

# Chapter 1

## Phase Composition and States of Water-Hydrocarbon Fluids at Elevated and High Temperatures and Pressures (Experiment with the Use of Synthetic Fluid Inclusions)



V. S. Balitsky, T. V. Setkova, L. V. Balitskaya, T. M. Bublikova,  
and M. A. Golunova

**Abstract** The article considers new approaches and methods for studying the phase composition and states of aqueous-hydrocarbon fluids in the temperature range of 240–700 °C and pressures of 5–150 MPa respectively. The essence of the approach is to conduct experiments in autoclaves on the formation of aqueous-hydrocarbon fluids through the interaction of hydrothermal solutions with bituminous and high-carbon rocks, as well as with crude oil. Simultaneous, in the same autoclaves, the quartz crystals and less other minerals with trapped aqueous-hydrocarbon inclusions are growing. These inclusions are the main objects of research that are carried out using modern micro thermometry methods, especially in combination with conventional and high-temperature FT-IR spectroscopy and microscopy with UV and natural light. This allows in situ monitoring of changes in the phase composition and states of aqueous-hydrocarbon fluids in a wide range of PT-parameters, to determine the effect of temperature and volume ratios of water and hydrocarbon (liquid and gas) phases on the occurrence of multiphase, three-phase and biphasic heterogeneous liquid and gas-liquid phases and homogeneous fluids. Studies have shown that with certain compositions of synthetic aqueous-hydrocarbon inclusions at heated and cooled is often appeared so-called imaginary homogenization in inclusions. This event associated with the periodic alignment of the refractive indices and densities of the aqueous and hydrocarbon liquid phases. The influence of the volume ratios of the aqueous and hydrocarbon phases on the cessation of cracking and metamorphic transformations of oil when the fluid goes into a homogeneous supercritical state, and the resumption of these processes after fluid heterogenization as a result of the temperature drop were established. In addition, a comparison of the effect of the PT-condition on the phase composition and the state of the hydrocarbon made it possible to estimate the maximum depths of the oil in the Earth's interior. Depending on the volume ratios of the water and oil phases this depth turned out to be equal from 14 to 22 km.

---

V. S. Balitsky (✉) · T. V. Setkova · L. V. Balitskaya · T. M. Bublikova · M. A. Golunova  
D.S. Korzhinskii Institute of Experimental Mineralogy, Russian Academy of Sciences,  
Academician Osipyan street 4, Chernogolovka, Moscow region 142432, Russia  
e-mail: [balvld@iem.ac.ru](mailto:balvld@iem.ac.ru)

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer  
Nature Switzerland AG 2020

Y. Litvin and O. Safonov (eds.), *Advances in Experimental and Genetic Mineralogy*,  
Springer Mineralogy, [https://doi.org/10.1007/978-3-030-42859-4\\_1](https://doi.org/10.1007/978-3-030-42859-4_1)

**Keywords** Water-hydrocarbon fluids · Oil stability · Depths of oil formation · Hydrothermal experiment

## 1.1 Introduction

It is known that oil in natural conditions is constantly associated with water. And this is not surprising, because these compounds, although sharply different in composition, but both are liquids that are stable in a wide range of temperatures and pressures. As liquids, they are subject to the same hydrodynamic laws and this largely predetermines their joint migration and concentration in certain areas of the Earth's crust.

Direct evidence of the joint migration of hydrothermal solutions, oil and hydrocarbon gases is found in many areas of modern volcanic and thermal activity, ocean floor spreading zones and other tectonically active parts of the Earth (Pikovskii et al. 1987; Simoneit 1995; Bazhenova and Lein 2002; Rokosova et al. 2001). The temperature of such fluids often reaches 400 °C and higher. At the same time, oil and gas provinces often show signs of hydrothermal activity. They are expressed in carburizing, sulphidization, quartzing and argyllization of rocks containing oil and gas fields. Sometimes these changes are accompanied by accumulations of uranium, mercury, antimony, gold and other minerals (Ivankin and Nazarova 2001). At the same time, gas, liquid and solid hydrocarbons (HC) are quite often found in magmatic and metamorphic rocks, contact-metasomatic formations, pegmatites and hydrothermal veins (Balitsky 1965; Beskrovnyi 1967; Ozerova 1986; Florovskaya et al. 1964; Chukanov et al. 2006). In addition to independent emissions, they are present in the fluid inclusions of various vein and ore minerals. All this indicates that hydrothermal solutions in the Earth's interior often interact with bituminous rocks and crude oil. The nature of such interactions at elevated and high temperatures and pressures is still not sufficiently studied. This is especially true for the phase composition and states of natural aqueous-hydrocarbon fluids, which are practically inaccessible for direct observation because of the great depths and associated high TR-parameters. However, many of their characteristics can be recreated with varying degrees of confidence in experimental studies using synthetic fluid inclusions in quartz and other minerals grown simultaneously with the interaction of hydrothermal solutions with bituminous rocks and crude oil (Balitsky et al. 2005, 2007, 2011, 2014, 2016; Teinturier et al. 2003).

Similar researches were carried out in the last 20 years in the Minerals Synthesis and Modification Laboratory of the D.S. Korzhinskii Institute of Experimental Mineralogy and led to the creation in the laboratory one of the new scientific directions connected with the solve of various problems of HC geochemistry. This article was also implemented within the framework of the abovementioned scientific direction. Its purpose is to demonstrate the possibility of using synthetic fluid inclusions in quartz to study and predict the phase composition and states of deep water-hydrocarbon fluids under various *PT*-conditions and to estimate on this basis

the oil and gas bearing capacity of bituminous rocks and the maximum depths of oil in the Earth's interior.

## **1.2 Approach to the Study of the Phase Composition and States of Water-Hydrocarbon Inclusions in Quartz and Methods of Their Research**

### ***1.2.1 Basic Approach***

The problems set in the article were solved on the basis of the approach developed by the authors of the article specifically to study the interaction of various bituminous rocks and crude oil with hydrothermal solutions (Balitsky et al. 2005, 2007). The essence of the approach is to conduct experiments on the formation of artificial aqueous-hydrocarbon fluids by means of interaction of hydrothermal solutions with bituminous rocks and crude oil at the same time growing quartz crystals with water-hydrocarbon inclusions. Such inclusions are essentially microsamples of mother solutions selected and hermetically preserved under *PT* conditions of experiments without disturbances in the system of dynamic equilibrium. Further inclusions are used to study in situ behavior, phase composition and states of their fluids by thermobarogeochemical methods (Ermakov 1972; Roedder 1984; Mel'nikov et al. 2008), especially microthermometry in combination with conventional and high-temperature local FT-IR spectroscopy and microscopy using UV lighting (Balitsky et al. 2016). It was assumed that if all syngenetic inclusions contained the same phases with the same volumetric ratios, they were captured from homogeneous fluids. When different phases or identical phases were observed in the inclusions, but with different volumetric ratios, this indicated that the mother fluids were in a heterogeneous state. Quartz was chosen to capture inclusions because it has high mechanical strength and chemical resistance - properties that are necessary both in the formation of fluid inclusions and subsequent thermometric studies. An important factor for the choice of quartz as a carrier of fluid inclusions is the relative ease of its growth on seed in aqueous solutions of different compositions in a wide range of temperatures (240–900 °C) and pressures (from the pressure of saturated steam to 150–200 MPa) (Balitsky et al. 2005).

### ***1.2.2 Methods of Growing Quartz Crystals with Synthetic Water-Hydrocarbon Inclusions***

All experiments on growing quartz with water-hydrocarbon inclusions were carried out by the hydrothermal method of temperature difference. Heat-resistant autoclaves of 30, 50, 100 and 280 ml volume made of stainless steel and Cr–Ni alloy were used

in experiments. Autoclaves were heated in electric shaft furnaces with two heaters. Depending on the design and size of the furnaces, they were equipped with 3 to 10 autoclaves at the same time. Temperature in furnaces and autoclaves was maintained and controlled by a set of standard devices (TYP 01 T4, TYP R3 and Thermodat-25M1). Temperature accuracy was  $\pm 2$  °C. The necessary pressure was set by pouring the solution with filling coefficients, which were determined by  $P$ - $V$ - $T$  diagrams for solutions of the corresponding composition (Samoilovich 1969), and in the absence of such—by tabular data  $P$ - $V$ - $T$ —dependencies for pure water (Naumov et al. 1971).

Crystals were grown on seed bars, mainly  $ZY$ - and  $ZX$ -orientations with the length of 140–210 mm, width of 5–8 mm and thickness of 2–4 mm. The absence of an autoclave diaphragm, which usually separates the dissolution and growth zones of quartz, led to a continuous convective mixing of the solution during the entire experiment and the formation of crystals of an unusual wedge-like shape, due to a gradual increase in the bottom-up growth rate as saturation increases (Fig. 1.1). Entering of autoclaves into the working mode was carried out with the speed of 50–70 °C/h. After reaching the set temperature the autoclave was maintained for 12–24 h in isothermal conditions or with a small (10–15 °C) inverse temperature difference. This made it possible to prepare pickling channels in the seed bars, which were infected with fluid inclusions when the direct temperature difference was restored (Balitskaya and Balitsky 2010).

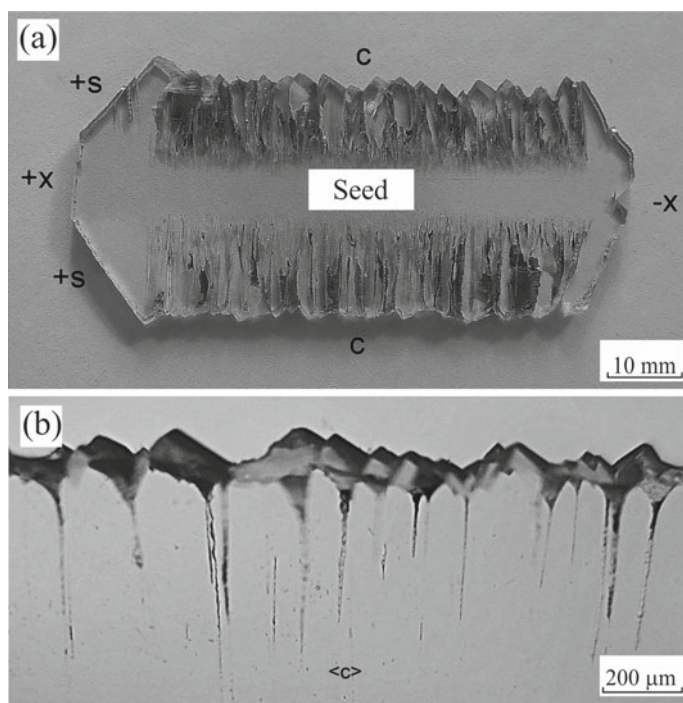
An important methodological task of the conducted researches was to find the conditions under which the formation of water-hydrocarbon inclusions would occur in quartz. The inevitability of the formation of such inclusions in quartz predetermined the choice of crystallographic orientations of seed cuts, stimulating the appearance of coarse regenerative relief on the growing surfaces (Balitsky et al. 2005). Anisotropy



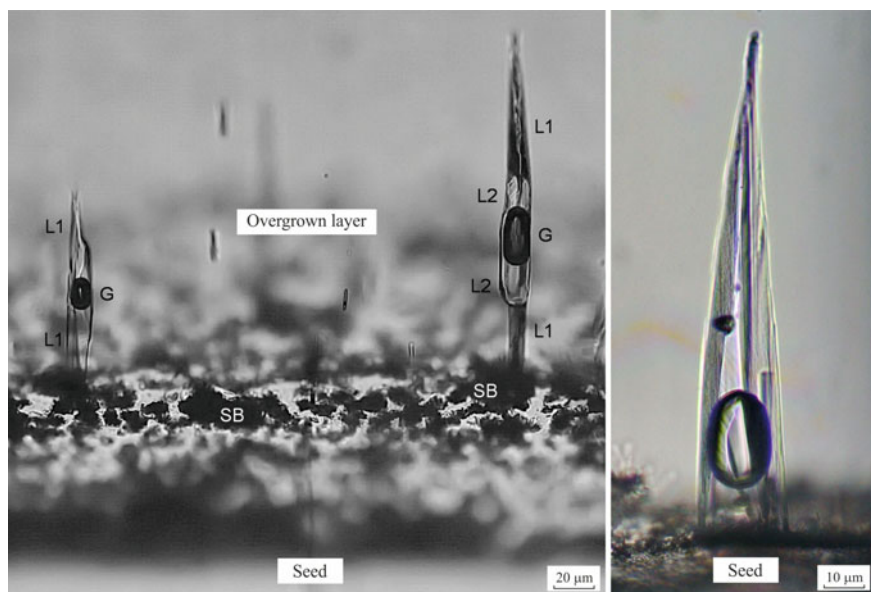
**Fig. 1.1** Examples of quartz crystals with water-hydrocarbon inclusions, grown in the temperature range of 240–670 °C and pressures of 5–150 MPa in alkaline and weakly alkaline solutions in the presence of bituminous rocks and crude oil

of the growth rates of the faces composing the pyramids of growth of such relief led at first to the appearance between them of micro-cavities, which at the subsequent overgrowth turned into fluid inclusions. The most actively similar inclusions are formed at growth of quartz on seed bars of *ZY*- and *ZX*-orientations. Regeneration pyramids of quartz relief growth are composed, as a rule, of faces of positive  $\{r\}$  and negative  $\{z\}$  rhombohedrons, hexagonal prism  $\{m\}$ , trigonal positive  $\{+a\}$  and trigonal negative  $\{-a\}$  prisms and trigonal positive  $\{+s\}$  dipyramids (Fig. 1.2a, b). In addition, fluid inclusions originate from particles of altered rocks, solid bitumen and oil droplets, which are usually deposited at the boundary between seed bars and newly formed quartz (Fig. 1.3). Fluid inclusions formed in the etching channels of dislocations in seed quartz bars are also no less informative for studies.

