

SUCCESSIVE, ISOTHERMAL HYDROCARBON MIGRATION EVENTS RECORDED BY FLUID INCLUSIONS IN FRACTURE-FILLING QUARTZ OF THE SZEGHALOM DOME (SE HUNGARY)

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ABSTRACT

The largest sub-basin in the south-eastern part of the Pannonian Basin is the Békés Basin (BB). The BB is surrounded by metamorphic and magmatic basement highs, which produce considerable amount of petroleum due to their high fracture porosity. One of the most intensively explored basement highs is located on the northern margin of the BB, called Szeghalom Dome (SzD). Former studies revealed remnants of an ancient hydrocarbon migration event preserved as fluid inclusions in the fracture-filling, idiomorphic quartz crystals of the SzD. This quartz phase occurs in 6 wells in the central part of the dome.

The several growth zones suggest that the quartz phase is the product of a successive cementation process. Two markedly different petroleum inclusion types could be distinguished along the growth zones characterised by different colours, vol. % of the gas phase and fluorescence emission. Simultaneously with the HC inclusions also aqueous inclusions occur in lower quantity and rather unequal spatial distribution.

The appearance of the different petroleum inclusions shows a well-defined temporal and spatial distribution during the HC-bearing fluid migration in the SzD. Based on co-genetic aqueous inclusions the quartz cementation preceded at isothermal conditions and decreasing salinity, while the HC-bearing fluid turned into a lower density (higher maturity?) type.

Key words: Pannonian Basin, metamorphic basement, fracture-filling minerals, fluid inclusion, microthermometry, petroleum migration.

INTRODUCTION

In the Pannonian Basin system (PB) hydrocarbon reservoirs exist not only in the basin-filling Neogene sediments, but also in its fractured metamorphic basement. The high fracture porosity of these rocks is the result of a multistage tectonic (in several parts brittle) evolution from the Pre-Variscan events up to present, which movements also produced a basement surface of remarkable orography. At present, the deepest sub-basins are as deep as 8000 metres below the present surface, while the mostly elevated highs are covered only with around 2000 metres of young (essentially Mio-Pliocene) clastic sediments. Thanks to all these structural and topographical reasons, a significant part of the crystalline mass can play an active role in the current hydrological system of the PB (Teleki et al., 1994). Incompatible chemical compositions of the oils (and water) produced from neighbouring wells, on the other hand suggest, that there also co-exist independent fluid regimes in the basement, which are not in hydrological contact (Pap et al., 1992).

There are several basement reservoirs throughout the PB, which even at present supply a significant amount of oil and gas. The largest one among them is called Szeghalom Dome (SzD), which is situated on the northern rim of the deepest sub-basin (Békés Basin).

Based on a detailed evaluation of organic geochemical data, the age of the currently explored hydrocarbons is thought to be of Middle-Upper Miocene age (Teleki et al., 1994) suggesting percolation into the basement coeval to the main subsidence phase of the basin. Juhász et al. (2002)

report HC-bearing fluid inclusions in fracture-filling quartz crystals from several basement cores. Including chemical and fluid inclusion data of the other vein forming minerals as well, they link this quartz phase to the exhumation stage of the basement high. Such a model suggests that the enclosed hydrocarbon migrated to the basement fractures prior to the sedimentation of the source rocks of the present-day oils, consequently it should be older and different from those produced currently.

The aim of this study is to determine the distribution of the fracture-filling, HC-bearing quartz phase in the SzD, to classify the temporal and spatial differences of the HC-bearing parent fluid, as well as to characterize the relationship between the petroleum migration and the quartz cementation. By means of the co-genetic aqueous inclusions we also aim to determine the variation of composition and the temperature of the brines co-genetic with the successive quartz precipitation events.

GEOLOGICAL SETTING

The Pannonian Basin (PB) system is a result of a rather complex, structural evolution from the Pre-Variscan events up to present. Currently, its Paleozoic-Mesozoic basement can be considered as an amalgamated mosaic of incompatible crystalline blocks, sedimentary nappes and sliders. Morphologically, PB consists of deep (down to -7000 m below surface) sub-basins and relatively uplifted basement highs (ca. -2000 m) among them. The deepest and largest sub-basin in the PB is the Békés Basin (BB), which is surrounded by basement highs from all directions.

During the Neogene, the BB developed due to a multistage subsidence history. According to current models (Teleki et al., 1994), the basin evolution of the BB can be divided into three main steps; the pre-rift, syn-rift and the post-rift episodes. Paleozoic and Mesozoic sediments represent the pre-rift formations, which are covered by Middle Miocene to Holocene sediments above a sharp erosional discordance surface. The syn-rift phase of the basin evolution started during the early Miocene and can be characterised by the uplift and exhumation of the basement highs as well as the subsidence of the sub-basins. The post-rift episode started with the coeval subsidence of both the basins and the previously elevated high regions. As a result, at present, pre-Neogene formations can exclusively be followed below the flat surface (2-7 kms) throughout the basin.

The subject of the present study is the Szeghalom Dome (SzD), which forms the boundary of BB in the north representing one of the most intensively explored basement highs all over the PB (Fig. 1A-C). The pre-Neogene basement of the SzD is composed mainly of medium and high-grade polymetamorphic rocks essentially representing the Variscan orogeny (M. Tóth et al., 2000). The most elevated central part of the high is covered by 1800 m thick Miocene-Holocene sediments at present.

Due to the Neogene movements, crystalline basement formed a horst/graben structure (Royden and Horváth, 1988; Tari et al., 1999), the basement rocks deformed rupturally

developing a dense fracture system. A detailed investigation of the microtectonic features on borecores of the SzD revealed a steeply-dipping (70-80°), conjugate system of normal faults and a set of sub-horizontal fractures (Szűcs, 2001). In some cases the members of the conjugate system are crosscut by the sub-horizontal fractures and are dragged away along them. The frequency and the aperture of the steeply dipping set are much higher than those of the low-angle one.

According to mineral chemical and fluid inclusion data (Juhász et al., 2002), exhumation is characterised by a general pyrite - illite - calcite1 - quartz - calcite2 - laumontite fracture-filling sequence in the steeply-dipping fractures. The sub-horizontal fractures are filled by laumontite, only (Szűcs, 2001). The early phases up to calcite1 form a very thin (< 1 mm) coating on the fracture walls. From the subsequent, free-standing quartz crystals Juhász et al. (2002) report presence of the hydrocarbon inclusions, which are focused in the present study.

