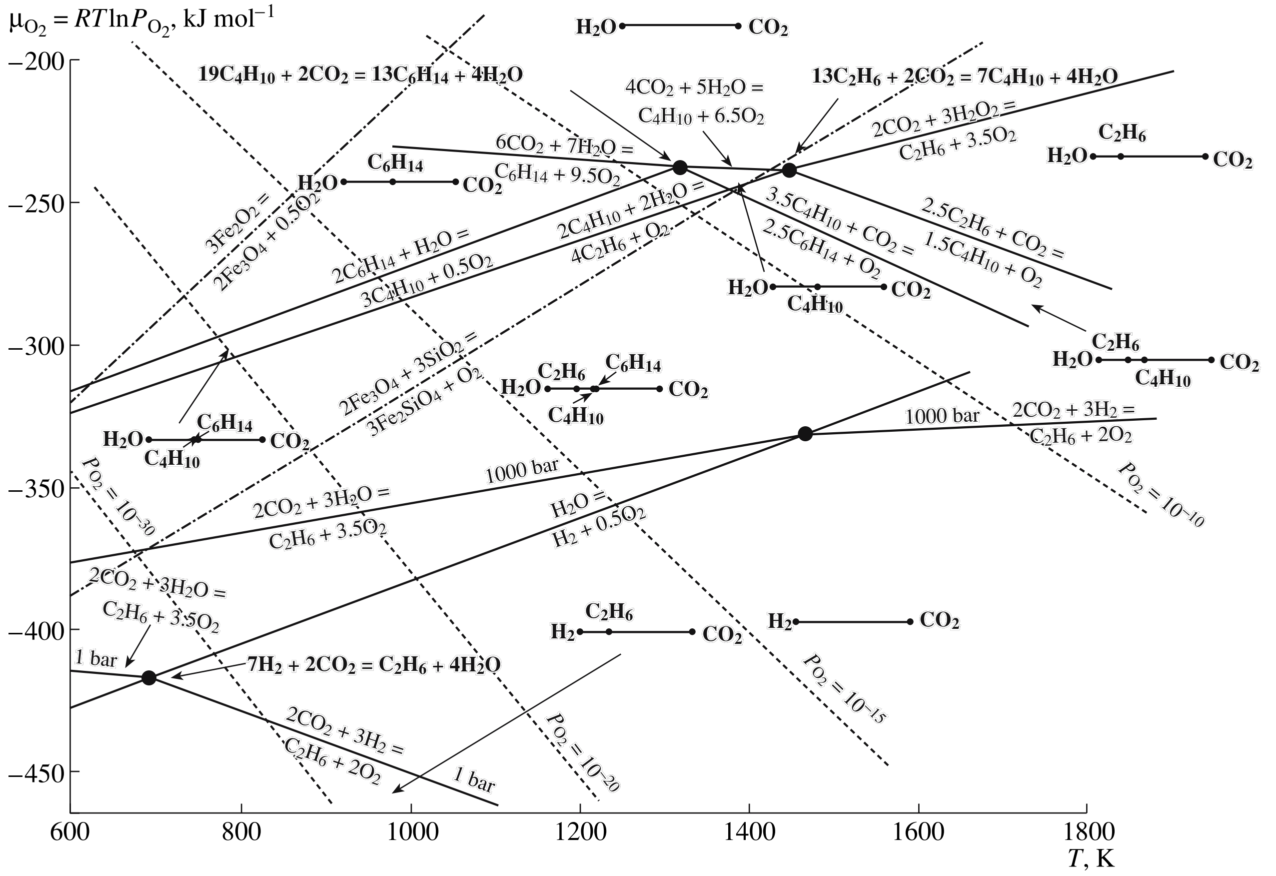

Fig. 2. Isobars that bound ethane (C_2H_6) facies in a pressure range of 1–1000 bar (Table 1) and approximately facies of ethane and heavy HCs (C_4H_{10} and C_6H_{14}) at a much higher pressure (upper portion of the diagram). The arrows point to the reactions of nonvariant equilibrium.

The considered models of the concentration of the heavy carbon isotope in hydrocarbons have different implications. The first model is inherent to extremely high-temperature conditions and is conjugated with the intensification of the reducing setting in magmatism. This model is only of theoretical significance because of its contradiction with petrologic data. The magma sources develop under the influence of aqueous fluids that markedly depress the melting temperature of magmatism. The evolution of magmatism is directed toward increasing alkalinity correlated with increase in the oxygen potential. These processes are consistent with the second model of the concentration of the heavy carbon isotope in hydrocarbons ($CH_3 \rightarrow CH$) owing to increase in the oxygen potential and decrease in temperature. This specific feature of the second model suggests its validity not only for magmatic processes of alkalinity growth in the abyssal melt, but also for the migration of hydrocarbon fluids from the melt into the crust with a higher oxygen potential.