To obtain water-hydrocarbon inclusions captured in quartz crystals, two series of experiments were conducted. In the experiments of the first series, liquid and gas hydrocarbons were supplied to the hydrothermal solution from bituminous rocks. The oil shale from the Kashpirskoye (near the town of Syzran) and Leningradskoye (near the town of Slantsy) deposits and high-bituminous rocks of the Bazhenov Formation (Western Siberia) and Domanikovyh sediments (Volga-Ural Province) were



**Fig. 1.2** Regeneration pyramids of quartz relief growth (a) and regeneration relief of rough faces of the basal pinacoid (b). Rough regeneration relief of rough faces, especially the basal pinacoid, favors to the generation of inclusions



**Fig. 1.3** The origin and formation of fluid water-hydrocarbon inclusions on particles of solid bitumen, oil droplets, altered bituminous rocks, micas and other minerals

used. Besides, hydrothermal treatment experiments were carried out with bituminous claystones of the Central Oil and Gas Basin of France.

The elementary composition of oil shale from the Kashpirskoye and Leningradskoye deposits includes, respectively (wt%): carbon—75.6 and 59.7–70; hydrogen—9.4 and 6.0–7.8; sulfur—1.4 and 6.0–14.2; nitrogen—0.5 and 1.7–2.5 and oxygen—13.1 and 22.3 (Lapidus and Strizhakova 2004). Organic matter, ash and total sulfur, respectively, are (wt%): 35.0, 46.0, 1.6 and 32.5, 57.5 and 5.8.

The Bazhenov Formation includes siliceous clay-carbonate rocks with hydro-mica, kaolinite, montmorillonite and carbonates. The share of initial organic carbon in them varies from 8 to 12 wt%, and the residual carbon decreases by 1–2 wt%. The content of chloroform bitumen rarely exceeds 1.0–1.5 wt%, although in general the soluble part of rocks reaches 10–14 wt%. Household deposits are similar in composition to the Bazhenov Formation in many respects. They also include bituminous siliceous clay-carbonate rocks enriched with organic matter. Its share is 2.5–10.0 wt% (Zaidelson et al. 1990). High bituminous rocks of both regions are attributed to oil and gas producing strata due to high content of microoil and combustible gas.

Fragments of initial rocks with the size of 5–8 mm in the cross section with the total mass of 10–12 g were placed in the lower (hotter) zone of the autoclave. In the same place on the perimeter of the inner wall of the autoclave charge quartz bars of 80–100 mm long, 4–8 mm wide and 2–4 mm thick were installed, which are necessary for feeding the solution with silica. Another ZY- and/or ZX-orientation quartz bar with a length of up to 208 mm was hung from a metal frame along the

vertical axis of the autoclave. This bar was a seed for the build-up of newly formed quartz with captured water-hydrocarbon inclusions.

Pure water, aqueous solutions of sodium chloride (10 and 20 wt% NaCl), sodium bicarbonate (5 and 7 wt% NaHCO<sub>3</sub>) and sodium carbonate (3 and 5 wt% Na<sub>2</sub>CO<sub>3</sub>) were used as initial solutions in experiments of this series. Solutions interaction with rocks was carried out at temperatures of 240/280, 300/320, 330/350, 360/380 and 370/400 and 420/450 °C at a pressure of 7, 20, 75, 90, 100 and 120 MPa, respectively. Here and below, the temperatures of the upper and lower end of the autoclave are indicated via a slant line, respectively.

In the second series of experiments, water-hydrocarbon inclusions in quartz were obtained by interaction of hydrothermal solutions directly with crude oil. Oil from the Bavlinskoye (Tatarstan) field was selected for testing. It included methane (67%), naphthenic (21%) and aromatic (12%) HC. Asphaltene content (wt%) did not exceed 7.5, sulfur 3.4 and resins 12.8. Specific weight is 0.9 g/cm<sup>3</sup>. The share of oil in the initial mixtures changed from 0.01 to 70 vol%.

The scheme of autoclave loading was slightly different from the experiments with oil shale and bituminous rocks. At first, the charge quartz and seed bars were placed in the autoclave. Then it was filled with clean water or aqueous solution of a given composition and then—with crude oil in given proportions in relation to the flooded water phase. The ratio of aqueous solutions to oil in an autoclave was controlled after the completion of experiments on the boundaries of their separation. These boundaries were clearly fixed on the grown crystals as their growth occurred only on that part of seed bars which were in an aqueous solution). Quartz crystals did not grow on the areas of the bars that were in the oil. Moreover, the seed bars under such conditions were partially dissolved by the penetration of water vapour into the oil. In addition, the areas with an overgrown quartz layer colored yellow with different intensities allowed to determine the levels of water and oil phases arising directly during the experiments and after the autoclave cooling.

Experiments of this series were carried out at temperatures from 280/300 to 650/670 °C and filling of autoclaves from 83 to 50%. This created pressure in autoclaves from 14 to 150 MPa, respectively.

Special experiments on autoclave heat treatment of primary water-hydrocarbon inclusions with sharply different volumetric ratios of water (L1) and oil (L2) phases were also carried out, schematically shown as follows:  $L1 \geq G > L2$  and  $L2 > L1 \geq G$ . Primary quartz crystals with such inclusions were grown at relatively low temperatures (240/260 and 280/300 °C) and saturated steam pressures (5 and 7 MPa respectively). Further, after detailed study of primary water-hydrocarbon inclusions, they were subjected to repeated autoclave thermobaric treatment in pure water at temperatures of 300, 320, 350 and 380 °C and pressure of 100 MPa for 12–15 days. Comparison of the results of experiments allowed to find out the influence of *PT*-parameters and volumetric ratios of water and oil phases on the processes of cracking and metamorphic transformations of oil, which were not manifested during short-term (60–90 min) heating and cooling of inclusions in a microthermometric chamber.

### ***1.2.3 Methods of Studying Products of Experiments, Phase Composition and States of Synthetic Water-Hydrocarbon Inclusions***

After completion of the experiments, the products of interaction of oil shale and other bituminous rocks and crude oil with hydrothermal solutions were studied under binocular (MBS-9) and polarization (Amplival po-d) microscopes. Diagnostics of solid phases was carried out with wide use of radiographs and microprobe analysis. Initial oil and oil-like hydrocarbons from the experiments were characterized by IR spectra recorded on the Avatar 320 FT-IR spectrometer by Nicolet Company and by chromatographic analyses using Perkin Elmer Clarus 5000 chromatograph with Sol-gel 60 cm capillary column and helium carrier gas. From grown quartz was prepared polished plates with thickness of 0.5–2.0 mm to study fluid and solid inclusions. Behavior, phase composition and states of inclusions were studied in situ at their heating and cooling (Mel'nikov et al. 2008; Prokof'ev et al. 2005) in the measuring microthermometric complex on the basis of microthermal camera THMSG-600 by Linkam (England) and microscope Amplival (Germany), equipped with an additional source of UV light, a set of long-focus lenses, video camera and control computer. The complex allows to observe in real time the behavior and phase states of fluids inclusions in the temperature range from  $-196$  to  $+600$  °C, record video films with continuous automatic recording of temperature and rate of temperature rise and fall. However, actually thermometric measurements were stopped at temperatures of  $405$ – $410$  °C, because at higher temperatures fluid inclusions lost their tightness due to their microscopic cracks, up to complete destruction.

Liquid and gaseous HC in fluid inclusions were identified by fundamental bands of IR spectra in the range of  $6000$ – $2600$   $\text{cm}^{-1}$ , recorded with IR microscope Continuum and single-beam FT-IR spectrometer Nicolet, Nexus with minimum aperture size of  $5$   $\mu\text{m}$  (resolution  $4$   $\text{cm}^{-1}$ ). Distribution of hydrocarbons in inclusions was controlled with the help of microspectrophotometer QDI 302 by CRAIC company on the basis of microscope LEICA DM 2500 P, as well as microscope ZEISS AXIO Imager (Germany), equipped with an additional source of UV light.

## **1.3 Results and Discussion**

### ***1.3.1 Phase Composition and States of Synthetic Aqueous-Hydrocarbon Inclusions in Quartz Grown at Interaction of Hydrothermal Solutions with Bituminous Rocks***

The interaction of hydrothermal solutions with oil shale and other bituminous rocks was studied in 20 experiments lasting from 14 to 60 days. Fragments of initial rocks

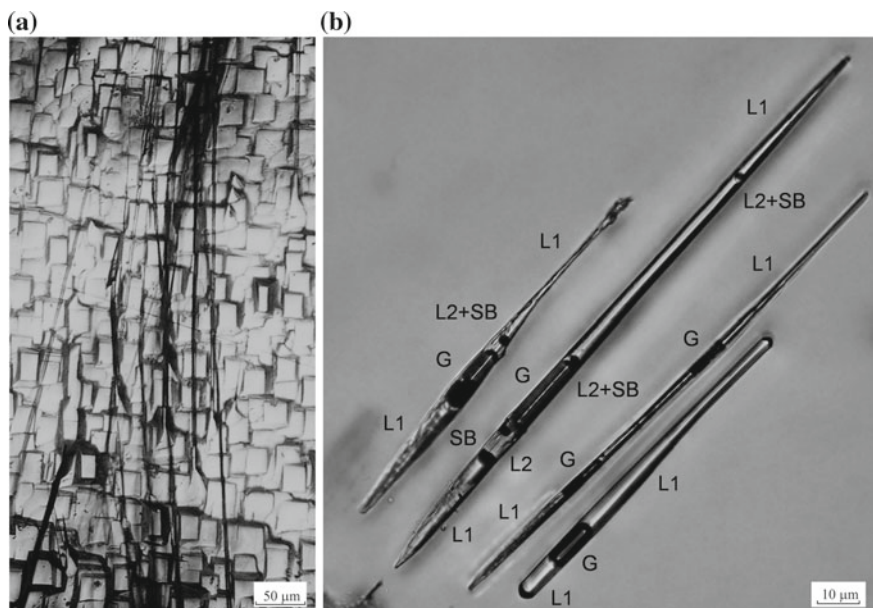




**Fig. 1.4** Quartz crystals of spontaneous nucleation covered with numerous spherical secretions of solid bitumen (asphalt)

after the experiments were usually completely or partially destroyed and turned into clay-like material. It contained hard and less often viscous bitumen in the form of shiny black spherical secretions (often hollow) and irregularly shaped clots (Fig. 1.4). Dimensions of solid bitumen emissions ranged from a hundredth of a millimetre to a few millimetres across. They were completely dissolved in chloroform and, according to diffractograms, were amorphous, which allowed them to be attributed to asphalt. In autoclaves after experiments at temperatures above 320 °C the residual gas pressure was fixed up to 0.3–0.5 MPa. A small clap, sometimes with partial escape of mother solution, accompanied autoclave opening. In the chromatograms of the samples of the sampled gas, methane and sharply subordinated amounts of propane and ethane were determined. On the surface of the residual solution, an oily film of light yellow to yellow-orange and almost black color was observed. The same film was observed on the surface of grown quartz crystals (see Fig. 1.1). Chromatograms and FT-IR film spectra practically do not differ from those of conventional crude oil.