During the exhumation, at the highest structural position of the SzD a pervasive calcite phase (calcite2) precipitated in the fractures. This phase contains pure liquid primary brine inclusions with Thom values as low as 50 °C. Its light $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ stable isotopic compositions suggest that the calcite precipitated from meteoric water typical of the Lower Pannonian time and not from former sea-water (Juhász et al., 2002). Calcite crystals also enclose terrestrial pollens not

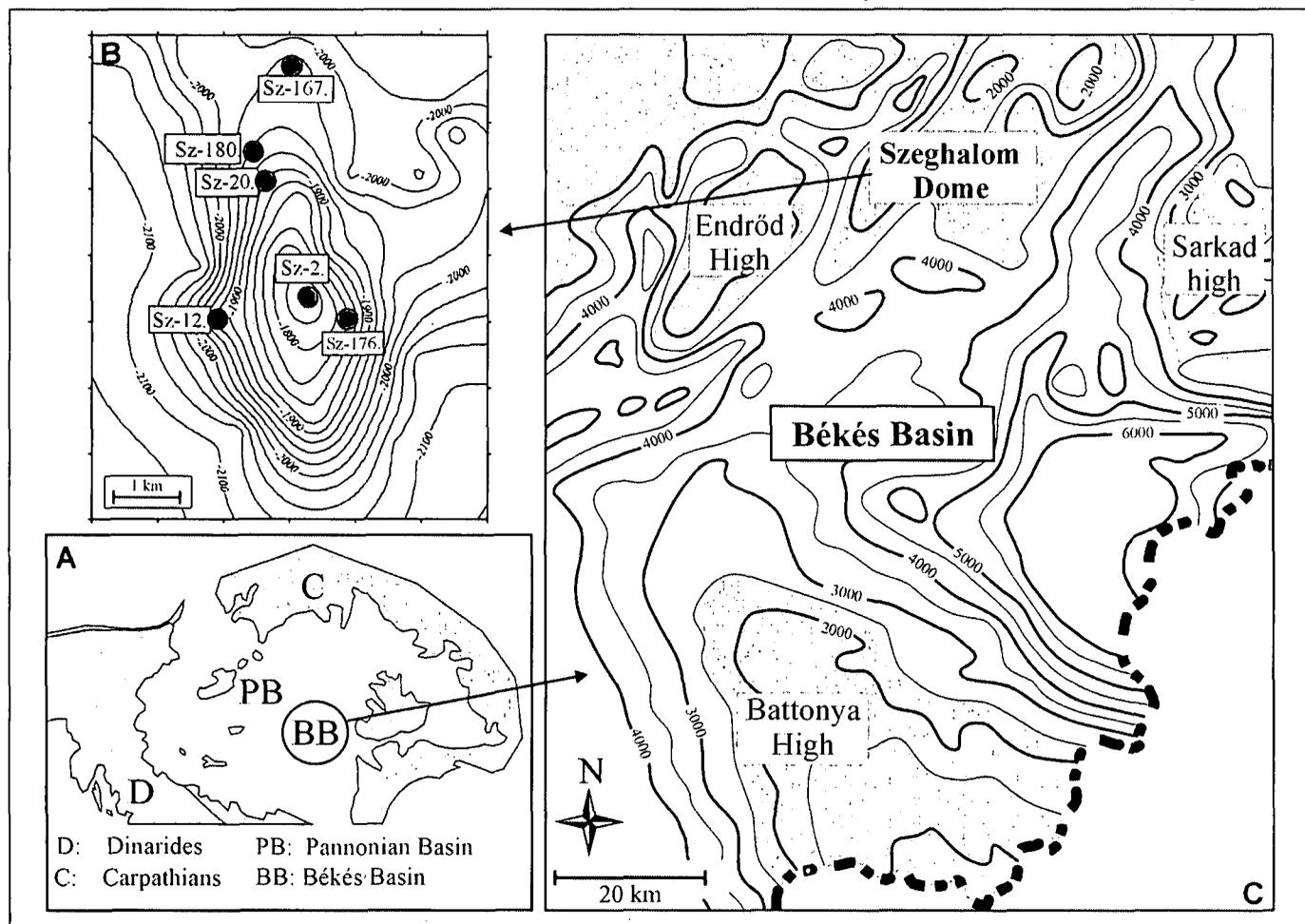


Fig. 1. (A) Location of the Pannonian Basin in the Alpine-Carpathian-Pannonian system. (B) Map of the Békés Basin and the surrounding basement highs. (C) The location of the wells on the Szeghalom Dome, which contain HC-bearing quartz crystals.

older than the Oligocene (*Chanepodiaceae*, *Ericaceae*) as well as other terrestrial plant fragments (M. Tóth et al., 2003) fixing the age of the fracture-filling mineralization to the Neogene.

The steep fractures stayed usually open even after the quartz precipitation but they were partially filled in due to the calcite phase.

ANALYTICAL METHODS

The walls of the fractures were investigated by hand-lens and by binocular microscope. A number of over 500 specimens were checked for open and filled fractures; grown-up quartz crystals were, however, found only in 6 wells. Fluid inclusions were observed on double polished single quartz crystals, using a modified spindle stage (Anderson and Bodnar, 1993) with immersion oil ($n=4.17$). During the use of UV-light, the immersion oil was omitted to avoid a disturbing emission.

Fluid inclusion measurements were carried out using a Linkam MDS-600 and a THMS-600 heating-freezing stage connected to an Olympus BX-60 microscope using objectives with a 40x and 100x magnification at the Montanuniversität in Leoben (Austria) and at the University of Szeged (Hungary). The instruments were calibrated using synthetic fluid inclusions of the *FLUID Inc.* at -56.6 (TmCO₂), 0.0 (TmH₂O) and 374 °C (ThH₂O). Prior to microthermometry, fluid inclusions were checked for any presence of petroleum, under UV-light. The petroleum-bearing aqueous inclusions were ruled out of this measurement. The salinity calculations were performed by the computer software Aqso2e developed by Bakker (2003) using the equation of Naden (1996).

The Raman spectra of the inclusions were detected by a LABRAM HR-800 microprobe at the Montanuniversität in Leoben (Austria) using 532.2 and 632.8 nm incident radiations. The spectral resolution of the vibration is 4 cm^{-1} ; the maximal size of the analysed circular area is about $3\text{ }\mu\text{m}$. The recording time generally was 150 s, the reference spectra were recorded on artificial silicon. The Raman spectra were evaluated using different literature data (Pironon et al., 1995; Orange et al., 1996)

SAMPLES

Open and healed fractures that contain fracture-filling quartz crystals were looked for in the cores of all 87 wells of the SzD. In agreement with the previous results (Szűcs, 2001), a mutual vertical/sub-vertical fracture network characterizes the cores. The shape and the dip of the fractures are highly variable depending on the host rock fabric, in which they formed. The average aperture of the steep fractures varies around 0.5-1 cm, but they locally form 3-5 cm deep vugs, as well. The wall of the fractures, especially, in the vugs is rough and is covered by different mineral phases.

Up-grown quartz crystals were found in six wells in the SzD (Sz-2, 12, 20, 167, 176, 180) (Fig. 1B). The crystals are faceted (prism: 10-10, trapezoid: 10-11) with a size of up to 10 millimetres; they are free from apparent imperfections. At some places the crystals show a well-developed bipyramidal habit. The crystals are colourless and translucent; except the samples of the Sz-167 wells, where the inner parts of the

crystals have a light brown colour. The extinction of the quartz crystals is homogenous, there could not be any subgrains or other microstructural features observed. The quartz phase of each of the six wells contains significant amount of petroleum inclusions, while HC-free quartz phase has not been found so far. Quartz crystals do not come out along the subsequent, sub-horizontal fractures.