The formation of heavy HCs started at an enormous fluid pressure. This is evident from the occurrence of hydrocarbons within fluid inclusions captured by diamonds and its mineral-satellites [8] genetically related to abyssal magmatic sources.

The alkaline trend of magmatic sources is inherent to the environment of mantle material compression that prevents selective escape of hydrogen. The latter process promotes the increase in fluid pressure and magmatic replacement of the mantle substrate that created the alkaline trend. The conjugation of the alkaline trend with the generation of heavy HCs is supported by the universal presence of a wide range of HCs in fluid inclusions captured by rock-forming minerals of alkaline rocks [9], particularly, minerals of the early mantle generation. The ascent of heavy HCs with a high energetic capacity is demonstrated by the development of deep sources of earthquakes related to detonation of metastable hydrocarbon accumulations [10]. These HCs probably participated in the formation of oil pools as may be judged from elevated seismicity of petroliferous provinces. However, methane and ethane make the major contribution to the ascent of hydrocarbons. In this process, methane behaves as an inert compound, whereas the highly reactive ethane is involved in the oxidative generation of water, giving rise to the formation of cognate heavy HCs ($CH_3 \rightarrow CH$) according to

Table 1. Free energy (ΔG_T°, kJ) of reactions of *n*-alkane oxidation at variable pressure and temperature calculated on the basis of constants taken from [5, 6]

Reaction	*P*, bar	*T*, K				
		298	600	900	1200	1500
See Fig. 1						
$CH_4 + 1.5O_2 = CO + 2H_2O$	1	−543.60	−569.62	−596.16	−622.16	−647.35
	100	−520.81	−523.74	−527.33	−530.39	−532.63
	1000	−509.41	−500.79	−492.91	−484.50	−475.27
$CH_4 + 0.5O_2 = CO + 2H_2$	1	−86.46	−141.67	−200.10	−259.41	−318.72
	100	−63.67	−95.78	−131.27	−167.64	−204.01
	1000	−52.27	−72.84	−96.85	−121.74	−146.64
See Fig. 2						
$C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$	1	−1441.54	−1457.19	−1473.37	−1486.96	−1499.01
	1000	−1390.27	−1319.53	−1266.89	−1211.63	−1154.85
$C_2H_6 + 2O_2 = 2CO_2 + 3H_2$	1	−755.82	−815.24	−879.25	−942.84	−1006.06
	1000	−687.44	−677.58	−672.75	−667.51	−661.90
$C_2H_6 + 0.5O_2 = C_4H_{10} + H_2O$	>1000	−179.86	−162.31	−146.44	−130.57	−114.71
$3C_4H_{10} + 0.5O_2 = 2C_6H_{14} + H_2O$		−177.62	−158.64	−141.11	−123.58	−106.05
$C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$		−1131.89	−1055.74	−979.58	−900.30	−821.02
$C_4H_{10} + 6.5O_2 = 4CO_2 + 5H_2O$		−1575.38	−1567.28	−1559.29	−1553.56	−1546.54
$C_6H_{14} + 9.5O_2 = 6CO_2 + 7H_2O$		−2118.42	−2160.96	−2203.43	−2338.77	−2276.20
$1.5C_4H_{10} + O_2 = 2.5C_2H_6 + CO_2$		−109.17	−143.22	−176.86	−210.98	−244.10
$2.5C_6H_{14} + O_2 = 3.5C_4H_{10} + CO_2$		−93.81	−136.07	−178.31	−220.55	−262.79

Table 2. Free energy of redox reactions of hydrocarbons in a hydrothermal system at *T* = 523 K and *P* = 48 bar calculated on the basis of constants taken from [11]