The grown quartz crystals, as noted above, have an unusual wedge-like shape (see Fig. 1.1), are very defective and contain numerous water-hydrocarbon inclusions. There are two main types of inclusions. The inclusions of the first type are confined to the pickling cavities of the growth dislocations (Fig. 1.5a, b). The inclusions have a drop-shaped, needle-shaped, spindle-shaped and tubular shape and are stretched in the direction of the optical axis of quartz crystals, often with a deviation from it by 5–15°. The diameter of inclusions varies widely—from the first to 20 μm, and the length—from 30 to 1500 μm. Often such inclusions completely cross the seed bar. The composition and phase volumetric ratios of such inclusions are characterized by a wide variety of inequalities, which can be represented by:  $L1 > G$ ,  $L1 \geq G > L2$ ,  $L1 \geq G > L2 \geq L3 \geq SB$ ,  $L1 \geq G$ ,  $L2 \geq L1 > G \geq SB$  and  $L2 > L1 \geq G \geq SB > L3$ , where L1 is an aqueous solution, G is a gas (mainly methane, water vapour and liquid hydrocarbons), L2 and L3—liquid hydrocarbons (synthetic oil), SB—solid bitumen (Fig. 1.6). Such diversity of phases and their volumetric ratios is



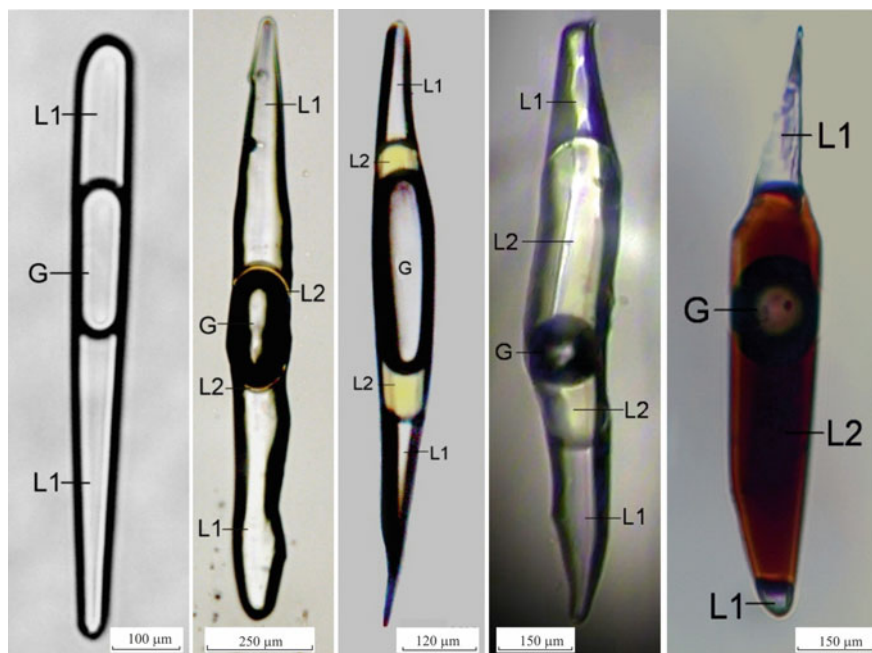
**Fig. 1.5** The etching cavities of growth dislocations formed in the process of entering the autoclave into the operating mode (a) and water-hydrocarbon inclusions of the first type formed in the cavities (b). Inclusions contain aqueous solution, liquid and gas hydrocarbons and solid bitumens in various volume ratios, sometimes with complete absence of some phases

probably connected with different duration of formation of etching cavity of growth dislocations and time of their refilling.

The phases in the inclusions have distinct partition boundaries and are determined on the basis of local FT-IR spectra. Liquid hydrocarbons are also clearly identified by bright blue fluorescence in UV light. It is obvious that the formation of inclusions with such a variety of phases and their volumetric ratios could occur only in heterogeneous fluids.

The formation of the second type of inclusions occurred in the overgrown layer of newly formed quartz, as a rule, near its boundary with the seed bar. They were less frequently recorded in the later growth zones of the basal pinacoid {c} and positive trigonal prism {+a}, and very rarely in the growth sectors of the positive dipyrmaid {+s}, main rhombohedrons {r} and {z} and hexagonal prism {m}. The inclusions are mainly of elongated conical and tubular shape (Fig. 1.7). However, in later growth zones, irregular and complicated form inclusions begin to predominate. Their length varies from 15–20 to 100 μm, rarely reaching 1000–1500 μm in diameter from 5 to 30 μm

The composition and volume ratios of phases in inclusions differ significantly from those of the first type. As a rule, these are four-phase inclusions with distinctly distinguishable phases of aqueous solution (L1), gas (G), mainly methane, liquid hydrocarbons (L2) and solid bitumen (SB) with volumetric phase ratios  $L1 \geq G \gg L2$



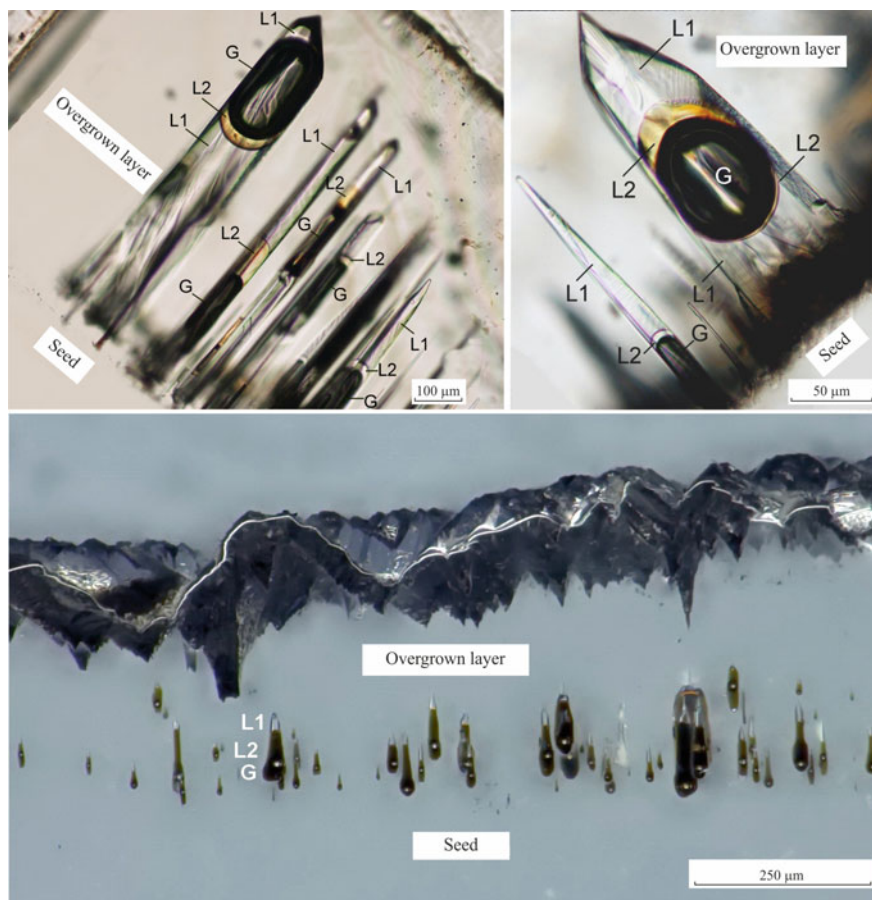
**Fig. 1.6** Synthetic water-hydrocarbon inclusions of the first type formed in heterogeneous water-oil fluids at temperatures of 240–310 °C, pressure 8–30 MPa. The volume ratio of phases: from  $L1 > G \gg L2$  to  $L2 > G \approx L1$

> SB. It is noteworthy that the proportion of liquid hydrocarbons inclusions formed in sub and supercritical fluids increases, while the proportion of solid bitumens decreases. However, in syngenetic inclusions, the real ratios of these phases are also subject to changes, although not as significant as in earlier inclusions in seed rods.

### ***1.3.2 Phase Transformations and Phenomena of Imaginary Homogenization in Water-Hydrocarbon Inclusions at Their Heating and Cooling***

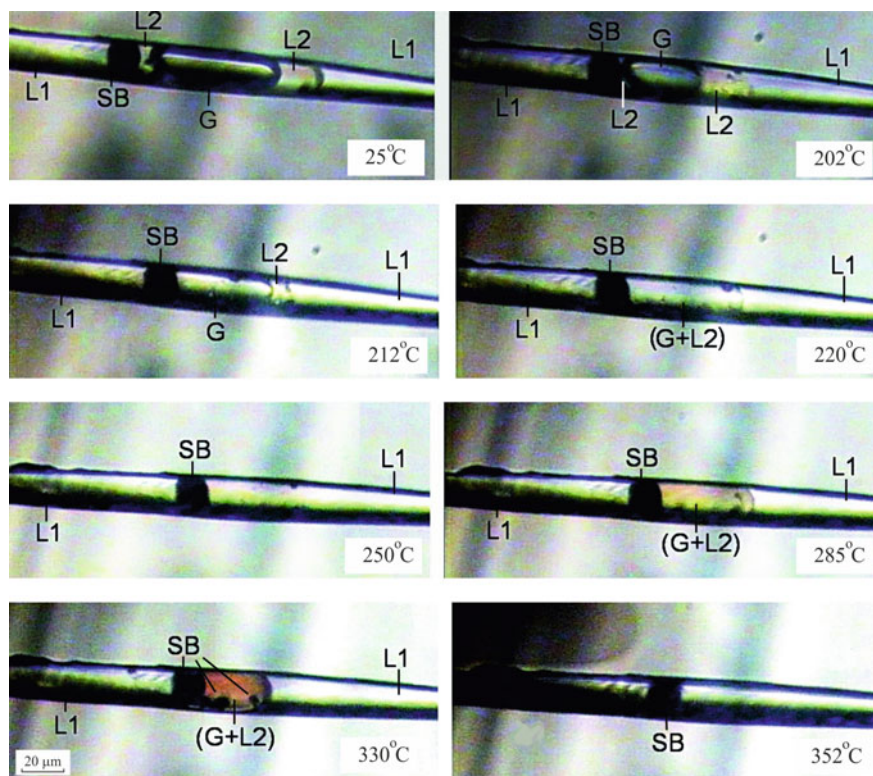
The behavior, phase composition and states of the most characteristic fluid inclusions of both types were studied by microthermometric method up to 400 °C at pressures in inclusions up to 90 MPa in combination with FT-IR spectroscopy and microscopy with natural and UV light.