FLUID INCLUSION PETROGRAPHY

The quantity and the distribution of the fluid inclusions (FIs) in the fracture-filling quartz phase are rather different from one crystal to another. The FIs contain either a brine- or a hydrocarbon-dominated fluid fill. Because the colour of the HC liquid phase in the FIs varies from dark brown to a completely colourless type, UV excitation was applied to distinguish them from the brine, and also to classify the single HC fluid inclusion assemblages (FIAs).

Size distribution and the amount of the FIs representing the two main fluid types (i.e. the brine- and hydrocarbon-dominated, respectively) show similar characteristic features in all of the six wells. Namely, the brine inclusions are several orders of magnitude smaller and less frequent than the other ones.

Based on the petrographic properties (colour, vol. % of the gas phase, fluorescence colour, etc.) three main FI types (and additional subtypes) can be distinguished in the quartz crystals:

Type IA: Two-phase inclusions showing a $V+L \rightarrow V$ type homogenisation. The vol. % of the gas phase is 0.8-0.9 (all vol. % values were measured on microphotographs). Both phases are colourless, during the UV excitation a weak, bluish fluorescent colour of the liquid phase can be observed. The inclusions might be as large as 1 mm in size. The shape of the inclusions is usually tabular, hand-like or rounded; they often form a tooth rack-like habit.

Type IB: The trapped fluid of this subtype is similar to that of Type IA but the homogenisation occurs as a $L+V \rightarrow L$ transition. The size of these inclusions never exceeds the size of Type IA inclusions; they usually are several orders of magnitude smaller.

The above subtypes sometimes occur within small, isolated inclusion clusters, whose members show highly variable liquid-vapour ratios.

When cooling, in some cases, a solid phase as black-coloured spots appears on the surface of the bubbles of the Type IA inclusions. During subsequent heating, this solid phase disappears between 20 and 22 °C. The occurrence adjacent to the (methane) bubble and the homogenisation temperature above 0 °C suggest that this solid phase is probably a gas-clathrate.

Type II: Type II inclusions can be characterised by a dark or pale brown liquid, a colourless vapour phase and solid phases of highly variable quantity ($L+V \pm S$). The liquid phase fluoresces very intensively with greenish blue colour under UV light. The vol. % of the gas phase varies between 0.2 and 0.3. These inclusions often show negative crystal shape. The size of Type-II petroleum inclusions (PIs) does not exceed $80\text{ }\mu\text{m}$.

In Type II PIs two solid phases (Sp and Sb) could be distinguished at room temperature, or during the cooling process (Fig. 2). At room temperature the Sp phase forms groups in the liquid phase, the particles show a dendrite-, needle-like or amorphous, translucent habit. The crystals show birefringent behaviour under crossed polarizers. During the cooling process the quantity of the solid phase increases, while below 0 °C it fills up the inclusions cavity, completely. The colourless, dendritic habit of the Sp phase prevents the estimation of its exact volumetric proportion.. Within the same FIA in some cases a yellowish brown, amorphous mass (Sb) occupies almost the whole inclusion cavity, while in other PIs it forms small (3-6 µm) particles, only. The extremely different quantity of the Sb phase relative to the liquid or vapour phases suggests an accidental origin.

Type III: The liquid phase of these FIIs consists of brine, while the composition of the vapour phase is in most cases unknown. The inclusions of Type III usually form isolated clusters with a maximal inclusion size of 15 µm. These aqueous inclusions are rather rare and they are distributed unevenly among and inside the growth zones. Type III inclusions occur together with Type I-II PIs in several growth zones.

Type I-II PIs occur either separated or in small groups. These groups define weakly developed planes, which usually terminate within the crystals. The small (< 10 µm) FIIs often form curved planes, which at places seemingly crosscut each other. Varying the position of the focal plane of the microscope, these FIIs-defined planes show a chaotic, often crosscutting texture. The clusters of Type III FIIs always occur within or along planes defined by the PIs.

In crystals, which contain only a few inclusions, the planar arrangement of the FIIs can be noticed by changing the point of view, only. Detailed petrographic observations using a modified spindle-stage (Anderson and Bodnar, 1993) show evidence for multistage quartz precipitation in each studied wells. The crystals can be characterised by several parallel growth zones with primary FIIs trapped along them. The angles between the planes defined by the FIIs give about 60°, the value corresponds to the angle between the faces of a hexagonal prism. The FIIs are often flat, parallel to each other and to certain faces of the enclosing crystal (Fig. 3).

The frequent occurrence of the sceptre-shaped quartz crystals is a macroscopic evidence of this multistage precipitation.

RAMAN MICROSCPECTROSCOPY

Although the spectra of Type IB inclusions were often masked by the (weak) fluorescence of the liquid phase as well, the composition of the IA subtype could be determined by this method, qualitatively. The major part of the vapour phase consists of methane with a subordinate quantity of ethane (Fig. 4). The characteristic peaks of the liquid phase are located on a hump between 2800 and 2950 cm^{-1} . The most intensive peak can be found at 2909 cm^{-1} referring to the presence of the methane dissolved in the liquid phase (Orange et al., 1996). Although they all occur systematically, the positions of the peaks at 2875, 2942 and 2963 cm^{-1} vary slightly in the different samples suggesting the contribution of diverse alkanes and/or cyloalkanes to the liquid phase. The

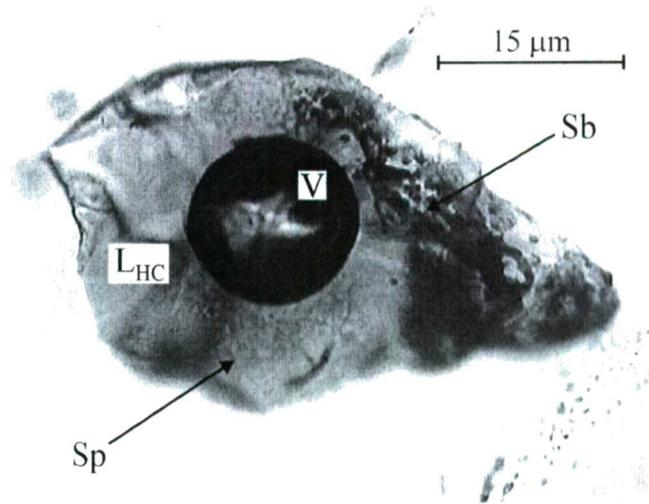


Fig. 2. Four phase (L+V+Sp+Sb), Type II petroleum inclusion from the Sz-167 well.

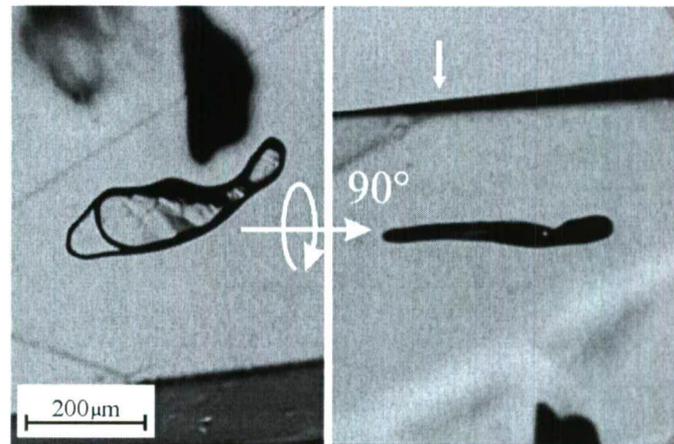


Fig. 3. Large, isolated Type Ia petroleum inclusion arranged parallel to the certain faces of the enclosing crystal (Sz-180 well).

