

Influence of cracking of crude oil in hydrothermal systems on formation of various types of oil-and-gas deposits

Balitsky, Vladimir S.*, Pironon Jacques **, Penteley, Svetlana V. ***, Novikova, Maria A.*, Balitskaya, Liudmila V.* and Bublikova Tatiyana, M*

*Institute of Experimental Mineralogy RAS, Osepiyan St, 4, Chernogolovka, Moscow District, Russia

**Université de Lorraine, G2R-CREGU laboratory – BP 239 • F-54506 Vandœuvre lès Nancy

***17, Allée des Noires Terres, 54850 Messein, France

Cracking of crude oil and of its heavy fractions is one of the principal processes of obtaining benzene and other oil-products. It is shown that sometimes the cracking took place in natural conditions. Precisely this fact explains the particularities of so-called hydrothermal oil's composition, which can be found in zones of spreading and in the fields of volcanic and thermal activities where the temperatures often achieve 400 °C and more (Simoneit, 1995; Bajenova & Lein, 2002). Experimental works have proved principal possibility of crude oil cracking in the hydrothermal systems (Bjoroy et al., 1992; Huang et al, 2001). The most convincing experiences related to such studies were a comparison of initial oil with residual oil and with hydrocarbons in synthetic fluid inclusions formed in the same systems (Teinturier et al., 2003).

In the present work the experimental study of crude oil cracking is attempted to understand its influence for formation of different types of oil & gas deposits. The investigations were carried out in a complex. The main attention was kept on fluid inclusions in quartz grown simultaneously with interaction of hydrothermal solutions and crude oil in a large range of temperatures and pressures.

Experiences were run by the hydrothermal method of thermal gradient, which was described in previous works (Balitsky et al., 2005, and others). Initial oil-water mixtures were prepared from oils with neutral, alkaline and alkaline solutions. Oil part in the mixtures varied from 0.01 to 50 vol%.

The temperatures of experiences were set from 220/260 °C up to 490/500 °C where the first value is the temperature of the upper part of autoclave and the second is the temperature of the bottom. The filling of autoclaves ranges from

50 to 80 %. More than 100 experiences with duration time between 14 to 30 days were carried out. The products of experiments were studied by optical microscope, X-ray, fluorescence, microprobe and were characterised by IR-spectra and by chromatograms. Fluid inclusions were studied in polished slices of quartz. Phase transformations in inclusions were observed in-situ during heating and cooling them in micro thermometric equipment THMSG-600 (Balitsky et al., 2007). Composition of oil fractions was defined by the boiling temperature and was characterised by local IR-spectra.

Fluid inclusions of quartz obtained at 220 to 320 °C are characterised by three-phase state with phase relation from $L1 \geq G > L2$ till $L2 \geq L1 > G$, where L1 is the water solution, G is the gas phase (water vapour) and L2 is oil (Fig. 1).

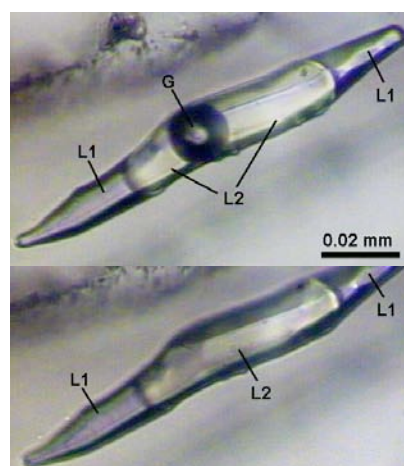


Fig. 1. Three-phase gas-liquid aqua-hydrocarbon inclusion in quartz, formed at 280 °C (upper picture), and the same inclusion in the two-phase state at 230 °C (bottom picture). Fragment of micro-thermogram.

The composition of initial and residual oils has not changed. During heating of inclusions up to 230 - 330 °C the gas phase disappears with the transformation of fluid to two-phase state liquid with a different L1/L2 ratio. Water-oil fluid existence can be evidence without a free gas-phase in earth crust under noted TP-parameters. Such fluids must be found at depths of about 3.5 to 4.5 km on the basis of average values of geothermic gradients and hydro- and litho-static pressures.

Fluid inclusions in quartz obtained at higher temperatures (330 to 490 °C) and saturation vapour pressures and more are characterised by different phase transformations. Such inclusions are polyphased under room conditions. Fluid in them can be essentially liquid ($L1 \geq G > L2 > SB$) or essentially gaseous ($G \gg L1 > L2 > SB$), where L1 is the water solution; L2 are liquid hydrocarbons, mainly light oil fractions (benzene, kerosene); G are gaseous hydrocarbons, essentially methane; and SB is solid bitumen.