**First type inclusions.** Such inclusions, as mentioned above, are concentrated in seed bars. Most often these are four-phase inclusions with volumetric phase ratios  $L1 > G \geq L2 > SB$ , where  $L1/G \approx 4$ ,  $L1/L2 \approx 12$  and  $L1/SB \approx 18$ . When heated to 100 °C, the phase composition and state of them remain practically unchanged (Fig. 1.8). The



**Fig. 1.7** Synthetic water-hydrocarbon inclusions of the second type formed in heterogeneous water-oil fluids at temperatures of 320–340 °C, pressure 50–80 MPa. The volume ratio of phases: from  $L1 > G \gg I2 > SB$  to  $L2 \approx SB \gg G \approx L1$

boundaries of the divide between all phases are clear. In the interval of 110–200 °C the volume of the gas phase (G) has sharply decreased by 8%. At the temperature above 210 °C the volume of liquid hydrocarbon phase (L2) began to decrease, and the phase G, on the contrary—to increase rapidly. The complete disappearance of phase L2 occurred at 220 °C due to its dissolution in phase G. This episode was accompanied by the release of numerous, rapidly disappearing gas bubbles. The new phase, designated as (G + L2), is pale yellow and has a clear boundary with the water phase (L1). When the temperature rises to 250 °C, the boundary between phases L1 and (G + L2), gradually pale, disappears completely. Visually, this is very similar to achieving homogenization of the solution. However, with further heating up to 270 °C, this boundary appeared again in the same area where it had disappeared. In the local FT-IR spectrum of inclusions, where the water phase L1 was located, there

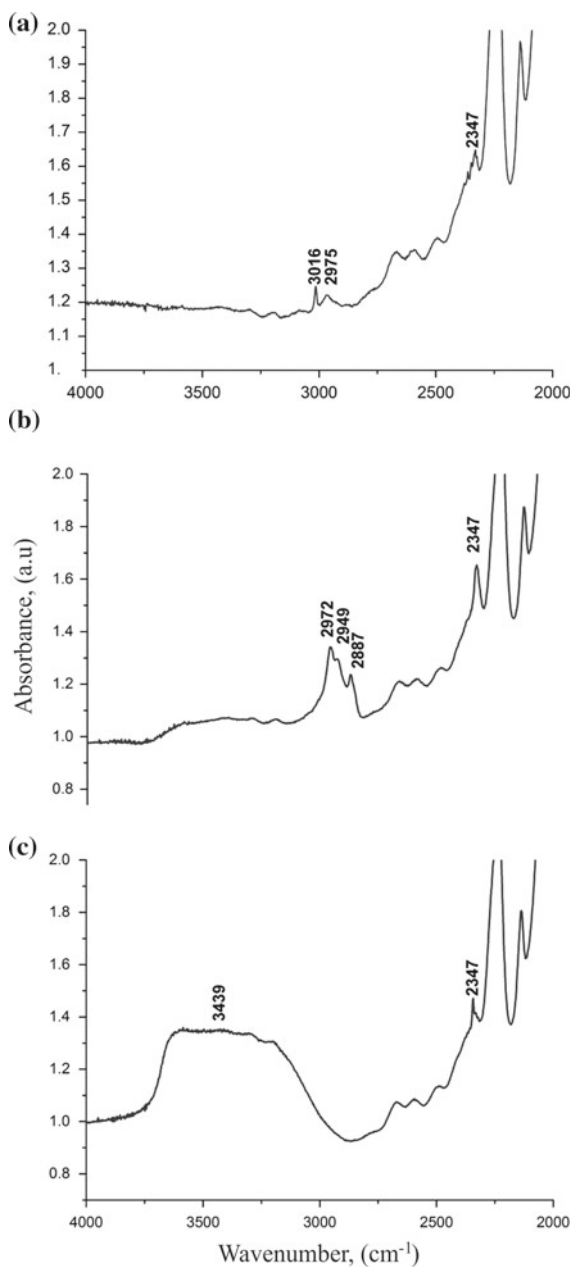


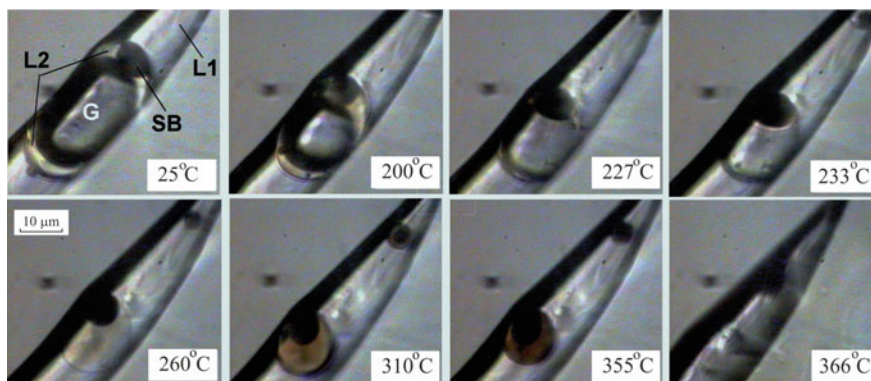
**Fig. 1.8** The thermogram of water-hydrocarbon inclusions with volume ratios of phases  $L1 > G > L2 > SB$ , where  $L1/G \approx 4$ ,  $L1/L2 \approx 12$  and  $L1/SB \approx 18$ . The thermogram illustrates the imaginary homogenization of hydrocarbon inclusion in quartz. Conditions of inclusions formation: 5 wt%  $\text{NaHCO}_3$ , 330/360 °C, ~80 MPa, the oil shale from the Kashpirskoye deposit

are only absorption bands of molecular water. But in the area where the allegedly extinct phase (G + L2) was located, the absorption bands around 2972, 2949 and 2887  $\text{cm}^{-1}$ , typical of crude oil, are clearly visible (Fig. 1.9a–c). Further increase of temperature up to 330 °C has led to colouring of this area of inclusion in yellow colour with an orange shade. At the same time, there was a decrease in the phase volume (G + L2), which at 350 °C was about 30% of its initial volume. The inclusion exploded at 352 °C.

In other, similar inclusions in terms of composition, intensive fluorescence appeared in the areas of the disappeared phase of liquid hydrocarbons when viewed in UV light, while in normal and polarized light there were no signs of the presence of liquid hydrocarbons. The disappearance of the boundary between the water (L1) and hydrocarbon (G + L2) phases at 250 °C, in our opinion, is not due to the real homogenization of the fluid, but is a consequence of the alignment of densities and refractive indices of these liquid phases in the process of heating the inclusion.

**Fig. 1.9** FT-IR absorption spectra of water-hydrocarbon inclusion (see Fig. 1.8), **a**—methane and liquid hydrocarbons dissolved in methane, **b**—liquid hydrocarbons, **c**—aqueous phase. In the spectra of all phases, an absorption band near  $2347\text{ cm}^{-1}$  is observed, due to the presence of  $\text{CO}_2$  in the inclusion

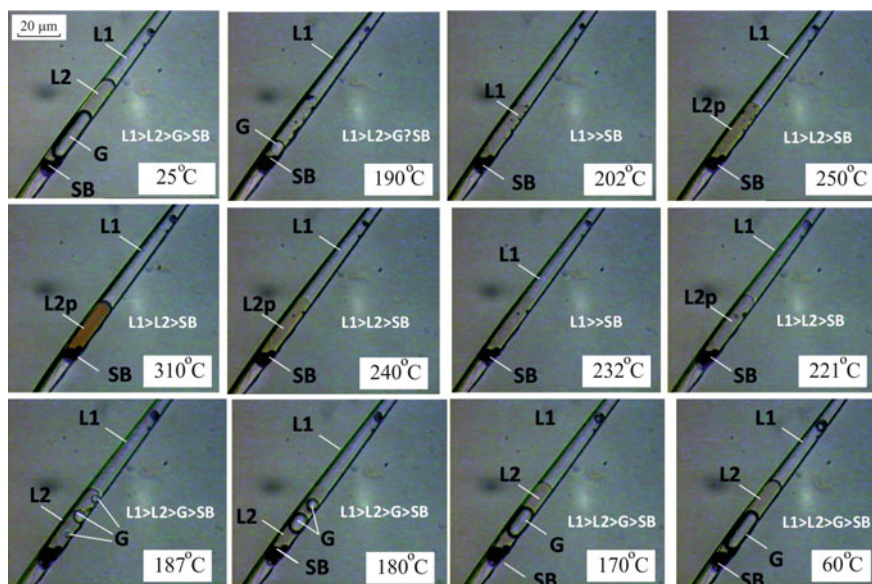




**Fig. 1.10** The thermogram of water-hydrocarbon inclusion of a similar nature as shown on Fig. 1.8, but the complete disappearance of the boundary between the gas and water phases was not achieved

The behavior of the next inclusions with similar phase volumetric ratios is close to that described above (Fig. 1.10). However, there was no complete disappearance of the boundary between the gas and water phases here, although at 260 °C the boundary between them became barely distinguishable. With a further increase in temperature, the gas phase, decreasing in volume, regained its yellow color, which changed to bright orange-yellow as the temperature increased. Then, the inclusion exploded at 366 °C.

Destruction of inclusions begins as shown earlier (Naumov et al. 1966), when the pressure inside inclusions rises to 80–90 MPa. The temperature should be 320 and 360 °C at the density ( $\rho$ ) of the solution  $\rho = 0.8 \text{ g/cm}^3$  and  $\rho = 0.6 \text{ g/cm}^3$  respectively. Therefore, the microthermometric study of other water-hydrocarbon inclusions did not raise the temperature of heating above 320 °C. This preserved the inclusions from destruction and made it possible to trace their behavior not only at the increase, but also at the decrease of temperature. Thus, heating of one of the four-phase inclusions with volumetric ratios of phases  $L1 > G \geq L2 > SB$  led at first, at 190 °C, to disappearance of the boundary between the phases of liquid hydrocarbons (L2) and aqueous solution (L1) (Fig. 1.11). Further, at 202 °C, the gas HC phase (G) disappeared completely. This created the illusion of complete homogenization of the solution. However, a close look at the inclusion showed that the area with the missing phases L2 and G had a subtle yellowish tinge. It was assumed that in this case the G phase dissolved in the L2 phase with the appearance of a new liquid hydrocarbon phase marked as (L2 + G). And really at the further increase of temperature to 250 °C intensity of yellow colouring of a phase (L2 + G) began to increase with simultaneous occurrence of its border with phase L1. At 310 °C, the phase (L2 + G) acquired an orange shade. Its volume decreased by about 30%. Due to the risk of depressurization of the switch at a higher temperature, heating was stopped and replaced by cooling. This first led to the loss of the orange shade of the phase (L2 + G) and then to its decomposition at 187 °C into L2 and G. At 60 °C, the phase composition and volumetric ratios of the phases in inclusion are fully restored.



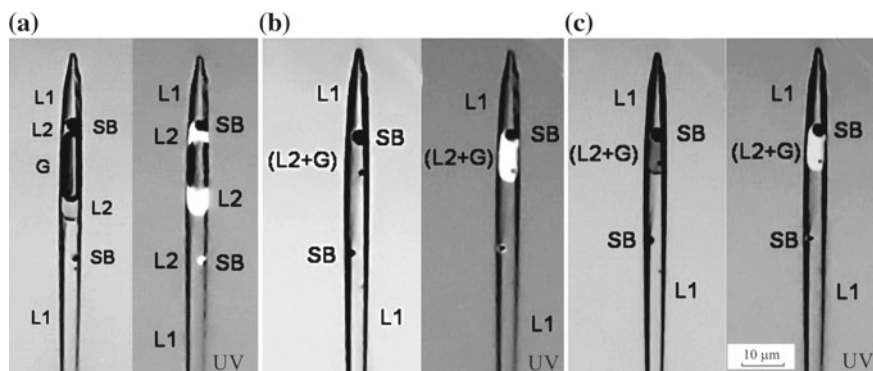
**Fig. 1.11** The thermogram of a multiphase inclusion with a volume ratio of the phases  $L1 > L2 > G > SB$  shows the behavior of the phases at heated and cooled in the temperature range 25–310–60 °C until the appearance of imaginary homogenization and inclusion destruction. Conditions of inclusions formation: 5 wt%  $\text{NaHCO}_3$ , 330/360 °C, ~80 MPa, the oil shale from the Kashpirskoye deposit

Another indisputable proof that the phase of liquid hydrocarbons does not disappear in inclusions at certain temperatures (and corresponding pressures), but remains in the form of an invisible phase, was obtained by simultaneous observation of inclusions in the thermometric chamber in normal and UV light. In particular, in contrast to the disappearance of the hydrocarbon phase ( $L2 + G$ ) and the onset of apparent homogenization observed during heating in the ordinary light, the presence of this phase in the inclusion is unequivocally proved by its bright fluorescence in UV light (Fig. 1.12). At the same site in the local FT-IR spectrum there are absorption bands typical for liquid hydrocarbons.

In general, all this indicates that at certain temperatures (and corresponding pressures) the disappearance and appearance of liquid and gas hydrocarbons inclusions can occur not only in connection with the real homogenization of the fluid, but also in the alignment of the density and refractive indices of two or more liquid phases due to their joint dissolution. This phenomenon we call as imaginary homogenization.