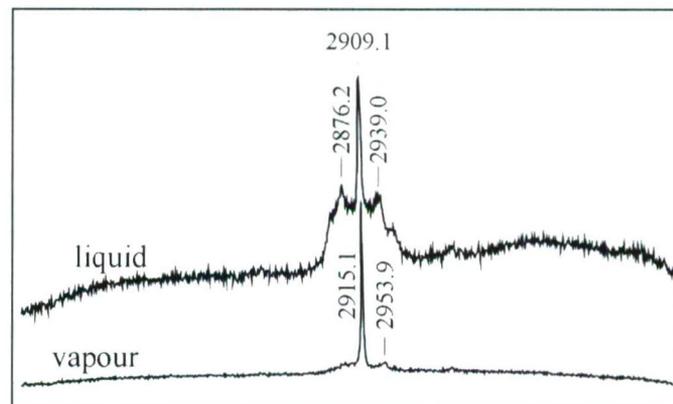


Fig. 4. Raman spectra of the liquid and vapour phases of Type Ia fluid inclusion.

weak fluorescence and the colourless habit of the Type I fluid inhibit the optical observation of the co-existing water phase probably present in the hydrocarbon inclusions.

The strong fluorescence inhibited the investigation of Type II inclusions by Raman spectroscopy.

Because of the small size and the arrangement of the aqueous inclusions (Type III), its semi-quantitative composition was specified only in two cases. In these cases

on the spectrum of the aqueous L phase the peak at 2909 cm^{-1} suggests the symmetric stretching band of dissolved methane (Dubessy et al., 2001). The determination of the composition of the vapour phase has been failed.

The distribution of Type I and II hydrocarbon inclusions shows a well-defined sequence in the studied wells and in the successive growth zones. Based on the results of petrography (performed under normal and UV light) and the micro-Raman spectroscopy, all of the petroleum inclusions occurring in quartz crystals of the Sz-20 and 180 wells belong to the Type I group, while the samples from the Sz167 well contain Type II PIs, exclusively. The precipitation of the quartz phase in the Sz-2, 12 and 176 wells took place in the presence of a more complex, changing fluid regime. The inner zones of the quartz crystals represent the above three wells contain Type II FIs, exclusively, while following a “sudden” change, in the outer (younger) growth zones Type I inclusions became dominant (Fig. 5). Both Type I and Type II FIs occur simultaneously within the same growth zone in one case, in the Sz-2 well.

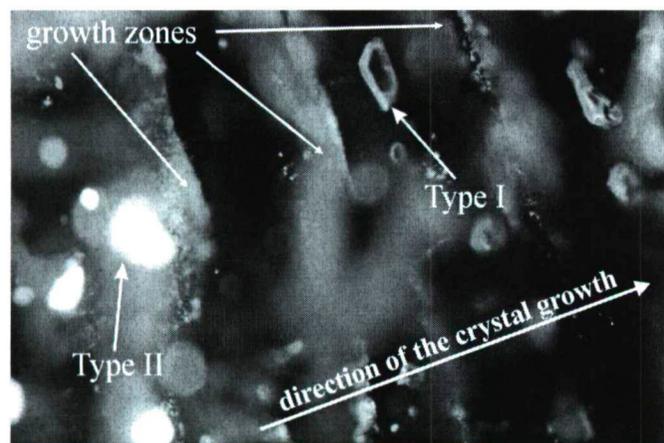


Fig. 5. Parallel growth zones with Type II petroleum inclusions occurring in the inner, and Type I PIs in the outer zones (Sz-173 well). The width of the picture is 1 mm.

MICROTHERMOMETRY

Aqueous FIAs suitable for microthermometry were found in three wells; Sz-2 (in two well sections: ÁGK-1131 (1900-1902.5 m) and 1134 (1990-1990.2 m), respectively), Sz-167 (2074 m) and Sz-180 (in well section: ÁGK-4644 (2011 m)). Because of the small size and the poor optical resolution, the homogenisation temperature in most cases was measured using the cycling method described by Goldstein and Reynolds (1994). We attempted to determine the final ice melting temperature in the presence of the vapour phase; in cases it was impossible, the temperature data are marked on the histograms.

Two aqueous FIAs of the Sz-2 well may be distinguished: in the well section ÁGK-1131 it is co-genetic with Type II PIs, while in the well section ÁGK-1134 it is co-genetic with Type I PIs. The measured Thom and TmICE values are shown in Fig. 6.

We were able to determine the homogenisation temperatures of Type IA and IB petroleum inclusions, which occur side by side in the same growth zone of the Sz-20 well (in well section ÁGK-4921 (2069 m)) Fig. 7. shows the distribution of the measured data. The flat morphology of the

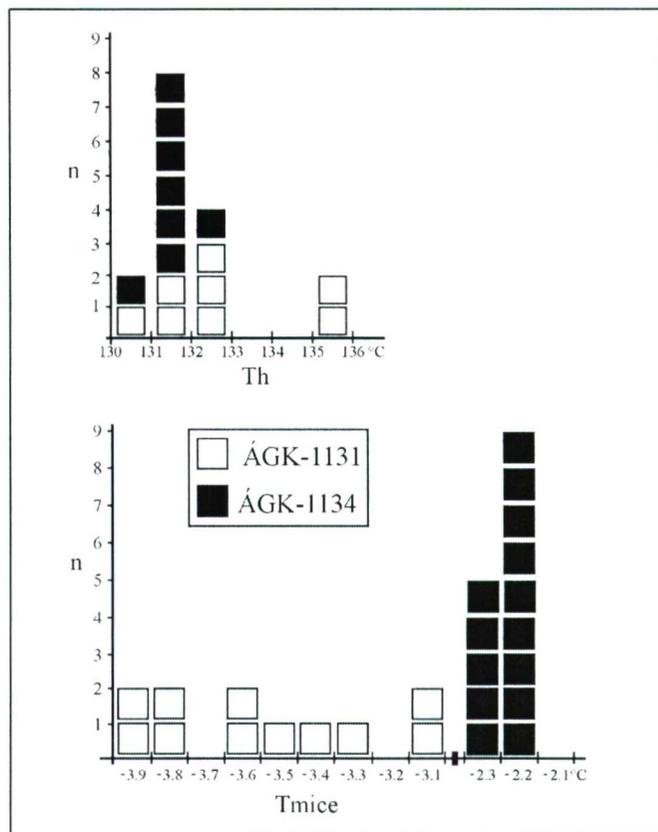


Fig. 6. Thom and Tmice values measured on aqueous inclusion of the ÁGK-1131 and -1134 well sections of the Sz-2 well.

