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Mantle-related CO_2, metasedimentary HC–N_2 gas and oil traces in the Répcelak and Mihályi accumulations, W-Hungary – mixing of three fluids of very different origin

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Numerous accumulations of CO_2 and nitrogen-rich natural gas are known in the hot Pannonian Basin System (PBS), where even the mixture of these two fluids is a common phenomenon. The Danube Basin, part of the PBS, is characterized by the predominance of CO_2 and nitrogen-rich natural gas over "normal" natural gas. The multistacked Répcelak and Mihályi gas accumulations (southern, Hungarian part of the Danube Basin) display an upward increase of nitrogen-rich natural gas at the expense of CO_2. This study, using the abundant public data, the published results and the new biomarker data obtained from oil traces, attempts to explain the formation of these multistacked accumulations. A synoptic view of the vertical changes in gas composition, the maturation history of the basin and its basement, the chronology of the Neogene basaltic volcanism and the biomarker pattern of the oil traces resulted in the recognition of the metasedimentary origin of the nitrogen-rich natural gas and in a relative chronology of the mixing of the two gases and the oil.

Key words: CO_2, nitrogen-rich gas, oil traces, magma degassing, metagenesis, Danube Basin

Introduction

Gas fields rich in CO_2 and to a lesser extent in nitrogen, are common in the Pannonian Basin System (PBS) (Koncz 1983; Clayton et al. 1990; Vass et al. 1990; Krupskij 1992; Sarkovic et al. 1992; Sachsenhofer 1994; Vető et al. 1997; Hrušecký 1999; Vető 2005). This is particularly true for the Danube Basin (see Fig. 1). In the southern part of the Danube Basin the CO_2 gas reserves are of one and half of order of magnitude greater than the natural gas reserves. This richness in inorganic gases is likely not a pure coincidence; it seems to be related to the shallow position of the mantle beneath the basin system.

During the development of the PBS the sediments and metasediments of the basement underwent reheating. Due to the high heat flow and the considerable

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thickness of the basin fill this reheating could/can led to the revival of the liberation of gases from kerogen and to the production of CO_2 and nitrogen via carbonate decomposition and release of nitrogen from silicates, respectively (Koncz 1983; Vető 2005; Vető et al. 1997). Obviously these processes depended on the depth, the pre-Neogene thermal history and/or the mineralogical composition of the rocks affected.

A portion of these fluids was/is able to enter the PBS

On the other hand, outgassing of the mantle or mantle-derived magmatic bodies produced/produces significant amount of CO_2, a part of which was/is able to enter the basin system (Cornides et al. 1986). These authors, studying the isotopic composition of the helium present in small amounts in the CO_2-rich gases accumulated in the southern, Hungarian part of the Danube Basin at Répcelak and Mihályi (for their locations see Fig. 1), supported a mantle-related origin for the CO_2.

Several multistacked accumulations, occurring in different parts of the PBS – at Répcelak in the Danube Basin (Mészáros 1979), at Mezőcsokonya in the Dráva Basin, SW Hungary (Kőrössy 1989) and some accumulations in the central part of the Great Plain Basin, eastern Hungary (Hatalyák et al. 2011; Vető et al. 1997; Vető