Other important and interesting from the point of view of generation and extraction of liquid and gas hydrocarbons from oil shale and other bituminous rocks is the experimental establishment of formation at 180–220 °C and pressures of about 10–20 MPa of homogeneous phases ( $G + L2$ ) and ( $L2 + G$ ). Their difference is determined by the predominance of gas, mainly methane, and liquid hydrocarbons



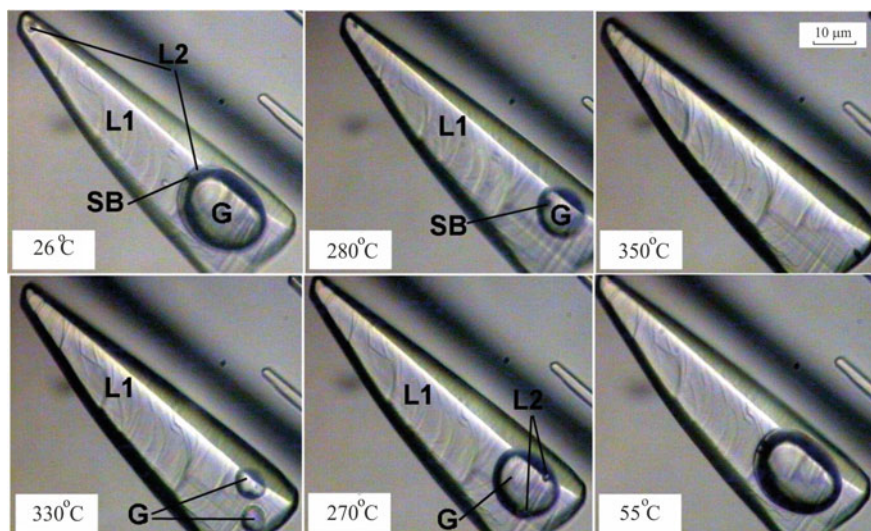


**Fig. 1.12** Fragment of the thermogram of water-hydrocarbon inclusion with simultaneous use of natural and UV light at **a**—30 °C, **b**—286 °C and **c**—305 °C. The combination of illumination allows to definitely seeing the apparent disappearance of the liquid hydrocarbon phase in daylight and its appearance (with bright fluorescence) in UV rays

in the initial fluid. Heterogenization of such phases with separation of liquid and gas hydrocarbons occurs at 187–200 °C.

**Second type inclusions.** The behavior of the second type of inclusions in the process of heating and cooling is much easier than in the first type of inclusions. This is demonstrated in the thermograms of the most characteristic inclusions in the overgrown layer of quartz crystals (Fig. 1.13). All fluid inclusions of this type include aqueous solution, gas (mainly methane) and liquid hydrocarbons. The volumetric phase relations are subject to the inequality of  $L1 > G \gg L2 \gg SB$ . As well as in inclusions of the first type, the character of behavior of fluids inclusions at heating and cooling does not change. But the absolute temperatures of occurrence and disappearance of gas and liquid phases of hydrocarbons inclusions can differ by tens of times. This indicates the heterogeneous state of the fluids during the capture of inclusions.

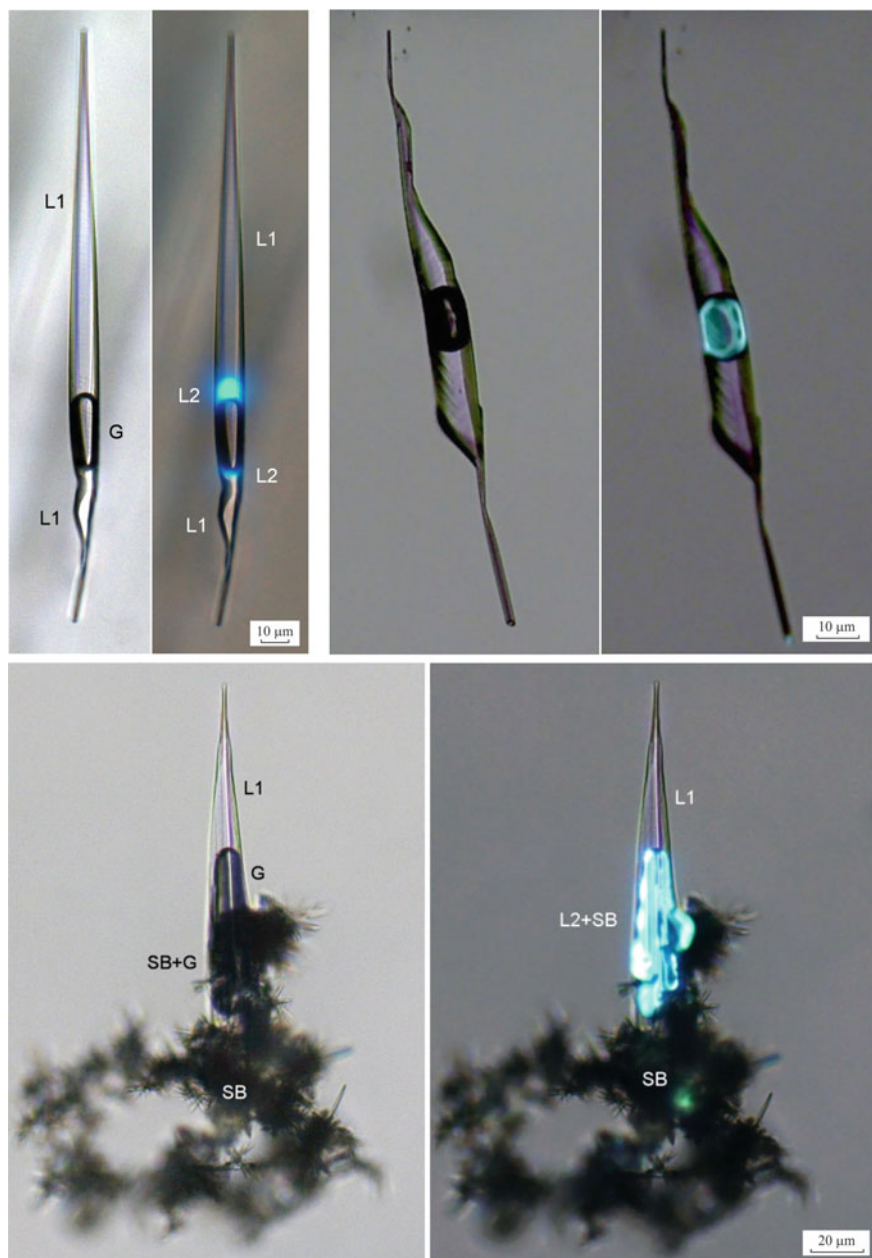
It should be especially noted that there are cases of hidden presence of liquid hydrocarbons in fluid inclusions at room temperature. Such inclusions were observed in the quartz grown at interaction of bituminous argillites of the Bazhenov Formation and the Central Oil and Gas Basin of France with pure water and slightly alkaline water solutions at temperatures from 350/380 to 420/450 °C and pressures from 80 to 120 MPa, respectively. The presence of liquid HC in fluid inclusions is usually recognized by the characteristic yellow or yellow-orange color. However, in many inclusions in quartz grown in sub- and supercritical fluids during their interaction with bituminous argillites, liquid hydrocarbons were not detected in ordinary and polarized light. But, as the study of numerous inclusions has shown, they are clearly fixed in UV light, combined UV and polarized light due to very intense fluorescence in the area adjacent to the boundary of the water phase (L1) and gas (G) phases (Fig. 1.14). The proof of the fact that the observed intensive fluorescence is caused by the presence of liquid hydrocarbons is the appearance of fluorescent inclusions of



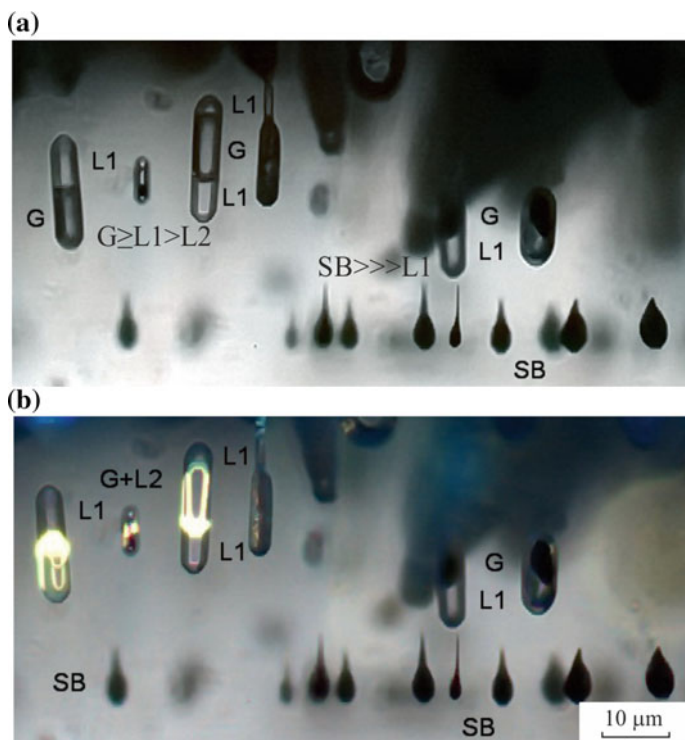
**Fig. 1.13** Thermogram of multiphase inclusion with the ratio of the phases  $L1 > G \gg L2 > SB$  formed in overgrown layer of quartz shows the behavior of the phases at heated in the temperature range of 26–350 °C and cooling in the range of 350–55 °C. Conditions of inclusions formation: 5 wt%  $\text{NaHCO}_3$ , 330/360 °C, ~80 MPa, oil shale of the Leningrad deposit

absorption bands in FT-IR spectra, which are usual for crude oil. At the same time, in the FT-IR spectra of the gas phase of such inclusions one can observe absorption bands of methane (near  $3016 \text{ cm}^{-1}$ ) and carbon dioxide (near  $2347 \text{ cm}^{-1}$ ). In the spectra of the rest of the inclusions outside the phases of liquid and gas hydrocarbons there is a diffuse band in the range of  $3000\text{--}3600 \text{ cm}^{-1}$  with a maximum at  $3400 \text{ cm}^{-1}$ , indicating the water composition of the phase. Mass viewing of such inclusions in quartz, grown during the interaction of sub- and supercritical fluids with bituminous mudguards, allows us to draw a conclusion about the broad development of this phenomenon, which was not previously noted.

In addition, the hidden presence of liquid hydrocarbons is constantly observed in inclusions formed in quartz, grown in sub and supercritical water-oil mixtures. In normal and polarized light, such inclusions usually have water and gas, mainly methane, and solid bitumen inclusions. The latter, as a rule, form myriads of the smallest (first  $\mu\text{m}$ ) droplet-shaped inclusions in the earliest quartz growth zones (Fig. 1.15a, b). There are no liquid and gas HC phases in such inclusions. However, in the later growth zones of the same crystals, much larger (up to 50–70  $\mu\text{m}$ ) two-phase inclusions with water (L1) and gas (G) phases are observed in normal and polarized light. When observing in UV light it is visible that the gas (methane) phase contains condensate of liquid hydrocarbons, which have a bright fluorescent glow. In FT-IR spectra of the same inclusion sites there are absorption bands typical for crude oil.