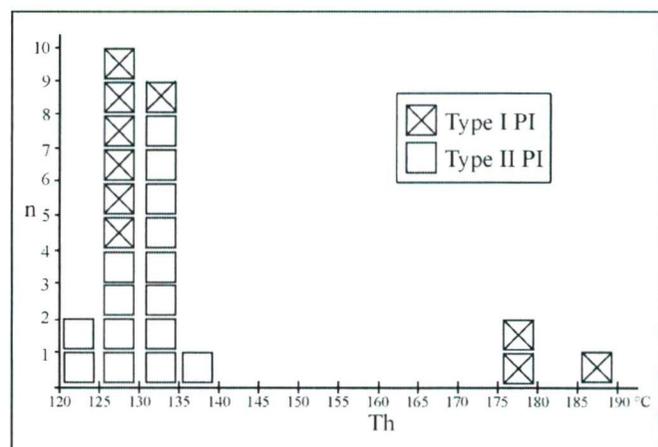


Fig. 7. Homogenization temperatures of the co-genetic Type Ia and Ib petroleum inclusions of the Sz-20 well (well section ÁGK-4921)

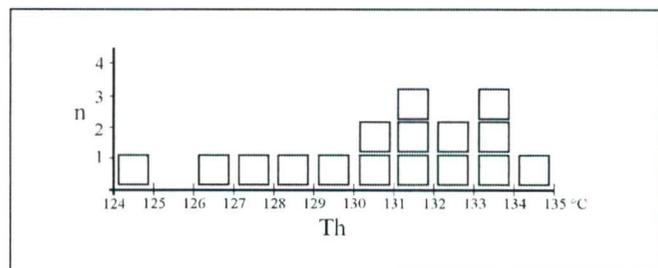


Fig. 8. Homogenization temperature values of Type IB petroleum inclusions of the Sz-180 well (well section ÁGK-4648).

Type IA inclusions make the observation of the temperature of the L→V mode homogenisation easier, however, these values must be regarded as minimal temperatures.

Measurable quantity of HC inclusions of the Sz-180 well was found in the 4848 well section (2020 m). The primary FIA exclusively contains Type IB fluid inclusions, which homogenized between 124 and 135 °C, by V→L transition (Fig. 8). In the 4644 well section (2011 m) of the same well aqueous FIA co-genetic with the Type I inclusions was observed. Thom values show a quite uniform distribution varying between 131 and 133 °C (Fig. 9).

Microthermometry was performed on both aqueous and petroleum inclusions (trapped along the same growth zone) of the Sz-167 well. The Thom and Tmice values are shown on Fig. 10.

At low temperatures, Type I FIIs show a characteristic phase transition of L+L+V→L+V type. During the cooling run, after the initial shrinkage of the vapour phase at about -77 °C a new liquid phase appears, which homogenises at about -63 °C during subsequent heating (Fig. 11). This transition can be observed on both Type IA and IB inclusions.

The S→L type homogenisation of the Sp phase occurs at slightly different temperatures in different wells containing Type II PIs. In Type II inclusions of the Sz-2, 12 and 176 wells the S→L homogenisation proceeds at 18 ± 5 °C, while in case of the Sz-167 well it occurs at 21 ± 8 °C. The S→L type homogenisation of the Sb solid phase proceeds above the V→L homogenisation temperature (it was not exactly determined).

DISCUSSION

In the central part of the SzD HC-bearing quartz were found in 6 wells, while quartz crystals free from organic fluid remnants were not observed (see Schubert and M. Tóth, 2001). The relative position of this quartz phase in the fracture-filling mineral sequence is of overriding importance in studied reservoir. Although fluid inclusion and stable isotope measurements of the subsequent calcite2 phase are available only from a few wells analysed by Juhász et al. (2002), our observations in all studied wells support their fracture-filling model. Namely, the precipitation of the quartz phase in the whole SzD precedes the formation of the calcite2 phase. Based on the newest palynological data of M. Tóth et al. (2003), the calcite2 phase precipitated at the most exhumed vertical position of the SzD during the Badenian. As a consequence, the HC fluid entrapped in the quartz crystals cannot be identical to the nowadays produced oil and gas, which have a source rock of Badenian, Sarmatian and lower Pannonian age (Teleki et al., 1994). So the known composition of the produced HC fluid could not be used even as a starting-point for investigation of the trapped fluid. Although there are some Mesozoic formations near the study area that contain members of high organic matter content (e.g. Szolnok Flysch Formation, Juhász et al., 2002), the source rock of the enclosed petroleum is still unidentified.

The studied fluid inclusions form planar arrangement supposing a secondary (or pseudosecondary) origin for the FIAs in question. The petrographical observations performed by the modified spindle stage (Anderson and Bodnar, 1993), however, suggest that the planar arrangement coincides well

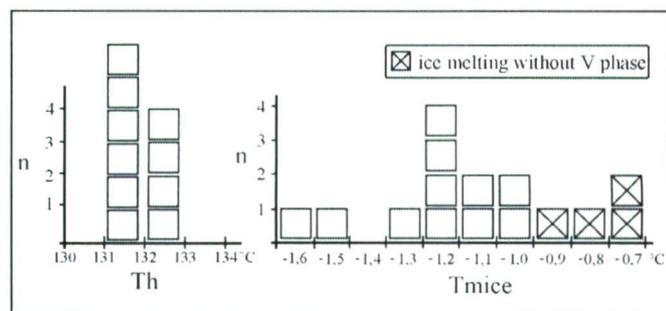


Fig. 9. Thom and Tmice values measured on aqueous inclusion from the Sz-180 well (well section ÁGK-4644).

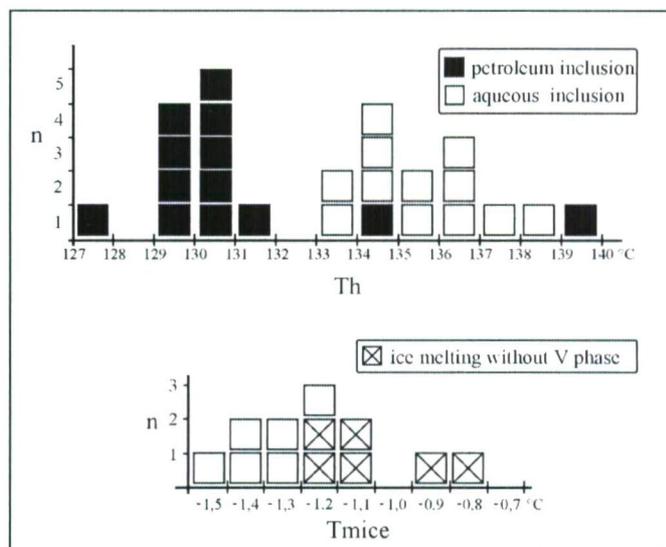


Fig. 10. Thom and Tmice values of the co-genetic aqueous and petroleum inclusions from the Sz-167 well.