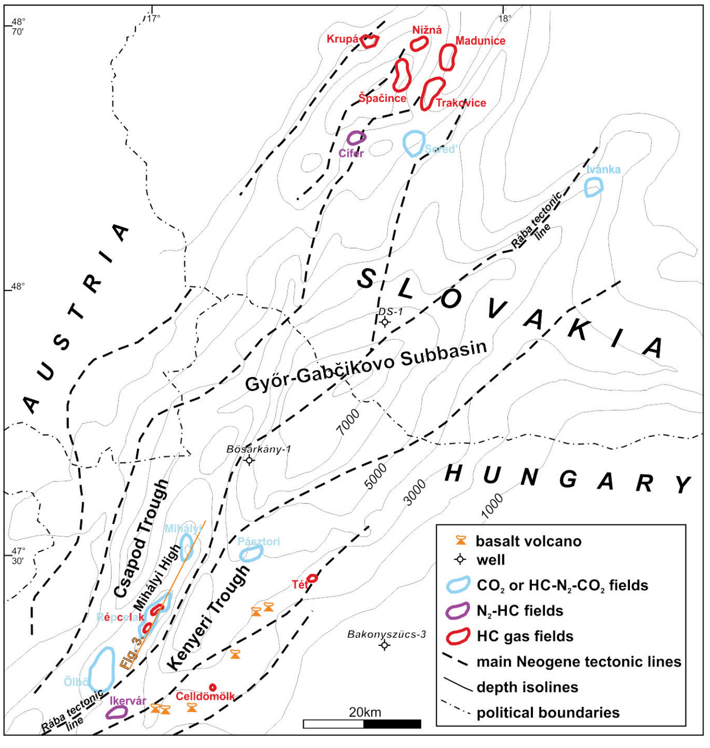

Fig. 1
Pre-Cenozoic basement map of the Danube Basin with known gas fields and the main Neogene tectonic lines (after Maros et al. 2011; Tari and Horváth 2010 and Hrušecký 1999)

2005) – show high variation in gas composition, ranging from "pure" CO_2 (over 95%) to N_2-rich natural gas with minor amount of CO_2 (1%). The large variation in gas composition displayed by these accumulations likely reflects mixing of gases of different origins.

In the following, after a short description of the geologic setting, the compositional variations of the Répcelak and the neighboring Mihályi CO_2 accumulations will be characterized and the previous research carried out on them will be summarized. A short chapter will deal with maturity and possible source rocks of the oil traces observed at Mihályi and Répcelak. Finally the evolution of the two multistacked accumulations will be highlighted with emphasis on sources of the fluids and the relative chronology of their mixing. This work, the geochemical study of the oil shows excepted, is based mostly on public data (Mészáros 1979) and published results (Cornides et al. 1986; Koncz and Etler 1994; Sherwood Lollar et al. 1997).

Geologic setting

The Danube basin is a Neogene pull-apart basin in the Pannonian Basin System with NE–SW orientation. It includes three main depocenters (Győr-Gabcikovo Sub-Basin, Csapod and Kenyeri Troughs) in the southern and four in the northern part surrounded by the Eastern Alps, the Carpathians and the Transdanubian Central Range (Vass et al. 1990; Tari 1994; Mattick et al. 1996; Hrušecký 1999).

Two main units built up the basement, which are separated by the NE to SW-trending Rába tectonic line: the Variscan metamorphic rocks of the Upper Austroalpine Unit in the western part and Permian siliciclastics, Triassic and Upper Cretaceous carbonates of the Transdanubian Central Range Unit in the eastern part of the basin (Haas et al. 2010).

In the southern (Hungarian) part of the basin there is one main structural high, the Mihályi High, in the center of the basin (Fig. 1), which is the hangingwall block of the Rába line belonging to the Upper Austroalpine Unit. It is built up by a Silurian low grade metamorphic sedimentary cycle that starts a sandy schist, continues as a phyllite and ends as a dolomite facies (Balázs 1971, 1975; Árkai et al. 1987; Fülöp 1990).

During the Middle Miocene a marine environment predominated, with mainly shale and marl deposited in the deeper basinal areas. The Mihályi High could have been in an uplifted position, resulting in the formation of reef limestone with limited spread and about 40–60 m thickness, on the Paleozoic rocks.

The Danube Basin was filled up by a prograding delta system during the Late Miocene (Pannonian) from about 10 My ago, in a east-southeast direction. At the border of the Kenyeri Trough and the Győr-Gabcikovo Subbasin an alkaline basalt-trachite-trachiandesite stratovolcano was built up during the Middle

Miocene. This volcano is covered by Pannonian sediments, deposited in the Late Miocene Lake Pannon (Harangi et al. 1995).

The Pannonian is not very well developed on the central Mihályi High because of its uplifted position. The basinal marl (Endrőd Fm.) is entirely absent; the turbiditic (Szolnok Sandstone Fm.) and the slope (Algyő Fm.) sediments are restricted, while the upper delta, delta plain, delta front (Újfalu Fm.) and the fluvial, alluvial plain (Zagyva Fm.) sediments exhibit large thickness within the entire basin (Fig. 2.; Juhász 1991; Uhrin 2011; Magyar et al. 1999, 2007, 2012; Kovać et al. 2011).