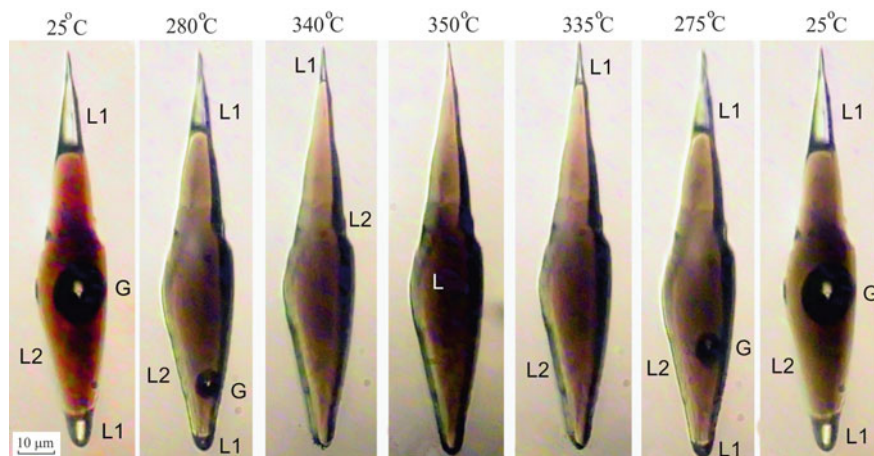
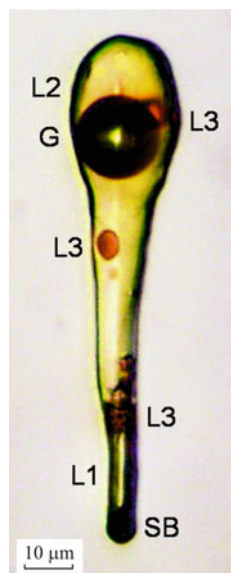
**Fig. 1.14** The presence of oil, including gas condensate in synthetic fluid inclusions in quartz grown in weakly alkaline aqueous sub- and supercritical fluids when they interact with bituminous argillites of the Bazhenov Formation and the Central Oil and Gas Basin of France at temperatures of 350–450 °C and pressure 80–120 MPa, respectively



**Fig. 1.15** Two types of inclusions in quartz crystal in natural light (a) and UV light (b). Intensive fluorescence of inclusions under UV light reveals the hidden presence of liquid oil hydrocarbons in fluid inclusions

Also consider the behavior of inclusions with volumetric phase ratios  $L2 > L1 \geq G > L3 \gg SB$  (Fig. 1.16). Such inclusions with oil-like liquid prevailing 3–5 times over all other phases are often found in quartz formed during interaction of hydrothermal solutions with oil shale. The inclusions are located in the overgrown quartz layer at some distance from the seed and are later in relation to the above mentioned three-phase inclusions. At heating of inclusions in them in the beginning (to temperatures 200–220 °C) liquid drops of phase L3 in the basic oil-like phase L2 are dissolved (Fig. 1.17). Then, at 260–280 °C, a gas bubble (mainly methane) is dissolved in the same phase. The inclusion is transformed to a two-phase state with two liquids—oil-like L2 and water L1, with a ratio of  $L2 > L1$ . Further temperature increase up to 353–360 °C leads to complete dissolution of L1 phase in oil-like liquid L2 with formation of homogeneous essentially hydrocarbon fluid. The share of dissolved in it water phase reaches 15–20 vol%. The cooling of inclusions in them in the reverse order completely restores the primary phase composition and volume ratios of the initial phases. This indicates a rapid establishment of equilibrium inclusions and stability of their phase composition.

**Fig. 1.16** Predominantly oil water-hydrocarbon inclusions with volumetric ratios of phases  $L2 > L1 \geq G > L3 > SB$  formed at hydrothermal solutions interact with oil shale. Inclusion forms in the overgrow layer of quartz near its boundary with the seed bar due to the massive precipitation of the smallest drops of oil saturated with dissolved water



**Fig. 1.17** The thermogram of predominantly oil inclusions shows reversible processes of sequential dissolution of the L3 phase (composition not yet installed) in the bulk of liquid hydrocarbons (L2), then dissolution of the gas bubble in the L2 phase and complete dissolution in the L2 phase of the aqueous phase and then transition of the fluid to the homogeneous state. As the temperature decreases, fluid heterogenization occurs with the sequential appearance of all previously dissolved phases

### ***1.3.3 Reflection of Oil Cracking in Synthetic Water-Hydrocarbon Inclusions in Quartz and Assessment of Possible Maximum Depths of Its Location in the Earth's Interior***

Cracking of crude oil and its heavy fractions is the main industrial process of obtaining gasoline and other hydrocarbon fuels, as well as raw materials for petrochemical and construction industries. At the same time, it has been established that to some extent oil cracking is manifested in natural conditions, especially when it is in direct contact with hydrothermal solutions and silicate (mica) and carbonate rocks with catalytic properties (Rokosova et al. 2001; Simoneit 1995; Huang and Otten 2001; Ping et al. 2010; Xiao et al. 2010; Zhao et al. 2008). If oil cracking really takes place in natural conditions, it can explain the vertical zoning observed in many oil and gas basins in the distribution of different types of hydrocarbons (Petrov 1984; Andreev et al. 1958; Samvelov 1995; Yeremenko and Botneva 1998).

Among the physico-chemical factors, the most significant changes in the vertical geological section of the Earth's strata undergo thermobaric parameters. It seems likely that their increase as the depth of oil and gas fields should inevitably lead to the cracking of oil and increase in its proportion of light and medium fractions, as well as gas HC, mainly methane, and residual solid bitumen. This assumption has been tested by us by conducting experiments using synthetic water-hydrocarbon inclusions.

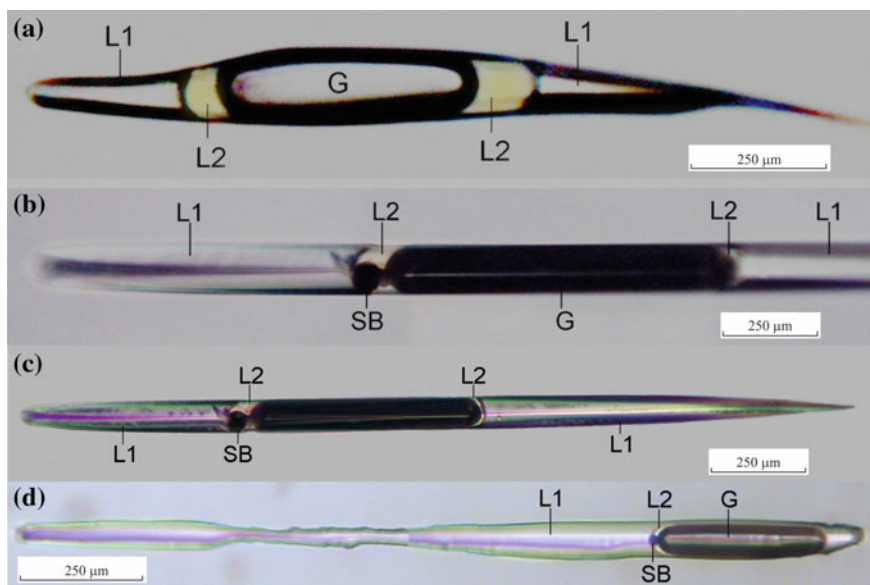
For this purpose, polished ZX- and ZY-orientation plates of 0.5–2.0 mm thickness with captured water-hydrocarbon inclusions were prepared from quartz crystals grown in water-oil solutions at temperatures of 240, 280 and 310 °C and pressures of 5, 7 and 20 MPa. Using the methods of thermobarogeochemistry, the phase composition, state and behavior at temperatures up to 400 °C were determined in inclusions. Then the plates with the studied inclusions were placed in autoclaves with the volume of 30 ml, poured with clean water and maintained at the temperatures of 300, 320, 350 and 380 °C and the pressure of 100 MPa for 7–14 days.

In total, about 30 quartz crystals have been re-treated and studied. All grown crystals contained two-phase (L1 + G) and three-phase (L1 + L2 + G) inclusions. Under room conditions, the fractions of the water (L1) and gas (G) phases in two-phase inclusions were in the volume ratios corresponding to the autoclave filling coefficients taking into account the reduction of their free volume by the amount of additives in aqueous crude oil solution. In three-phase inclusions, the volume ratios of phases L1/G/L2 varied widely—from  $L1 > G \gg L2$  to  $L2 > L1 > G$ , regardless of the share of liquid hydrocarbons in the initial water-oil mixtures. This indicated the heterogeneous state of mother fluids during the capture of inclusions by quartz crystals. No hydrocarbon gases were detected in the gas bubble of inclusions. When the inclusions are heated, they disappear first. The two-phase inclusions become homogeneous and the three-phase inclusions become liquid two-phase, with practically the same volumetric L1/L2 phase ratios as before the disappearance of the gas phase. In the process of further heating liquid two-phase inclusions are stored

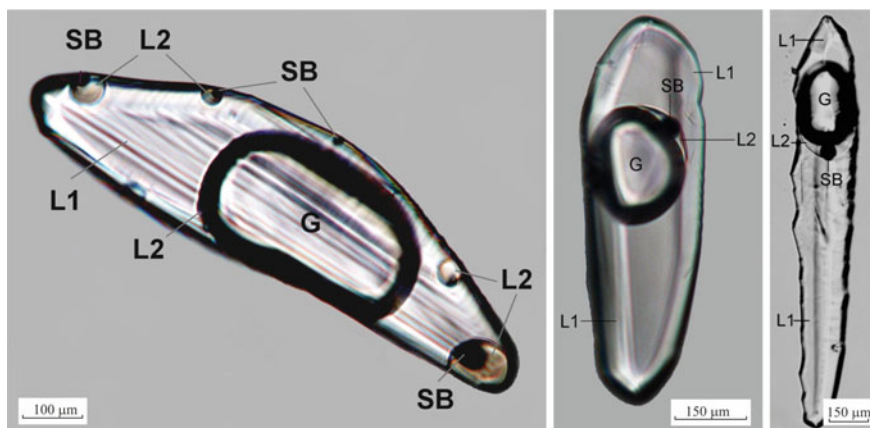
up to 365–405 °C (depending on the density of the solution) with an insignificant (1.5–2.0 vol%) decrease in the proportion of L2 phase. At higher temperatures, most of these inclusions lose their hermetic state, often with an explosion.

After the autoclave heat treatment at 350 °C and 150 MPa, the two-phase (L1 + G) inclusions remain identical to the initial inclusions. At the same time, the phase composition and volumetric ratios of phases in three-phase inclusions of the composition (L1 > L2 > G) undergo significant changes at temperatures above 300 °C, while the inclusions, heat-treated at lower temperatures do not bear any changes.

In the gas phase of three-phase inclusions, according to the data of the local FT-IR, at 320 °C there appears methane with an insignificant admixture of propane and ethane, the content of which increases with increasing temperature and fraction inclusions of liquid hydrocarbons. Spherical releases of SB solid bitumen always occur in droplets and the liquid hydrocarbon trimming at the boundary of water and gas phases, and the share of gasoline fraction increases in the liquid hydrocarbon phase according to chromatogram data (Fig. 1.18). This is also confirmed by the beginning of boiling of the liquid hydrocarbon phase at 90 °C. Boiling continues up to 280 °C up to disappearance (dissolution) of L2 phase and transition of inclusion into two-phase state (L1 + G). Further heating of the inclusion leads to a gradual reduction of the gas bubble and its disappearance at 350 °C with the transition to a homogeneous state of inclusion. Solid bitumen SB emissions are maintained virtually



**Fig. 1.18** Initial water-hydrocarbon inclusions formed in heterogeneous water-oil fluids 350–380 °C and 100 MPa, SB—absent (a), inclusions after heat treatment at 350 °C (b–d) with the appearance of solid bitumen, methane and with increase proportion of light fractions. The change in the composition of heat treated inclusions is result of oil cracking



**Fig. 1.19** Initial water-hydrocarbon inclusions in quartz grown at temperatures of 350–370 °C and pressure ~90 MPa. The phase composition of the inclusions is identical to the composition of low-temperature inclusions heat-treated at 350–380 °C and 100 MPa

unchanged. When cooling to 335 °C, a gas bubble appears in the inclusion, indicating the beginning of its heterogenization. At the further cooling the phase composition and volumetric ratios of water phase, liquid hydrocarbons and gas phase were fully restored. The data obtained show that fluid inclusions in low-temperature quartz subjected to heat treatment at temperatures of 300, 320, 350 and 380 °C become identical in terms of phase composition, states and behavior during heating and cooling of primary inclusions in quartz grown at similar and close temperatures (Fig. 1.19). This is due, in our opinion, to the same reason—the cracking of crude oil, which in the presence of hydrothermal solutions becomes noticeable at 320 °C and reaches maximum activity in the temperature range of 350–380 °C. At the same time, the thermometry of individual inclusions with different phase volumetric ratios made it possible to find out at what temperatures (and corresponding pressures) such inclusions can be in heterogeneous and homogeneous state. It turned out that during short-term (60–90 min) heating of inclusions with a share of phase L2 from 3 to 40 vol% at 266–308 °C the phase G disappears with transition of inclusion into a liquid two-phase state with a ratio of phases  $L1 > L2$ . At further increase of temperature in inclusions with a share of phase L2 less than 4–5 vol% homogenization occurs at 350–357 °C, while inclusions with a higher share of phase L2 explode at 355–385 °C.

Other behaviour at short-term heating is characterized essentially by oil inclusions with volume ratio of phases  $L2 \gg L1 \approx G$ . At first, the G phase disappears at 270–285 °C and the inclusion becomes two-phase with a phase ratio of  $L2 \gg L1$ . This state is maintained up to the temperature of 345–355 °C, above which the aqueous phase (L1) is completely dissolved in the phase of liquid hydrocarbons (L2) with the transition to a homogeneous state. Decrease in temperature leads to



heterogenization of inclusion with appearance at 335–350 °C of phase L1 and further, at 265–270 °C—gas, basically methane phase G.