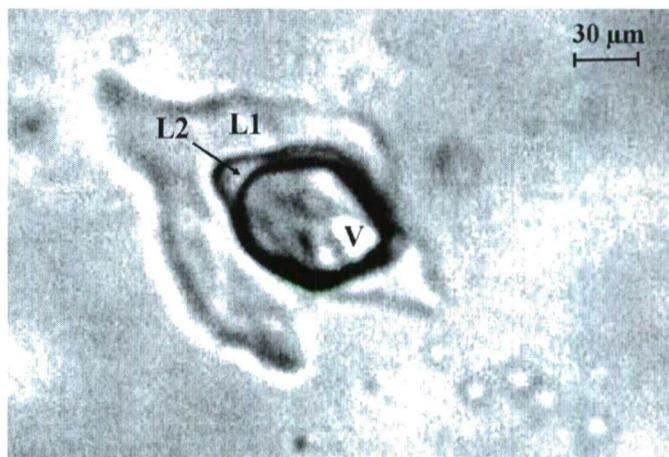


Fig. 11. Type Ib fluid inclusion from the Sz-180 well (well section ÁGK-4648) showing L + L + V equilibrium at -89 °C.

with an early-late primary origin of these inclusions (Roedder, 1979), which were probably trapped along the faces of the earlier quartz crystals. Thus the petroleum (and aqueous) inclusions trapped along parallel growth zones were formed simultaneously with the precipitation of the host quartz (primary inclusions; Goldstein and Reynolds, 1994).

HC-bearing idiomorphic quartz crystals were reported from several localities in the world, e.g. the so-called "Marmarosh diamonds" (Dudok et al., 2000), "Québec diamonds" (Levine

et al., 1991), etc. Several works studied the obvious relationship between the precipitation of quartz and the host rock rich in organic matter, as well (e.g. Levine et al., 1991; Bennett, 1991; Wilkinson et al., 1998). Wilkinson et al. (1998) suppose that the organic acids, which liberate during the thermal maturation of the organic matter, could be of primary importance in the local silica transport.

Based on the negligible solubility of silica in petroleum, in spite of the extremely low amount of aqueous inclusions relative to the HC-bearing ones, it can be supposed that even those quartz crystals, which exclusively enclose petroleum inclusions, were precipitated from an aqueous solution. Nedkvitne et al. (1993) studied the temporal relationship between diagenesis and oil emplacement in sandstone reservoirs of the North Sea. They could demonstrate that in contrast to the former conception, cementation does not terminate after oil emplacement in all geological situations.

The fracture-filling quartz phase of the SzD contains two markedly different HC fluids. They differ in colour, density, presence of solid phases, intensity and colour of fluorescence, (relative) time of trapping, as well as spatial occurrence in the SzD. The PIs of Type I and II occur either separated or together in the studied wells, but the temporal sequence of these fluid types is identical everywhere.

The colourless liquid phase, the different vol. % of the gas phase and the lack of the solid phases unambiguously distinguish Type I fluid from Type II, although, these deviations may account for completely different reasons. The above-mentioned features of Type I fluid suggest a low density; possibly mature HC fluid (light oil/condensate). Similar HC-bearing FIAs were introduced by Munz et al. (1999) from the Brent Group Reservoirs among many others. Based on the observed bluish fluorescent colour, they considered the trapped fluid as a condensate. Referring to the results of Luks et al (1983), Teinturier et al (2002) classified PIs from the Haltenbanken Area as condensate based on appearance of a new liquid phase during cooling. The new liquid phase homogenised below 0°C by $L+L+V \rightarrow L+V$ transition.

The usually typical low amount of the aromatic components of the gas condensates (e.g. Goldstein and Reynolds, 1994) is proved indirectly by the applicability of the visible Raman spectroscopy in case of Type I fluid inclusions. The contribution of methane and ethane to the vapour and alkanes/cycloalkanes to the liquid phase is revealed by the Raman microspectroscopy. Even if their compositions agree, there is not unquestionable evidence that the Type I fluid must be a condensate, because the measured components are most common in crude oils, too (Tissot and Welte, 1978). The termogenic formation of condensate is typical of the higher part of the oil window (Tissot and Welte, 1978). Nevertheless, there also are other mechanisms (e.g. evaporative fractionation, Thompson, 1987), which may produce condensates that are seemingly similar to those produced by thermal maturation.

By reason of the coloured liquid phase, the lower API gravity (presence of different solid phases) and the bluish green fluorescence colour (red shift relative to the emission of the Type I fluid), Type II HC fluid can unambiguously be distinguished from the Type I fluid. To form subcategories within the Type II fluid using the above-mentioned indirect methods is not possible. Therefore, the Type II fluid found in

the Sz-167 well cannot undoubtedly be correlated with those of Sz-2, 12, 176 wells, whose outer growth zones contain even the Type I fluid. The similar homogenisation temperature data (about 130 °C) of the co-genetic aqueous inclusions and occurrence of the solid phases stand for the relationship to the other three wells, while the significantly lower salinity (2.07-2.57 wt% NaCl_{eq}) and the uniquely coloured host quartz tell against.

We have constructed a relative sequence for the different HC fluid types using the occurrence of the different HC-bearing FIAs in the subsequent growth zones of the six wells. Then the studied wells of the SzD were classified based on similar PIs or PI sequences.

The most common HC FIAs in the SzD belong to Type IA and IB. In the Sz-20 and 180 wells these two HC types occur exclusively. The FIAs arise along several parallel growth zones but there is no systematic difference in the appearance (vol. % of the gas phase, colour, fluorescence properties) of the HC-bearing FIAs of the adjacent zones. The succeeding growth zones of the Sz-167 well contain Type II PIs, without any difference between the FIAs. A well-defined temporal difference can be observed in the appearance of Type I and Type II fluids in the centre and the southern flank of the SzD; in case of the Sz-2, 12, 176 wells. While the inner growth zones are defined, exclusively, by Type II PIs, following a sudden appearance of Type I inclusions (Fig. 5), this type becomes dominant in the outer zones. In these wells Type I fluid appears only in the outer (younger) growth zones.

There is not any significant change in any measured properties of the FIAs/PIs with depth.

If the aqueous inclusions at the time of entrapment were saturated respecting methane, then the homogenisation temperature coincidences with the trapping temperature (Hanor, 1980; Pironon et al., 2001). Because of the minute size, rarity and position of the aqueous inclusions, we were able to prove the presence of methane by Raman microprobe in the vapour (and the liquid) phase in two cases only. As the common occurrence of petroleum and aqueous fluids within the same inclusion unambiguously prove the co-genetic trapping of the two fluids (Fig. 12), we consider that the aqueous phase was methane-saturated at the time of trapping (Munz, 2001).

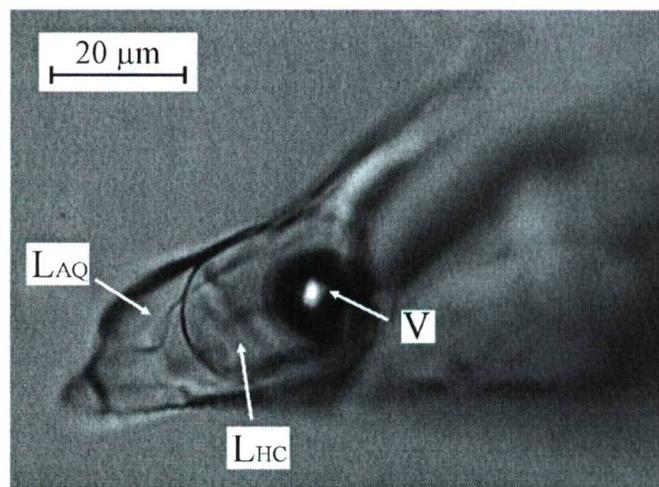


Fig. 12. Three phase ($L_{AQ} + L_{HC} + V$) petroleum inclusion from the Sz-167 well.