During the Pliocene volcanic activity was renewed (Balogh et al. 1982, 1986; Borsy et al. 1986; Harangi et al. 1995; Wijbrans et al. 2007) and small basalt volcanoes formed in the southeastern part of the Danube Basin (see Fig. 1). Basaltic rocks occur in the subsurface as well. They have been identified in wells, on seismic lines and are displayed on the magnetic anomaly map (Balogh et al. 1982; Gulyás et al. 2006).

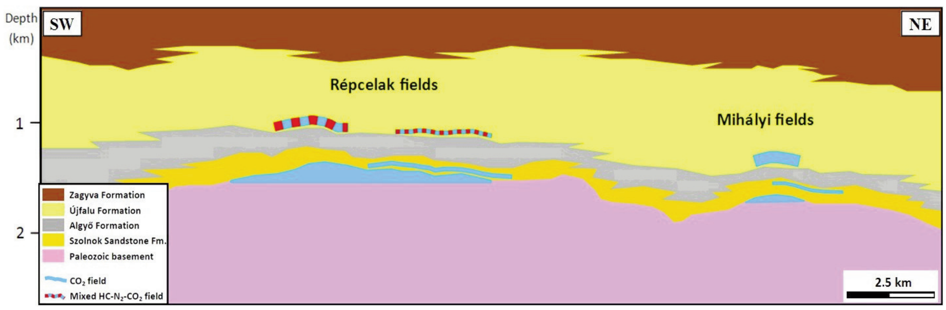

Fig. 2
Schematic cross-section of the Répcelak and Mihályi gas fields

Description of the fields and previous research

The Répcelak and Mihályi accumulations are located on the Mihályi High (Fig. 1), a prominent structural element developed along the Rába tectonic line, which was likely acting as the main migration pathway for the CO_2 fluids. The short description below of the two accumulations is after Mészáros (1970, 1979). At Répcelak the weathered surface part of the basement forms the lowermost reservoir, followed by two marine Middle Miocene sandstone reservoirs; the bulk of the gas is stored in the sandstone and sand layers of the overlying lacustrine strata. The stratigraphy of the individual reservoirs is similar at Mihályi, the only difference being that no Middle Miocene reservoirs were developed there.

The change of gas composition along depth in the two accumulations is displayed in Fig. 3 and the corresponding data are listed in Table 1. At Répcelak the CO_2 content decreases upsection, with some scatter from 95 to 87% in the

Table 1
Average gas composition of the individual reservoirs at Répcelak and Mihályi with reservoir names and GWC positions (after Mészáros et al. 1979)

reservoir	GWC position relative to sea level (m)	CO_2 %	HC %	N_2 %	CH/N_2	$^3He/^4He$* X10^6
Répcelak						
	–810	1.06	71.91	27.03	2.7	
	–840	1.25	71.88	26.87	2.7	
	–850	1.89	72.29	25.82	2.8	
	–855	1.67	73.28	25.05	2.9	
	–875	2.42	71.91	25.67	2.8	
	–940	12.87	65.38	21.75	3	
lac. lM fp II	–1025	68.61	22.18	9.21	2.4	
lac. lM fp I	–1068	88.96	7.53	3.51	2.1	
lac. lM ap VII	–1187.5	87.13	9.55	3.32	2.9	
lac. lM ap VI	–1200	86	7.63	6.37	1.2	
lac. lM ap IV	–1230	88.4	8.43	3.17	2.7	
lac. lM ap III	–1270	90.33	6.64	3.03	2.2	
lac. lM ap II	–1290	94.89	2.96	2.15	1.4	2.6
lac. lM ap I	–1305	95.56	2.74	1.7	1.6	2.9
marine mM	–1280	96.67	1.45	1.88	0.8	
basement	–1310	94.42	4.18	1.4	3	
Mihályi						
Fp X	–982	83.42	12.91	3.67	3.5	
Fp IX	–1006.5	88.3	9.29	2.59	3.6	
Fp VIII	–1092.5	96.33	2.79	0.88	3.2	
Fp VIIb	–1145	94.51	4.32	1.17	3.7	
Fp VIIa	–1128	96.52	2.91	0.57	5.1	
Fp VI	–1158	95.96	3.32	0.72	4.6	
Fp V	–1181	96.36	2.9	0.74	3.9	
Fp IV	–1195	95.94	2.34	1.72	1.4	
Fp III	–1245	96.39	2.79	0.82	3.4	
Fp II	–1285	96.71	2.54	0.75	3.4	
Fp I	–1294	97.04	2.45	0.51	4.8	5.5
Ap IIB	–1332.5	88.2	9.76	2.04	4.8	
Ap IIA	–1348	95.56	3.84	0.6	6.4	
Ap I	–1522.5	94.07	4.7	1.23	3.8	
basement	–1492.5	98	1.62	0.38	4.3	