Reaction	ΔG_{523}, kJ	Reaction	ΔG_{523}, kJ
$2C_3H_8 + H_2 = 3C_2H_6$	−50.76	$6C_2H_6 + O_2 = 4C_3H_8 + 2H_2O$	−382.53
$3C_4H_{10} + H_2 = C_3H_8$	−50.85	$8C_3H_8 + O_2 = 6C_4H_{10} + 2H_2O$	−382.35
$2C_6H_{14} + H_2 = 3C_4H_{10}$	−57.17	$6C_4H_{10} + O_2 = 4C_6H_{14} + 2H_2O$	−369.71
$3C_8H_{18} + H_2 = 4C_6H_{14}$	−59.39	$8C_6H_{14} + O_2 = 6C_8H_{18} + 2H_2O$	−365.27
$C_{16}H_{34} + H_2 = 2C_8H_{18}$	−59.79	$4C_8H_{18} + O_2 = 2C_{16}H_{34} + 2H_2O$	−364.47
$4C_{20}H_{42} + H_2 = 5C_{16}H_{34}$	−59.86	$10C_{16}H_{34} + O_2 = 8C_{20}H_{42} + 2H_2O$	−364.33

the second model. This is illustrated in the diagram (Fig. 3) and Table 2 for low-temperature (liquid) aqueous solutions. The diagram is based on the thermodynamic constants of substances in aqueous solutions calculated at the pressure of water vapor saturation and temperature of 25–350°C [11].

The difference in the behavior of methane and ethane in geological processes follows from thermodynamic calculations of the chemical potentials of oxygen $\mu_{O_2} = RT\ln P_{O_2}$ in reactions of the formation of heavy HCs in hydrothermal solutions, for example, propane C_3H_8 ($T = 523$ K, $P = 48$ bar): $4CH_4 + O_2 = 2C_2H_6 + 2H_2O$, $\mu_{O_2} = -338.69$ kJ; $3CH_4 + O_2 = C_3H_8 + 2H_2O$, $\mu_{O_2} = -349.65$ kJ; and $6C_2H_6 + O_2 = 4C_3H_8 + 2H_2O$, $\mu_{O_2} = -382.53$ kJ. According to these data, ethane participates in oxidizing reactions more readily than methane and produces a series of heavy HCs (Fig. 3) that are involved in several processes of the formation of the Earth's sedimentary shell, such as creation of anomalies of isotopically light carbon due to the loss of hydrogen and formation of not only carbonates, but also bitumen deposits ("cahytolites," i.e., deposits of carbon–hydrogen compounds), which serve as a basis for the formation of black shales. The black shales were peri-