The generally observable small size and unequal distribution of the aqueous inclusions makes comparison of the studied wells concerning the trapping temperature problematic. Nevertheless, we suppose that the measured aqueous FIAs do not represent contemporaneous growth zones of the different wells, on the contrary they record different moments of the quartz precipitation. Accepting the above assumption, the precipitation of the fracture-filling quartz phase of the SzD took place during static temperature regime but intensively changing fluid composition.

The common recrystallisation phenomenon (e.g. by necks connected inclusions) and the overall observable size difference between Type IA and IB inclusions may suggest that the liquid-rich (Type IB) inclusions were possibly formed by post-entrapment modification of the originally Type IA PIs. In this case Type IB inclusions should give a rather scattering Thom pattern caused by the accidental change in the volume of the inclusion cavity yielded by recrystallisation (Sheppard et al., 1985). In the present case, however the Thom values of Type IB inclusions are quite similar (Fig. 7), and the typical range falls near that of Type IA. Although the fact that the size of Type IA inclusions always exceeds the dimension of Type IB would support the above assumption, the size difference may be explained by the different wetting properties of the co-existing vapour and liquid phases, as well (Diamond personal communication, 2003).

Considering a multi-component hydrocarbon fluid, there are mechanisms that may result in formation of heterogeneous FIAs, i.e. simultaneous trapping of liquid- and vapour-rich petroleum inclusions introduced by Teinturier et al. (2002). They described condensate-type fluid showing analogous behaviour to ours from the Haltenbanken area (North Sea). Based on the similar Thom values of the L→V and V→L type fluid inclusions they supposed a near critical trapping. However, they have found several inclusions with critical homogenisation behaviour as well, which was not observable in the studied SzD samples. Here, the frequent occurrence of the partially necking-downed FIs, the negative crystal shape, the pointed inclusion shape as well as some Thom values differing from the average suggest that the effect of recrystallisation could not be ignored either.

Since the measurable aqueous FIAs of the Sz-2 well were found in different samples (crystals), the temporal relationship between the two growth zones (FIAs) were identified based on the co-genetic petroleum inclusions. Systematic sequence of Type I and II HC inclusions is well-defined in the studied wells, i.e. the growth zones containing Type I fluid inclusions always post-date the Type II-bearing zones. Therefore we consider the aqueous FIA in the sample 1131 co-genetic with Type II petroleum inclusions as a marker of the former stage of quartz precipitation in the SzD. Since the aqueous inclusions of the sample 1134 co-exist exclusively with Type I HC fluid, it must represent the parent fluid composition of the later (younger) stage. A similar change in the composition of the HC fluid during the charging of a hydrocarbon reservoir is a common phenomenon (e.g. Munz et al., 2002). The types and distribution of the petroleum inclusions in the Sz-12 and 176 wells are identical to those observed in the Sz-2 well, in these cases, however, aqueous inclusions occur sporadically.

Although, formation temperatures of the quartz phase in the early and late growth zones (Sz-2) are similar, a significant change in the salinity can be observed. While the aqueous inclusions of the well section 1131 show a salinity of 5.1-6.3 wt% NaCl_{eq}, those values of the well section 1134 vary between 3.7-3.8 wt% NaCl_{eq}. The salinity measured on the aqueous inclusions of the Sz-180 well changes between 1.2-2.7 wt% NaCl_{eq}, while the trapping temperature is identical to those measured in the Sz-2.

Although, the relative time of precipitation of the quartz phase between the Sz-180 and the outer growth zones of the Sz-2 wells is unclear, we suppose a trend of decreasing salinity from the time of migration of Type II petroleum towards the appearance of Type I fluid. So, the intermediate salinity received from the outer growth zones of the Sz-2 well may probably represent the mixing "event" of Type I and Type II fluids. There is no reason for changing salinity if we assume that the Type I fluid formed by phase separation from the "original" Type II fluid, to further discuss this dilemma quantitative information of the petroleum inclusions of the three growth zones is needed.

CONCLUSIONS

- Six wells of the central part of the SzD contain HC-bearing, euhedral quartz crystals, which was formed unambiguously prior to the calcite₂ phase, which represents the most exhumed state of the SzD.
- The several growth zones and the flat PIs arranging parallel to certain crystallographic directions of the host quartz suggest a primary origin of the HC-bearing FIs and the co-genetic brine inclusions.
- Based on colour, fluorescent properties and low temperature phase transition, the HC fluid of the Sz-20 and 180 wells probably represent a condensate-like fluid (Type I).
- In the Sz-2, 12 and 176 wells the precipitation of the quartz phase took place in a changing HC fluid regime. The early liquid-rich PIs (Type II) are followed by the condensate-like, translucent HC fluid in the outer (younger) growth zones of the quartz crystals. Based on the introduced data it is impossible to decide whether this condensate is the product of advanced thermal maturation or was formed by phase separation from a former petroleum fluid (e.g. by evaporation fractionation).
- Based on the aqueous inclusions co-genetic with the PIs, the trapping of the primary FIAs and the precipitation of the different quartz phases happened at isothermal conditions (at about 130 °C) but in the presence of different HC fluids. The quartz cementation in Sz-167 well took place at a temperature identical to those observed in the other five wells.
- During the fluid evolution devised using the subsequent PIs, a decreasing salinity (5.1-6.3 → 3.7-3.8 → 1.2-2.7 wt% NaCl_{eq}) of the aqueous inclusions can be revealed. The significant salinity change relates to the abrupt appearance of the condensate-like fluid suggesting a phase separation rather than the increasing thermal maturation of the same organic matter.
- Based on colour, fluorescence properties, trapping temperature, vol. % of the gas phase and the presence of higher molecular weight components (solid phases), the Type II PIs of the Sz-167 well seem to be related to those found in the Sz-2, 12 and 176 wells. Because Sz-167 well

can be found rather far from the three wells mentioned, and Type II fluid is completely missing from the two wells (Sz-20 and 180, respectively), which are situated among them (c.f. Fig. 1C), we suppose that the Type II fluid of the Sz-167 well is probably different from that found in the Sz-2, 12 and 176 wells. The lower salinity of the aqueous inclusions measured in the Sz-167 well support this assumption, however, to decide this question compositional data of the different HC types are needed.

- Although, the different liquid-vapour ratios of Type I PIs were presumably resulted from heterogeneous trapping, the morphology of the inclusions suggest a possible effect of the recrystallization, as well.