The helium isotope ratios after Cornides et al., 1986
GWC = gas-water contact, Ap and ap = Lower Pannonian, Fp and fp = Upper Pannonian, mM = Middle Miocene, lac = lacustrine

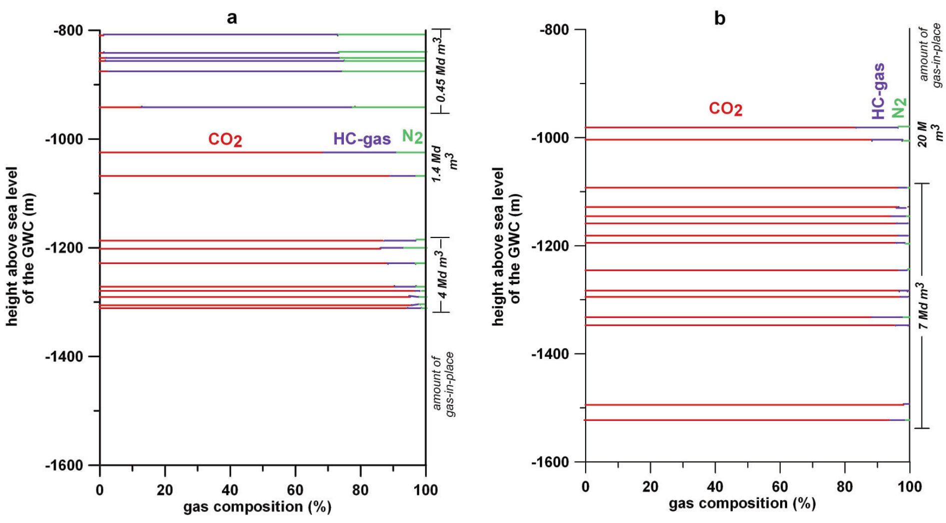

Fig. 3
Change of gas composition with depth at Répcelak (a) and Mihályi (b) (based on data reported by Mészáros 1979)

lower reservoirs (1310–1068 m BSL depth interval). Thereafter it rapidly but progressively drops below 2% in the upper reservoirs (1025–810 m BSL). At Mihályi most of the reservoirs contain 94–98% CO_2, but in the uppermost ones its concentration upsection decreases to 83%. The HC-gas to N_2 ratio of the CO_2-dominated reservoirs (over 80%) varies between 0.8 to 3 at Répcelak and between 1.4 to 6.4 at Mihályi, while it is relatively constant in the upper HC-dominated reservoirs at Répcelak, where it ranges between 2.7 to 3 (Table 1).

The bulk of the HC-gas consists of methane. Since most of the gas analyses were carried out in the sixties/early seventies of the last century, when the gas chromatography was in its infancy, the calculation of the wetness of the HC-gas would be meaningless (oral comm. of I. Koncz).

Mészáros (1970, 1979) described that before completion of the wells M 1 at Mihályi and M 5/b at Répcelak (for their locations see Fig. 4), traces of oil (a black one at Répcelak) accompanied the CO_2 flux from the lower sandstone reservoirs. The open tracts were between 1603.6–1512 and 1466–1452 m in the wells M1 and M5/b, respectively. Oil traces were found in some other wells as well. The locations of the wells from which oil traces have been studied for biomarkers are shown in Fig. 4.

The Hungarian National Oil and Gas Co began producing CO_2 from the two fields in the fifties. The modest amount of burnable natural gas pooled in the uppermost reservoirs at Répcelak (Fig. 3a) has already been depleted.