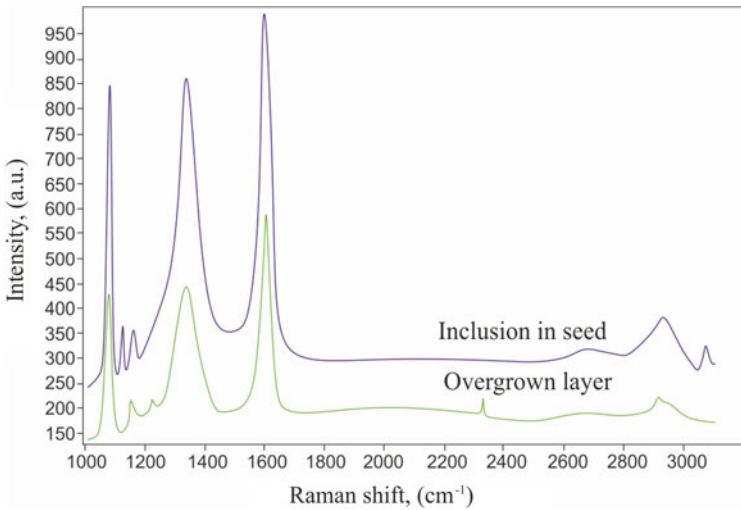
Inclusions formed at temperatures from 335 to 495 °C produce solid bitumen, methane and, less frequently, propane, ethane and CO<sub>2</sub>, while the L2 phase is substantially (up to 70%) enriched with light gasoline-kerosene fractions. In the highest temperature inclusions on the periphery of L2 phase secretions the appearance of one or two phases of liquid hydrocarbons—L3 and L4—is recorded. They disappear (dissolve) in phase L2 at 95 and 126 °C accordingly.

Inclusions captured by quartz at 335–355 °C are characterized by a phase ratio of  $L1 \geq G > L2 > SB$ . The share of L2 phase in different inclusions varies from one hundredths to 30%. At heating of inclusions with a share of phase L2 to 4 vol% it disappears at 160–180 °C with transition of a fluid in a two-phase condition (L1 + G). Homogenization of such inclusions occurs at 287–322 °C. At higher fractions of phase L2, the increase in temperature up to 308–315 °C leads to disappearance of phase G, and then, at 340–360 °C inclusions explode, not having reached homogenization.

In water-hydrocarbon inclusions formed at 420–490 °C, the share of L2 phase in inclusions corresponds to its volume in initial solutions, changing from 5 to 35 vol%. Short-term heating of inclusions with the ratio of phases  $L1 \geq G > L2 > SB$  has allowed to establish that phase L2 (at a share of phase L2 10–12 vol%) are disappears (dissolves) at 250–285 °C with transition of inclusion in a two-phase condition with a parity of phases  $L1 \geq G$ ; at the further heating to 370 °C the phase G disappears with transition of inclusion in a homogeneous condition. Hard bitumen is retained without change. Cooling of inclusions leads to the appearance of all these phases in reverse order at temperatures that are 12–15 °C below their disappearance temperatures. Increasing the share of L2 phase up to 25 and 36 vol% increases the temperature of its disappearance up to 315 and 335 °C, respectively. Complete homogenization of such inclusions occurs at 380–395 °C.

In experiments at 650/670 °C, the autoclaved oil captured in the inclusions is completely transformed into graphite and methane (Fig. 1.20).

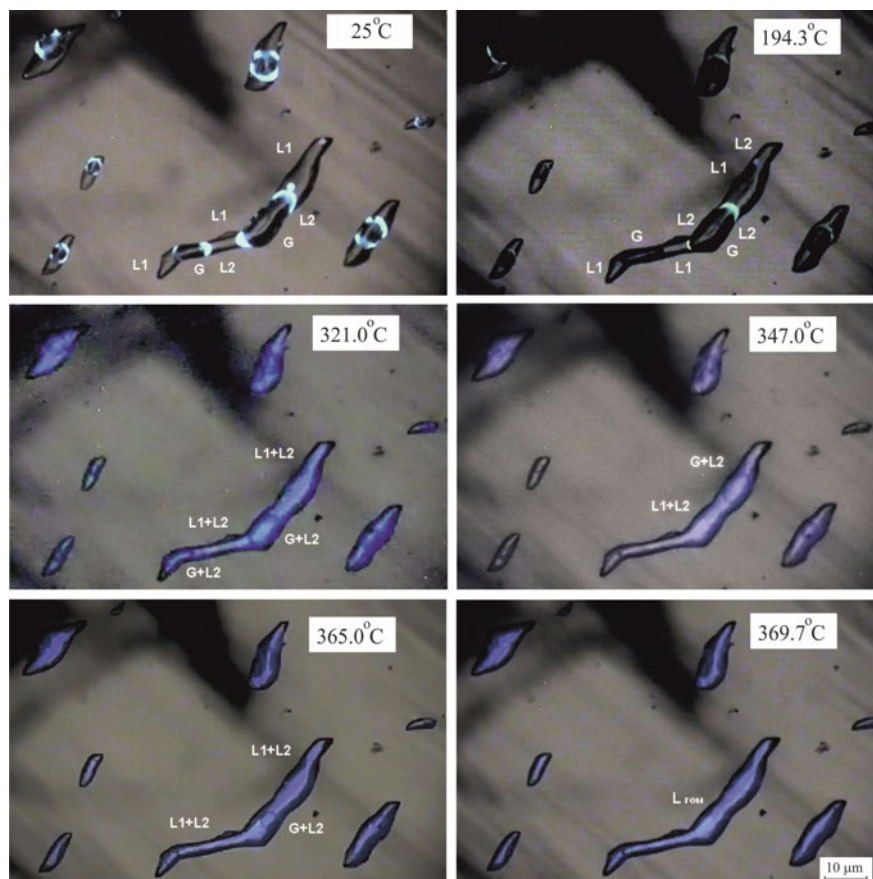
As noted above, the nature of oil transformations at high temperatures largely depends on the volume ratios in the fluid of the oil, water and gas phases. When the phase volumetric ratios in high-temperature inclusions are subject to the inequality of  $L1 \geq L2 > G$  and the fluids are in a homogeneous state, the oil is stored in them, at least up to 500 °C. This is indicated by the very presence of oil in the primary fluid inclusions captured by quartz at temperatures of 335–500 °C (Fig. 1.21), and its preservation in the secondary inclusions after repeated treatment in homogeneous solutions of supercritical fluids for 30–40 days. In our opinion, this is due to the fact that oil hydrocarbons do not exist as individual compounds with their inherent properties when dissolved in aqueous solution. This is indicated by the disappearance in the high-temperature (400 °C) FT-IR spectra of typical oil absorption bands near 2972, 2949 and 2287 cm<sup>-1</sup> (Fig. 1.22), as well as the characteristic greenish-blue fluorescent glow in UV light. At cooling and heterogenization of inclusions all disappeared phases, their volume ratios, typical absorption bands in FT-IR spectra and characteristic fluorescent glow are completely restored.



**Fig. 1.20** Raman spectra of the inclusion in the seed and spectra the overgrown layer of quartz testifies to the transformation of water-hydrocarbon fluid into fine crystalline graphite

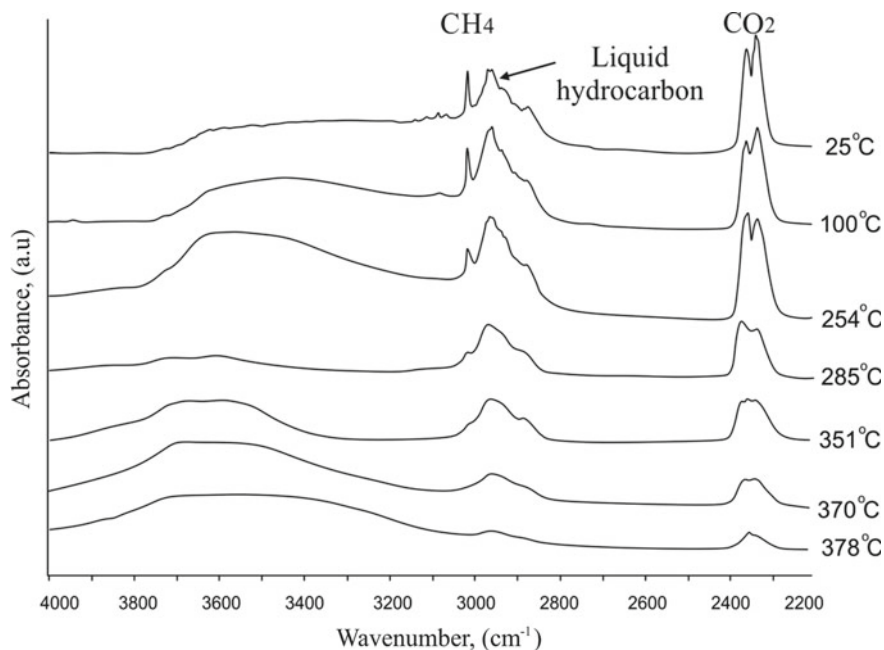
Essentially oil inclusions with a phase ratio of  $L2 \gg L1 \approx G$  behave differently during heat treatment. In the local high-temperature FT-IR spectra, when the homogenization of inclusions with the dissolution of gas G (270–285 °C) and water L1 (350–357 °C) phases is achieved, the specified absorption bands typical of oil (Fig. 1.23) are completely preserved, as well as its characteristic fluorescent glow. When the inclusions are cooled down, the composition and volume ratios of the phases are fully restored. After 14 days of heat treatment at 300 °C, the composition and volume ratios of the phases inclusions, as noted above, remain unchanged. However, already at 320 °C residual solid bitumen appears in them and the share of light oil fractions increases by 10–15%. The increase in temperature up to 350 and especially 380 °C leads to complete conversion of oil into solid bitumen, methane and, to a lesser extent, carbon dioxide (Fig. 1.24).

Thus, the experimental data obtained testify to the heterogeneous (three- and two-phase) state of water-oil systems at relatively low temperatures (up to 240–310 °C) and pressures (up to 30–50 MPa). Even in the longest (up to 120 days) experiments at the specified *PT*-parameters the oil remains stable without being subjected to any changes. But already at 320 °C and especially in a range of temperatures 350–380 °C it undergoes essential changes. The nature of these depends largely on the volume ratios of the oil, water and gas phases. Under conditions of water solution predominance over oil, dissolved in homogeneous, including supercritical fluids, oil hydrocarbons lose their ability to split due to the formation of true solutions with water. At least under such conditions, the oil present to the gas condensate of fluid inclusions remains stable up to 490 °C. However, in cases where oil prevails over aqueous solution, HC in its composition when reaching a homogeneous state are preserved as such and continue to be cracked until irreversible transformation into



**Fig. 1.21** Fragment of the thermogram of water-hydrocarbon inclusion in quartz. Quartz growth conditions: 5 wt%  $\text{Na}_2\text{CO}_3$  + 10 vol% oil, 390/400 °C, ~120 MPa

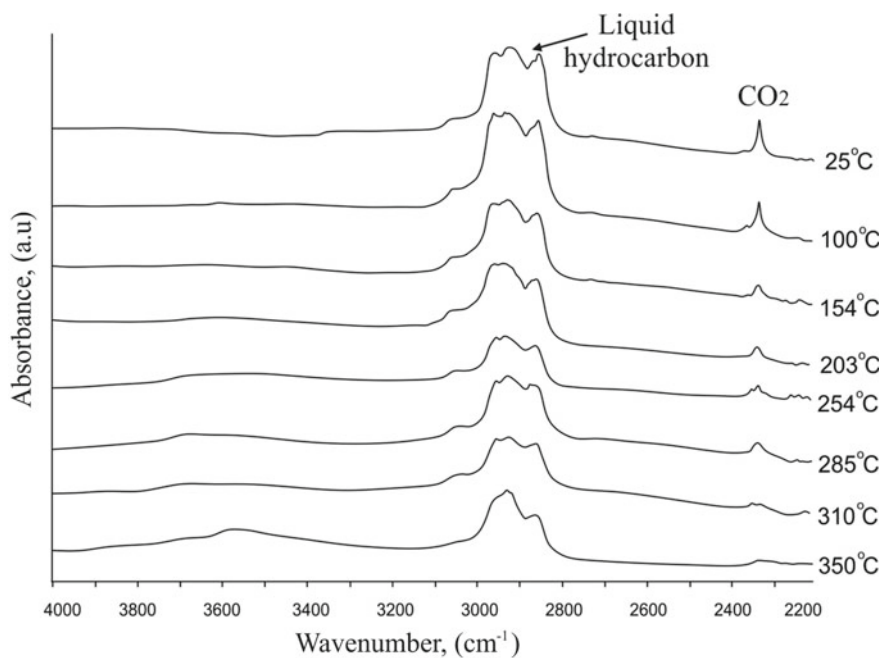
methane and residual solid bitumen, up to graphite. All this makes it possible to consider that those oil deposits, where oil prevails over the water phase, can spread taking into account the actual thermal gradients of oil and gas bearing strata of 2–30 °C/km up to the depth of 12–14 km. But if the water component exceeds the share of oil in the reservoirs, such water-oil fluids can reach a depth of 18–20 km. In this case, the safety of oil is ensured by finding it together with associating aqueous solutions in sub and supercritical states.