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REFERENCES

- ANDERSON, A. J., BODNAR, R. J. (1993): An adaption of the spindle stage for geometric analysis of fluid inclusion. *American Mineralogist*, **78**, 657-664.
- BAKKER, R. J. (2002): <http://www.unileoben.ac.at/~buero62/minpet/Ronald/Programs/Computer.html>. accessed: November 15, 2003.
- BENNETT, P., SIEGEL, D. I. (1987): Increased solubility of quartz in water due to complexation by dissolved organic compounds. *Nature*, **326**, 684-687.
- BENNETT, P. (1991): Quartz dissolution in organic-rich aqueous systems. *Geochimica et Cosmochimica Acta*, **55**, 1781-1797.
- CSONTOS, L., NAGYMAROSI, A. (1999): Late Miocene inversion versus extension in the Pannonian Basin. *Tübinger Geowissenschaftliche Arbeiten, Series A*, **52**, 132.
- DUBESSY, J., BUSCHAERT S., LAMB, W., PIRONON, J., THIÉRY, R. (2001): Methane-bearing aqueous fluid inclusions: Raman analysis, thermodynamic modelling and application to petroleum basins. *Chemical Geology*, **173**, 193-205.
- DUDOK, I., JARMOLOWICZ-SZULC, K. (2000): Hydrocarbon inclusions in vein quartz (the „Marmarosh diamonds”) from the Krosno and Dukla zones of the Ukrainian Carpathians. *Geological Quarterly*, **44**, 415-425.
- GOLDSTEIN, R. H., REYNOLDS, T. J. (1994): Systematics of fluid inclusions in diagenetic minerals. *SEPM Short Course* 31.
- HANOR, J. S. (1980): Dissolved methane in sedimentary brines: potential effect on the PVT properties of fluid inclusions. *Economic Geology*, **75**, 603-617.
- JUHÁSZ, A., M. TÓTH, T., RAMSEYER, K., MATTER, A. (2002): Connected fluid evolution in fractured crystalline basement and overlying sediments, Pannonian Basin, SE Hungary. *Chemical Geology*, **182**, 91-120.
- KARLSEN, D. A., NEDKVITNE, T., LARTER, S. R., BJORLYKKE, K. (1993): Hydrocarbon composition of authigenic inclusions: Application to elucidation of petroleum reservoir filling history. *Geochimica et Cosmochimica Acta*, **57**, 3641-3659.
- LEVINE, J. R., SAMSON, I. M., HESSE, R. (1991): Occurrence of fracture-hosted impsomite and petroleum fluid inclusions, Quebec City Region, Canada. *AAPG Bulletin*, **75**(1), 139-155.
- LUKS, K. D., MERRILL, R. C., KOHN, J. P. (1983): Partial miscibility behavior in cryogenic natural gas systems. *Fluid Phase Equilibria*, **14**, 193-201.
- M. TÓTH, T., SCHUBERT, F., ZACHAR, J. (2000): Neogene exhumation of the Variscan Szeghalom Dome, Pannonian Basin, E. Hungary. *Geological Journal*, **35**, 265-284.
- M. TÓTH, T., KEDVES, M., SCHUBERT, F. (2003): Az Alföld metamorf aljzatának exhumációja a Szeghalom-dóm területén: palinológiai bizonyítékok. *Földtani Közlemény*, **133/4**, 547-562.
- MUNZ, I. A., JOHANSEN, H., HOLM, K., LACHARPAGNE, J.-C. (1999): The petroleum characteristics and filling history of the Froy field and the Rind discovery, Norwegian North Sea. *Marine and Petroleum Geology*, **16**, 633-651.
- MUNZ, I. A. (2001): Petroleum inclusions in sedimentary basins: systematics, analytical methods and applications. *Lithos*, **55**, 195-212.
- MUNZ, I. A., YARDLEY, B. W. D., GLEESON, S. A. (2002): Petroleum infiltration of high-grade basement, South Norway: Pressure-Temperature-time-composition (P-T-t-X) constraints. *Geofluids*, **2**, 41-53.
- NEDKVITNE, T., KARLSEN, D. A., BJORLYKKE, K., LARTER, S. R. (1993): Relationship between reservoir diagenetic evolution and petroleum emplacement in the Ula Field, North Sea. *Marine and Petroleum Geology*, **10**, 255-270.
- ORANGE, D., KNITTLE, E., FARBER D., WILLIAMS, Q. (1996): Raman spectroscopy of crude oils and hydrocarbon fluid inclusions: A feasibility study. In Dyar, M. D., McCammon, C., Schaefer, M. W. (eds): *The Geochemical Society, Special Publication No. 5*.
- PAP, S., SÖREG, V., PAPNÉ HASZNOS, I. (1992): A Dévaványa-déli metamorf medencealjzati szerkezet szénhidrogénkutatói problémái - esettanulmány. *Geophysical Transactions*, **37**(2-3), 211-228. (in Hungarian)
- ROEDDER, E. (1979): Fluid inclusion: Mineralogical Society of America, *Reviews in Mineralogy*, v. 12.
- ROYDEN, L. H., HORVÁTH, F. (eds.) (1988): *The Pannonian Basin: A Study in Basin Evolution*. AAPG, Tulsa, Oklahoma. *Memoir* **45**, 27-48.
- SCHUBERT, F., M. TÓTH, T. (2001): Structural evolution of mylonitized gneiss zone from the northern flank of the Szeghalom dome (Pannonian Basin, SE Hungary). *Acta Mineralogica et Petrographica Szeged*, **42**, 59-64.
- SHEPHERD, T. J., RANKIN, A. H., ALBERTON, D. H. M. (1985): *A Practical Guide to Fluid Inclusion Studies*. Blackie.
- SZÜCS, É. (2001): Polimetamorfitok mikrotektonikai vizsgálata a Békési-medence északi részén. *Kézirat, SZTE, Ásványtani, Geokémiai és Közettani Tanszék*. (in Hungarian)
- TARI, G., DÖVÉNYI, P., DUNKL, I., HORVÁTH, F., LENKEY, L., STEFANESCU, M., SZAFIÁN, P., TÓTH, T. (1999): Lithospheric structure of the Pannonian Basin derived from seismic, gravity and geothermal data. In Durand, B., Jolivet, L., Horváth, F., Séranne, M. (eds): *The Mediterranean Basins: Tertiary Extension within the Alpine Orogen*. Geological Society: London. *Special Publications* **156**, 215-250.
- TEINTURIER, S., PIRONON, J., WALGENWITZ, F. (2002): Fluid inclusion and PVTX modelling: examples from the Garn Formation in well 6507/2-2, Haltenbanken, Mid-Norway. *Marine and Petroleum Geology*, **19**, 755-765.
- TISSOT, B. P., WELTE, D. H. (1978): *Petroleum Formation and Occurrence*. Springer-Verlag.
- WILKINSON, J. J., LONERGAN, L., FAIRS, T., HERRINGTON, R. J. (1998): Fluid inclusion constraints on conditions and timing of hydrocarbon migration and quartz cementation in Brent Group reservoir sandstones, Columba Terrace, northern North Sea. In Parkell, J. (ed): *Dating and Duration of Fluid Flow and Fluid-Rock Interaction*. Geological Society Special Publications **144**, 69-89.

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