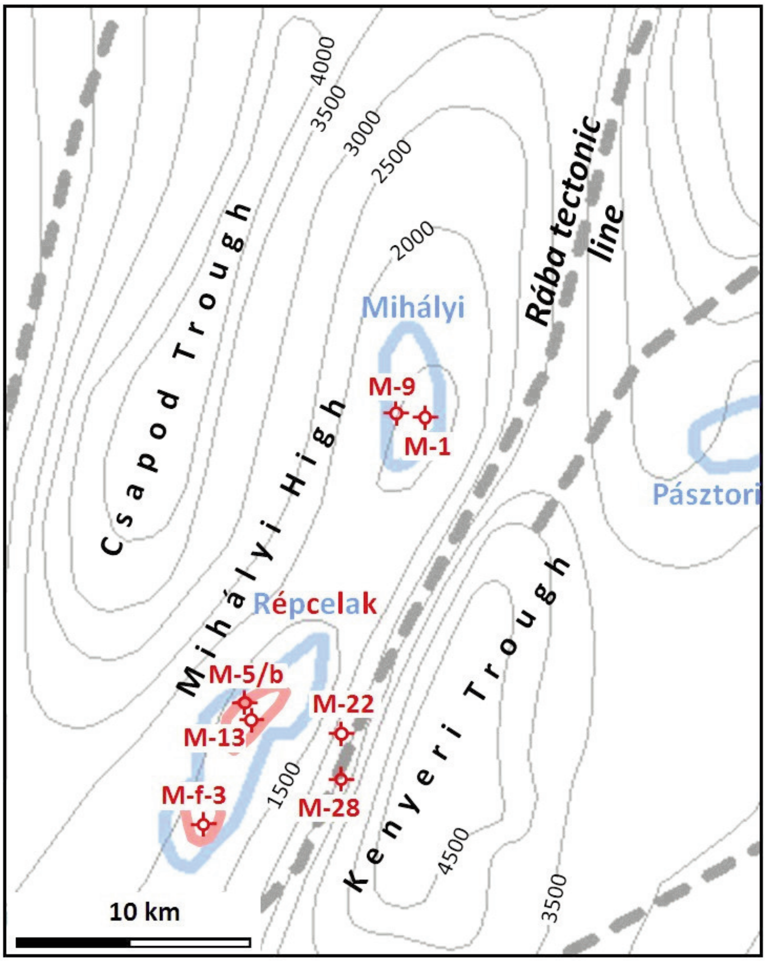

Fig. 4
Location of the wells drilled on the Mihályi High, discussed in the text

Based on the high values of $^3He/^4He$ ratio, ranging between 2.6 to 5.5×10^{-6}, Cornides et al. (1986) assumed that an important part of the CO_2 at Répcelak and Mihályi is of mantle origin. It is worth mentioning that Sherwood Lollar et al. (1997) report 3.2 for helium R/Ra from a non-named CO_2 field in the Hungarian part of the Danube Basin (sample LHP in their Table 1). LHP is the abbreviation of Little Hungarian Plain, the geographic equivalent of the southern, Hungarian part of the Danube Basin.

Koncz and Etler (1994) discussed the origins of the CO_2 and the accompanying methane pooled in Neogene reservoirs and in the top part of the basement in a non-named multistacked accumulation, developed on the Mihályi High. They pointed out that the range of $\delta^{13}C$ of the CO_2 (–9 to –6‰) supports both carbonate decomposition and volcanic origin. Koncz and Etler (1994) report –45.2 and –36.2‰ $\delta^{13}C$ for the methane contained in two CO_2-rich (over 90%) reservoirs and assume that these values match the maturity of the Neogene source rocks of the Danube basin. They argued that the heptane and iso-heptane values (sensu Thompson 1979) of the gas condensates, co-produced with the CO_2-rich gases, correspond to an early to intermediate stage of oil generation.

Geochemical characterization of the oil traces

Saturate fractions of condensate and oil traces (in the following they will be named together as oil trace), obtained from four wells drilled on the Mihályi High and from well M22 drilled E of the Répcelak accumulation (for locations see Fig. 4), have been studied using gas chromatography. The oils, the M22 one excepted, have been co-produced with gas. The M22 oil accompanied the drilling mud during penetration of the basinal marls of the Pannonian strata.