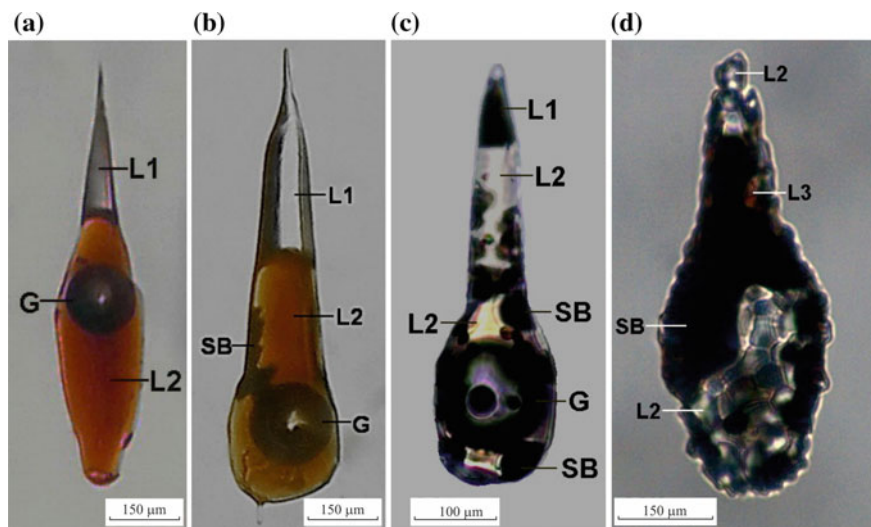
**Fig. 1.22** FT-IR spectra of phase absorption of water-hydrocarbon inclusion in the temperature range 25–378 °C. An increase in temperature leads to the disappearance of the absorption bands of methane (3016  $\text{cm}^{-1}$ ) and liquid hydrocarbons (2800–3000  $\text{cm}^{-1}$ ). The band associated with the presence of  $\text{CO}_2$  (2450  $\text{cm}^{-1}$ ) almost completely disappears

## 1.4 Conclusions

1. Modified method of hydrothermal growth of quartz crystals allows to form fluid inclusions of stimulated and spontaneous nucleation. These inclusions are essentially microsamples of fluids formed during the interaction of hydrothermal solutions with bituminous rocks and crude oil.
2. Numerous experiments and especially data on in situ study of fluid inclusions by thermobarogeochemical methods testify to fundamentally different behavior and phase states of water-hydrocarbon fluids formed in temperature ranges: 240–320 °C, 320–380 °C and 380–500 °C at pressures of saturated steam and higher. These differences are due to the cracking of crude oil (or, more precisely, its heavy fractions) in hydrothermal solutions at temperatures above 330 °C with the formation of predominantly light and medium fractions.
3. Water-hydrocarbon fluids formed at temperatures up to 300–320 °C and pressures above saturated steam (experimentally traced 90 MPa) turn into liquid two-phase oil-water fluids without free gas when heated. Their existence in this state is traced up to the depressurization of inclusions at 365–405 °C. It is possible that at higher temperatures and pressures such fluids may become homogeneous. But



**Fig. 1.23** FT-IR spectra of phase absorption of predominantly oil water-hydrocarbon inclusion in the temperature range 25–378 °C. The spectra shows a stable existence of oil up to 350 °C



**Fig. 1.24** Predominantly oil water-hydrocarbon inclusion after autoclave treatment at **a**—300 °C, **b**—320 °C, **c**—350 °C, **d**—380 °C and 100 MPa for 14 days

oil should be enriched with light and medium fractions due to cracking and other specific hydrocarbons and other compounds.

4. Water-hydrocarbon fluids formed at temperatures of 330–500 °C behave differently when heated: first, they pass into two-phase gas-liquid state with light oil fractions dissolved in gas hydrocarbons, and then, when the critical point of water is exceeded, they transform into homogeneous, probably supercritical fluids.
5. Different ratios of the same phases and their different compositions in the captured inclusions indicate the heterogeneous state of aqueous-hydrocarbon fluids formed during the interaction of hydrothermal solutions with bituminous rocks and crude oil. And only fluids, in which the share of dissolved hydrocarbons at given thermobaric parameters is lower than their solubility, are homogeneous.
6. Oil content in hydrothermal slightly alkaline and alkaline solutions, established by the visual method, in the temperature range of 260–400 °C and pressure up to 90 MPa increases from the hundredth and first tenths of shares up to 8–10 vol. At the same time, the total content of hydrocarbons formed as a result of oil cracking at 380–450 °C and pressure up to 110 MPa, is about 10–20% in the same solutions.

**Acknowledgements** The authors are grateful to J. Pironon, A. Randy and O. Barres (GeoResources Laboratory of the Nancy University, France), G. V. Bondarenko and S. V. Penteley for the cooperation in carrying out the research. The study was support by the IEM RAS project № AAAA-A18-118020590150-6

## References

- Andreev PF, Bogomolov AI, Dobryansky AF, Kartsev AA (1958) Oil transformation in nature. Gostoptehizdat, Leningrad, p 416
- Balitskaya OV, Balitsky VS (2010) Mechanisms of the formation and morphogenetic types of fluid inclusions. *Dokl Earth Sci* 435(1):1442–1445
- Balitsky VS (1965) On occurrence of bitumen in the mercury and mercury-antimony deposits in the Northwestern Caucasus. *Sov Geol* 3:144–150
- Balitsky VS, Balitskaya LV, Bublikova TM, Borkov FP (2005) Water-hydrocarbon inclusions in synthetic quartz, calcite, and fluorite crystals grown from oil-bearing hydrothermal solutions (experimental data). *Dokl Earth Sci* 404(1):1050–1053
- Balitsky VS, Prokof'ev VY, Balitskaya LV, Bublikova TM, Pentelei SV (2007) Experimental study of the interaction of mineral-forming hydrothermal solutions with oil and their coupled migration. *Petrology* 15(3):211–223
- Balitsky VS, Penteley SV, Balitskaya LV, Novikova MA, Bublikova TM (2011) Visual in-situ monitoring of the behavior and phase states of water-hydrocarbon inclusions at high temperatures and pressures. *Petrology* 19(7):653–674
- Balitsky VS, Bondarenko GV, Pironon J, Penteley SV, Balitskaya LV, Golunova MA, Bublikova TM (2014) The causes of vertical zonation in the distribution of hydrocarbons over the Earth's interior: Experimental evidence of the cracking of crude oil in high-temperature water-hydrocarbon fluids. *Russ J Phys Chem B* 8(7):901–918

- Balitsky VS, Penteley SV, Pironon J, Barres O, Balitskaya LV, Setkova TV (2016) Phase states of hydrous–hydrocarbon fluids at elevated and high temperatures and pressures: study of the forms and maximal depths of oil occurrence in the earth’s interior. *Dokl Earth Sci* 466(2):130–134
- Bazhenova OK, Lein AY (2002) Geochemistry of carbonaceous rocks in modern hydrothermal systems. In: *Proceedings of Russian conference on organic mineralogy*. SPb Gos. Univ., St. Petersburg, pp 95–96
- Beskrovnyi NS (1967) Oil bitumen and hydrocarbon gases accompanying hydrothermal activity. VNIGNI, Leningrad, p 209
- Chukanov NV, Pekov IV, Sokolov SV, Nekrasov AN, Ermolaeva VN, Naumova IS (2006) On the problem of the formation and geochemical role of bituminous matter in pegmatites of the Khibiny and Lovozero alkaline massifs, Kola Peninsula, Russia. *Geochem Int* 44(7):715–728
- Ermakov NP (1972) Geochemical systems of mineral inclusions. Nedra, Moscow, p 376
- Florovskaya VN, Zارايسкий GP, Zezin RB (1964) Kerites and other carbon compounds at the Komsomol’skoe sulfide deposits, Southern Urals. *Dokl Akad Nauk SSSR* 157(5):1131–1134
- Huang WL, Otten GA (2001) Cracking kinetics of crude oil and alkanes determined by diamond anvil cell-fluorescence spectroscopy pyrolysis: technique development and preliminary results. *Org Geochem* (32):817–830
- Ivankin PF, Nazarova NI (2001) Deep fluidization of the earth’s crust and its role in petro-uregenesis, salt and oil formation. *TSNIGRI*, Moscow, p 206
- Lapidus AL, Strizhakova YuA (2004) Oil shale—an alternative raw material for chemistry. *Bull Russ Acad Sci* 74(9):823–829
- Mel’nikov FP, Prokof’ev VY, Shatagin NN (2008) Thermobarogeochemistry. Academic project, Moscow, 244 p
- Naumov VB, Balitsky VS, Khetchikov LN (1966) On relations between the capture, homogenization, and decrepitation temperatures of gas-liquid inclusions. *Dokl Akad Nauk SSSR* 171(1):146–148
- Naumov GB, Ryzhenko BN, Khodakovskii IL (1971) Thermodynamic data handbook. Atomizdat, Moscow, p 240
- Ozerova NA (1986) Mercury and endogenous ore-forming processes. Nauka, Moscow, p 232
- Petrov AA (1984) Hydrocarbons of oil. Nauka, Moscow, p 263
- Pikovskii YuI, Karpov GA, Ogloblina AI (1987) Polycyclic aromatic hydrocarbons in the products of Uzon oil in Kamchatka. *Geokhimiya* 6:869–876
- Ping H, Chen H, Song G, Liu H (2010) Oil cracking of deep petroleum in Minfeng sag in north Dongying depression, Bohai Bay basin, China: evidence from natural fluid inclusions. *J Earth Sci* 21(4):455–470
- Prokof’ev VY, Balitsky VS, Balitskaya LV, Bublikova TM, Borkov FP (2005) Study using IR Spectroscopy of Fluid Inclusions with hydrocarbons in synthetic quartz. In: *Proceedings of 15th Russian conference on experimental mineralogy*. Geoprint, Syktyvkar, pp 194–196
- Roedder E (1984) Fluid inclusions. *Rev. Mineral. Mineralogical Society of America*, 12, 644p
- Rokosova NN, Rokosov YuV, Uskov SI, Bodoev NV (2001) Simulation of transformations of organic matter into hydrothermal petroleum (a review). *Pet Chem* 41:221–233
- Samoilovich LA (1969) Relations between the pressure, temperature, and density of aqueous salt solutions. VNIISIMS, Moscow, p 48
- Samvelov RG (1995) Features of hydrocarbon pools formation at greater depths. *Geol Neft Gaz* (9):5–15
- Simoneit BRT (1995) Organic geochemistry of aqueous systems at high temperatures and elevated pressures: hydrothermal petroleum. *Main research avenues in geochemistry*. Nauka, Moscow, pp 236–259
- Teinturier S, Elie M, Pironon J (2003) Oil-cracking processes evidence from synthetic petroleum inclusions. *J Geochem Explor* 78:421–425
- Xiao QL, Sun YG, Zhang YD (2010) The role of reservoir mediums in natural oil cracking: preliminary experimental results in a confined system. *Chin Sci Bull* 55(33):3787–3793
- Yeremenko NA, Botneva TA (1998) Hydrocarbon deposits at great depth. *Geol Oil Gas* 1:6–11

- Zaidelson MI, Vaynbaum SY, Koprova NA (1990) Formation and oil and gas content of domanicoid formations. Nauka, Moscow, 79 p
- Zhao WZ, Wang ZY, Zhang SC (2008) Cracking conditions of crude oil under different geological environments. *Sci China Ser D Earth Sci* 51:77–83