At the beginning of heating inclusions up to 250 - 290 °C dissolved liquid hydrocarbons in gas hydrocarbons form a bi-phase fluid ($L1 > G$). Then homogenization of the fluid at 365 to 372 °C occurs (Fig. 2).

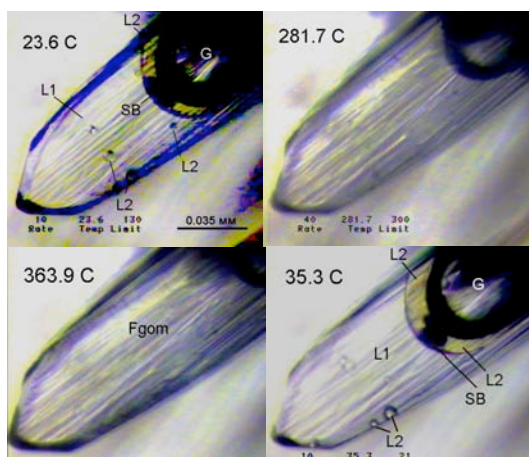


Fig. 2. Fragment of micro-thermogram: Formation of bi-phase aqua-hydrocarbon fluid ($L1 > G$) at 280 °C followed by its homogenization at 363.9 °C. Inclusion's cooling gives a restoration of all disappeared phases. Temperature of inclusion's formation is 490 °C.

This is a principle difference of such type of inclusions from bi-phase aqua-oil fluid inclusions formed at lower TP-parameters. The heavy oil fractions in high temperatures solutions (above 330 °C) undergo cracking. Formation of light hydrocarbon fractions is fixed with their boiling temperature from 60 till 240 - 270 °C in inclusions. Gas hydrocarbons, especially methane, and the presence of solid bitumen is also observed. Chromatograms' comparison of oil and its heavy fractions before and after experiments definitely evidences the hydrocarbon cracking both, by appearance of light fractions and by the increase of their quantity. The heating of such fluids up to critical point of water, transforms them into a homogeneous supercritical state. It indicates the possibility of the existence of light and medium oil fractions and their migration as supercritical fluids in the earth crust. This process probably demonstrates the conditions of formation of gas condensate and oil condensate deposits.

Thus, the investigations show the principle phase compositions and phase states of aqua-hydrocarbon fluids formed at temperatures lower than 320 °C and above 330 °C at saturated vapour pressure and more. Such differences are related with crude oil cracking, which results in the appearance of light oil fractions (benzene and kerosene), gaseous hydrocarbons and solid bitumen. That is clearly observed by the influence of high temperatures on primary aqua-oil inclusions formed in quartz at temperatures between 280 - 320 °C (Fig. 3).

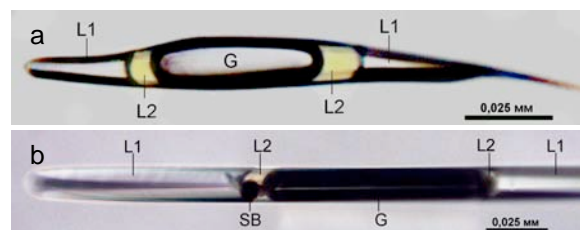


Fig. 3. a An inclusion formed in quartz at 280 °C: L1 – water solution, G – water vapour, L2 – hydrocarbons identical to the composition of oil used as initial charge; b The same kind of inclusion after high-temperature (400 °C) treatment within 12 days: L1 – water solution, G – gas, mainly methane, L2 - light oil fractions as well benzene and kerosene, and residual asphalts (SB).

Thermo-baric parameters in the earth crust depend on real thermo-gradients and hydro- and litho-static pressures. Such parameters inevitably reach with depth the values, which lead to hydrocarbon cracking. This fact has an important meaning on hydrocarbon composition and formation of corresponding types of oil and gas deposits.

REFERENCES

- Balitsky V.S., Pironon J., Penteley S.V., Novikova M.A., and Balitskaya L.V. (2011) *Doklady Earth Sciences*, p. 383–386.
- Bazhenova O.K., Lein A.Yu. (2002) V kn.: Organicheskaya mineralogiya. *Materialy Rossiiskogo soveshchaniya po organicheskoi mineralogii*. SPb: SPbGU, p. 95–96. (in russian)
- Behar F., Kressman S., Rudkiewicz J.L., Vandenbroucke M. (1992) *Organic Geochemistry*, 19, p. 173-189.
- Huang W.-L., Otten G.A. (2001) *Organic Geochemistry*, 32, p. 817-830.
- Simoneit B.R.T. (1995) Osnovnye napravleniya geokhimii. M.: Nauka, c. 236-259. (in russian)
- Teinturier S., Elie M., Pironon J. (2003) *Journal of Geochemical Exploration*, 78-79, p. 421 - 425.