The obtained isoprenoid and light to heavy *n*-alkane ratios are listed on Table 2. On the basis of the pristane/phytane ratio the studied oil traces form two clearly separate groups: in Group A oil traces, obtained from the wells M1 and M22 this ratio ranges between 0.8 to 0.9, while it varies between 1.64 to 2.14 in the Group B oil traces, obtained from wells M9, M13 and Mf3.

Table 2
Biomarker indices of the oil shows. Locations of the wells are shown in Fig. 4

well	reservoir	depth interval (m)	nor/pr	pr/ph	pr/nC17	ph/nC18	nC15-/nC15+
Mihályi							
M9	U. Pann. I	1414–1419	0.71	1.66	0.74	0.64	3.65
M9	L. Pann. IIb	1455–1461	0.62	1.85	0.64	0.34	1.29
M1	n. id.	1510–1515	0.92	0.87	0.57	0.81	0.31
M1	bas.+ mM.	1553–1602*	0.93	0.90	1.01	1.01	0.52
Répcelak							
Mf3	burnable IIIe	1000–1003	0.77	2.14	1.39	0.99	6.93
M13	U. Pann. II	1149–1153	0.75	1.64	0.91	1.02	2.83
M22**		2368–2372	0.70	0.80	1.26	1.54	0.83

* production from two perfored intervals (1553–1556 m and 1600–1602 m) together
** drilled E of the Répcelak accumulation, nor = norpristane, pr = pristane, ph = phytane, nC17 = n-heptadecane, nC18= n-octadecane, nC15-= the sum of alkanes upto n-pentadecane, nC15+ = the sum of alkanes from n-pentadecane, bas = basement, mM = Middle Miocene, L. Pann. = Lower Pannonian, U. Pann. = Upper Pannonian, n. id. = non identified

It is worth mentioning that these ratios (o/h: 0.37, m/h: 0.22, nh/h: 0.44., h/st: 0.34) do not differ from those of the oils studied from the giant Algyő field (Great Plain Basin, SE Hungary), reported by Sajgó (1984 and 2000).

The M22 oil trace, found beyond the Répcelak accumulation and in a much deeper position, is likely on a migration pathway.

Discussion

The gradual change in gas composition observed at Répcelak suggests that this accumulation was formed by in-reservoir mixing of two end-members, a mantle-derived CO_2 fluid and a HC-gas – N_2 fluid of likely metasedimentary origin.

It is very likely that the CO_2 fluid contained a minor amount of N_2. On the other hand, the minor amount of HC-gas in the CO_2-dominated reservoirs is considered here as genetically linked to the oil traces, in other words it is oil-associated gas. The relatively light carbon isotopic composition of the methane reported by Koncz and Etler (1994) from CO_2-rich gases of a non-named gas field located on the Mihályi High agrees well with presence of oil-associated gas.

Now we must return to the clear difference in HC-gas/N_2 ratio between the CO_2-rich gases and the nitrogen rich HC-gases filling the uppermost reservoirs at Répcelak (see section Description of the fields and previous research). The different origins of the HC-gas and the N_2 present in the CO_2-dominated reservoirs discussed above explain the great scatter of their ratio. On the other hand, the relative constancy of their ratio in the uppermost reservoirs at Répcelak agrees well with their common metasedimentary origin.

The carbon isotopic composition of the methane in the uppermost, HC-gas dominated reservoirs at Répcelak is unknown, but the very low HC-gas/N_2 ratio (2.7–3) characterizing them clearly contradicts an early mature/mature nature of the corresponding HC-gas. Hence HC gases present in the CO_2-rich and the N_2-HC-gas dominated reservoirs at Répcelak are of quite different origins; oil-associated gas in the first and metasedimentary gas in the second case.

In the following, sources will be tentatively proposed for the two end-members as well as for the oil traces and the oil-associated gases.

Source of the CO_2 fluid

We agree with Cornides et al. (1986) that an important part of the CO_2 stored in the two accumulations is of mantle origin. This CO_2 (and that studied for helium isotope composition by Sherwood Lollar et al. 1997) was produced by degassing of melts ascending from the shallow asthenospheric mantle beneath the basin. However, the corresponding basaltic intrusions have not been identified yet. It is possible that the Rába Line, considered as the main migration pathway, had direct connection with basaltic dykes and vents belonging to the deeper-lying intrusions.