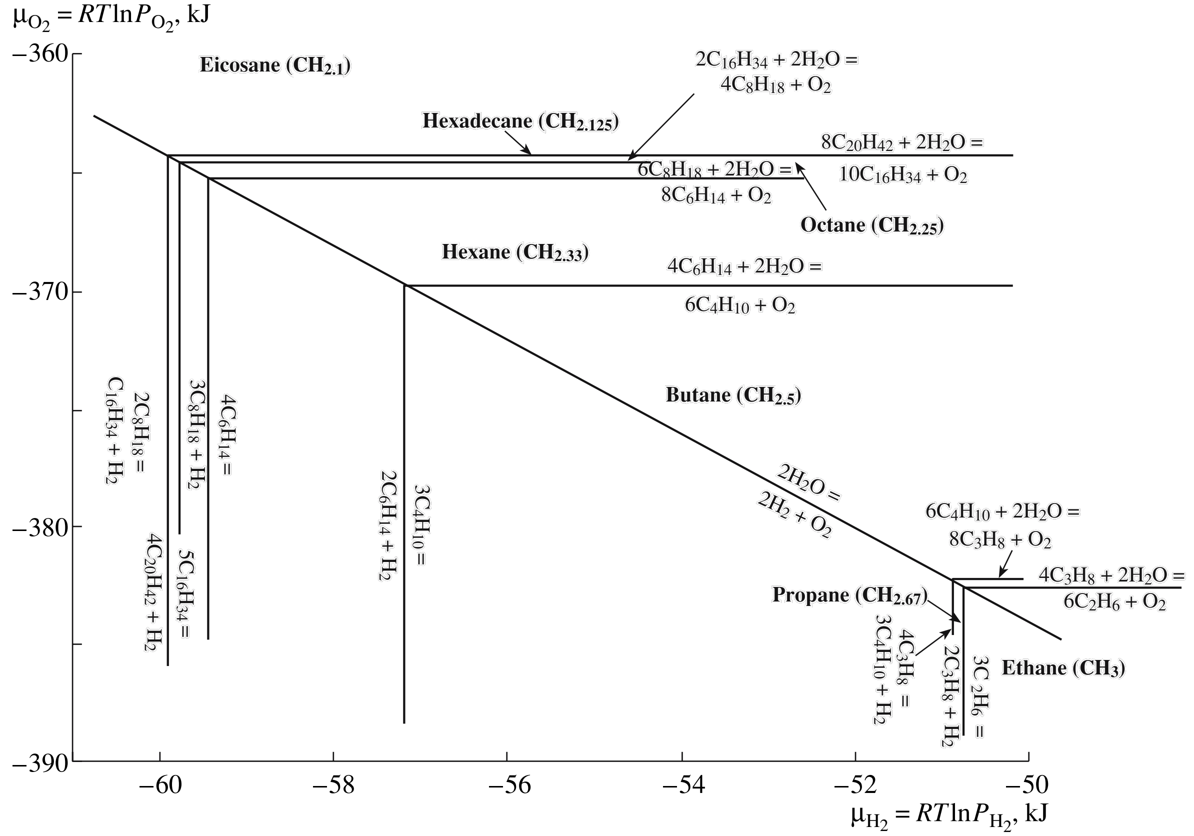

Fig. 3. The μ_{H_2}–μ_{O_2} diagram of redox facies of hydrocarbons of petroleum series (*n*-alkanes) in a hydrothermal system at $T = 523$ K and $P = 48$ bar (Table 2).

odically developed on a global scale in the Earth's sedimentary shell and correlated to a certain extent with impulses of oil formation [12]. However, the formation of oil is an abyssal process under conditions preventing the selective migration of hydrogens and transformation of oil into bitumen. Nevertheless, according to [2–4], hydrothermal vents in the aforementioned Rainbow and Juan de Fuca fields are accompanied by heavy hydrocarbon seeps that represent specific embryos of oil formation. In black shales [13] related to the input of heavy HCs, conjugation of the processes discussed above with oil formation is emphasized by the occurrence of transitional oil shales.

Judging from the occurrence of HCs of the oil series (alkanes and alkylbenzens) in hydrothermal vents of the Juan de Fuca Ridge, the formation of oil is possible at a great depth of the sedimentary basin under the fluid pressure inhibiting the loss of hydrogen. In this regard, marginal ocean ridges of the Juan de Fuca type occupy a transitional position between the mid-ocean ridges, which are not accompanied by sedimentary basins, and the shelf and continental margins of oceans and seas accompanied by sedimentary basins regarded as the major oil reservoirs. This structural difference in terms of hydrocarbon potential is related to the formation of oil after the impact of acid fluids upon the rocks [7]. Owing to percolation in the abyssal mafic and ultramafic magmas, the fluids are aggressive with respect to sialic rocks of terrigenous basins and their granitic–gneissic basements. The acid leaching of these rocks augments the porosity of sedimentary rocks and the formation of reservoirs necessary for the subsequent accumulation of oil. Owing to this process, the oil pools replace considerable volumes of sedimentary rocks. Conduits of the fluid-mediated exhumation of an incompletely dissolved material of sedimentary basins are expressed in geological sections as peculiar roots of mud volcanoes [14] spatially associated with petroleum provinces in some regions. The necessity of fluid leaching of sialic rocks before the formation of oil is clearly seen in the fields where the oil pools extend beyond the limits of sedimentary basins and penetrate deep into upthrown blocks of the granitic, gneissic, or carbonate basement [15].

The heavy HCs of oil pools in sedimentary basins of the Earth's crust probably are heterogeneous. On the one hand, they were transported from mantle magma sources. On the other hand, they were synthesized from light HCs (Fig. 3) in the course of separation of oil ($4C_6H_{14} + 0.5O_2 = 3C_8H_{18} + H_2O$, etc.) from water commonly underlying oil pools. The transition of oil from the gaseous (fluid) phase into liquid state naturally