It is very probable that the remnants of the basalt volcanoes, occurring in the 10–20 km vicinity of the Mihályi High, are the surface/shallow subsurface expression of the above-mentioned ascending melts. According to K/Ar and $^{40}Ar/^{39}Ar$ geochronology these volcanoes formed between 5.5 to 4.2 My (Balogh et al. 1982; Borsy et al. 1986; Wijbrans et al. 2007). This makes it likely that the accumulation of CO_2 occurred at about 5.5 to 4.2 My.

Source(s) of the HC-gas – N_2 fluid

Laboratory studies and geologic considerations (Littke et al. 1995; Krooss et al. 2005; Boudou et al. 2008) led to the conclusion that significant portions of the nitrogen fixed in the kerogen and in clay minerals in form of K-substituting ammonium, are liberated during very low-grade metamorphism of shaly sediments and coal. On the other hand, kerogen reached the remaining, relatively small part of its HC-gas potential, in roughly the same metamorphic phase. The N_2-rich gas fields, found in Rotliegendes reservoirs of North Germany, are thought to be formed by liberation of nitrogen and HC-gases in already very mature Carboniferous shale and coal or in even older sediments, and are trapped separately from the main mass of thermogenic HC-gases, formed during catagenesis and at the very beginning of metagenesis (Littke et al. 1995; Gerling et al. 1997). According to Gerling et al. (1997) the relative importance of the organically and inorganically fixed sedimentary nitrogen as sources of N_2 cannot be judged. The results of the pyrolysis experiments of Krooss et al. (2005), carried out on shale and coal of very different maturity, are of particular importance for our work. These authors have found that in a part of the studied shale the bulk of the organically-bound nitrogen was already liberated as N_2 at a maturity level corresponding to 3–4% vitrinite Ro.

Vitrinite Ro trends reported from the central part of the Danube Basin, both in Hungary and Slovakia, reveal a surprisingly rapid downward increase of maturity in the Middle Miocene strata (Fig. 5). The downward extrapolation of these trends makes it probable that in the deepest part of the Middle Miocene the vitrinite Ro reaches 3–4%. Hence, in light of the findings of Krooss et al. (2005) it cannot be a priori excluded that (i) nitrogen gas formed intensely in the deepest part of the Danube Basin and (ii) the modest volume of N_2-rich gas pooled in the uppermost reservoirs of the Répcelak accumulation (045 Md m^3, see Fig. 3) was sourced by the corresponding metasediments.