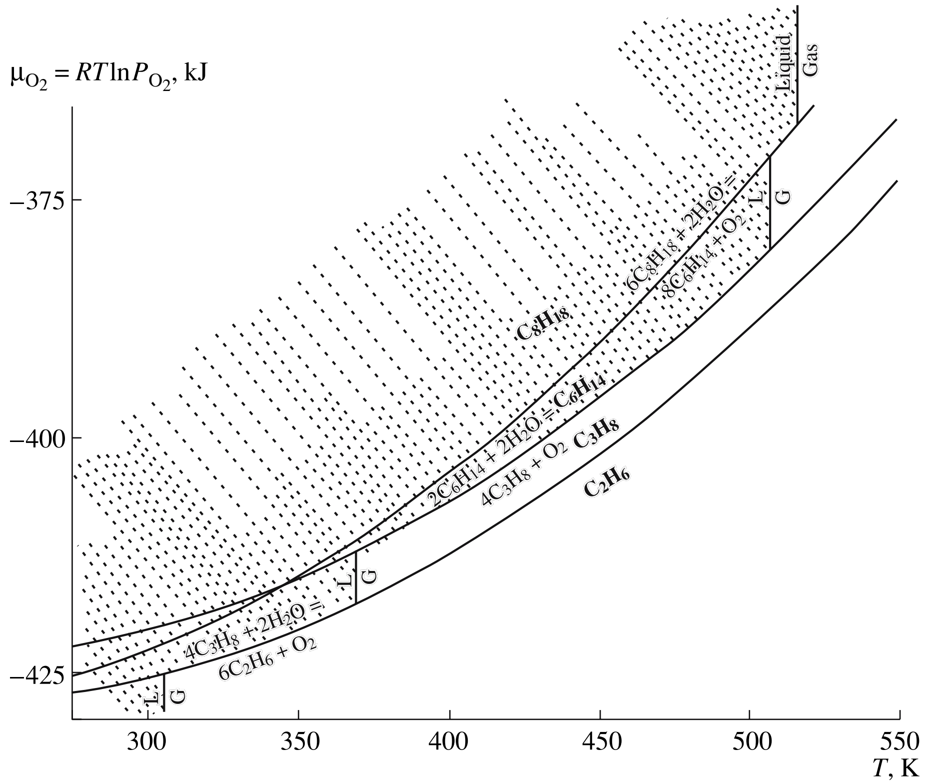

Fig. 4. Temperature relationships of redox facies of hydrocarbons (ethane, propane, hexane, and octane) in water solutions at a pressure of water vapor saturation calculated on the basis of the constants taken from [11]. The vertical lines designate phase (gas–liquid) transitions of HCs that control their incorporation into liquid oil (hatched field).

fits the scenario of consecutive transformations of specific HCs in accordance with their critical *PT* parameters. The oil, which is immiscible with the liquid water released in this process, is formed in a wide temperature range (Fig. 4). The process is completed with release of the gaseous phase that migrates elsewhere or makes up gas pools in the overlying rocks.

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REFERENCES

1. D. C. Kelley, J. Geophys. Res. **101**, 2943 (1996).
2. N. G. Holm and J. L. Charlou, Earth Planet. Sci. Lett. **191**, 1 (2001).
3. J. L. Charlou, J. P. Donval, Y. Fouquet, et al., Chem. Geol. **191**, 345 (2002).
4. A. M. Cruse and J. S. Seewald, Geochim. Cosmochim. Acta **70**, 2073 (2006).
5. R. A. Robie and B. S. Hemingway, *Thermodynamic Properties of Substances at 298.15 K and 1 Bar (105 Pascals) Pressure and Higher Temperatures* (US Geol. Surv., Washington, DC, 1995).
6. D. R. Stull, E. F. Westrum, Jr., and G. C. Zinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969; Mir, Moscow, 1971).
7. A. A. Marakushev and S. A. Marakushev, Dokl. Earth Sci. **406**, 141 (2006) [Dokl. Akad. Nauk **406**, 521 (2006)].
8. C. E. Melton and A. A. Giardini, Am. Mineral. **59**, 775 (1974).
9. J. Potter, A. H. Rankin, and P. J. Treloar, Lithos **75**, 311 (2004).
10. I. K. Karpov, V. S. Zubkov, V. A. Bychinsky, and M. V. Artimenko, Russ. Geol. Geofiz. **39**, 754 (1998).
11. E. H. Oelkers, H. C. Helgeson, E. L. Shock, et al., J. Phys. Chem. Ref. Data **24** (4), 1401 (1995).
12. A. E. Kontorovich and V. S. Vyshemirsky, Dokl. Earth Sci. **357**, 1154 (1997) [Dokl. Akad. Sci. **356**, 794 (1997)].
13. Ya. E. Yudovich, Vestn. Inst. Geol., No. 2, 9 (2006).
14. V. N. Kholodov, Lithol. Miner. Res. **37**, 293 (2002) [Litol. Polezn. Iskop. **37**, 339 (2002)].
15. E. G. Areshev, *Petroliferous Basins of the Pacific Mobile Belt* (AVANTI, Moscow, 2004) [in Russian].