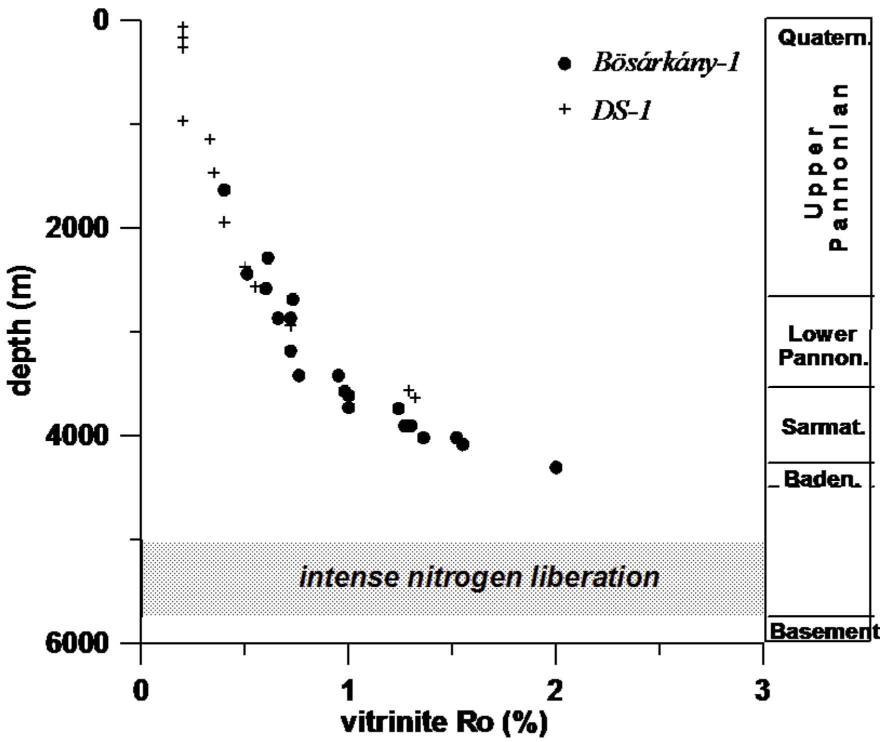

Fig. 5
Increase of vitrinite Ro with depth in the central part of the Danube Basin
Ro data of well Bősárkány-1 after Lenkey et al. (2002) and well DS-1 after Franko et al. (1992) The stratigraphic column of well Bősárkány-1 is shown on the right. Dashed line is the bottom of well Bősárkány-1. For locations of the two wells see Fig. 1

On the other hand, it cannot be excluded that the grade of metamorphism of the Silurian strata lying beneath the depocenters increased during the build-up of the PBS. A second step of metamorphosis could also have taken place locally in the Silurian metasediments because of their heating by the mantle-derived intrusive bodies, the supposed sources of the CO_2 accumulations of Répcelak and Mihályi. Hence the Silurian metasediments, known to contain high amounts of organic matter in different parts of the basement of the PBS (Badics and Vető 2012), also would have been able to generate HC gases and nitrogen.

Vető (1988) reports a gas show containing 37% N_2 from the Lower Triassic of the well Bakonyszűcs-3, drilled at the eastern margin of the basin (its location see in Fig. 1). This gas show, found at 930 m depth, beneath Triassic sediments of about 900 m thickness, supports the basement origin of the N_2-rich gases.

Source rocks of the oil traces

On the basis of the nor/pr, pr/nC17, ph/nC18 and nC15⁻/nC15⁺ values (Table 2), the samples belong to the least-mature and low-mature oil groups of Sajgó (2000).

The pr/ph ratio is one of the indicators used most frequently for assessing the oxygen content of the depositional environment. Roughly speaking, its values of below and above 1 indicate anoxic and oxic depositional settings, if all other conditions are the same (Didyk et al. 1978). Both the increase in contribution of terrestrial land plant matter to the kerogen and the advance of maturation result in increase of the pr/ph ratio. On the other hand, hypersaline conditions favor its decrease.

The sharp difference in pr/ph ratio between the two groups of oils suggests actual difference in oxygen content between the corresponding depositional environments. This assumption is supported by the fact that the oil traces of the two groups do not differ substantially in maturity. Hence the Group A oil traces have been generated from an anoxic (hypersaline?) source rock, while the source rock of the Group B oil traces was deposited in oxic conditions.

Since the oil traces of the two groups preserved their differences during migration, one must conclude that they used different migration pathways. These considerations suggest that the two source rocks are developed in different parts of the basin and/or they belong to different stratigraphic horizons.

The Group A oil trace of the well M22, drilled east of the Répcelak accumulation (Fig. 4), on the western flank of the Kenyeri Trough, is a strong argument to suppose the presence of an anoxic source rock in this sub-basin. Mattick et al. (1996) report that the Middle Miocene strata penetrated by the well M28, drilled only some km distance from well M22, are characterized by relatively high TOC content; six of the nine samples studied contain more than 1% TOC. It seems likely that the anoxic source rock of the Group A oils is developed in the Middle Miocene strata of the Kenyeri Trough. The few Rock-Eval data reported by Mattick et al. (1996) support the presence of oil source rock(s) in the southern Danube Basin.

History of filling

It is obvious that the trapping of the three fluids did not take place at the same time. The question arises: what was the succession of their arrival and trapping?

We have no decisive arguments to establish a relative chronology for the build-up of the two gas accumulations, but we can use strong indirect arguments for proposing one.

It seems reasonable to suppose that the lower reservoirs were filled earlier than the upper ones. In the cases of some important multistacked accumulations of the Vienna Basin (Ladwein 1988) and the giant Algyő oil and gas accumulation in the Great Hungarian Plain (Sajgó 1984) convincing geochemical reasons led these authors to conclude that the lower reservoirs were filled earlier than the upper ones.

By analogy with these well-documented case histories from the PBS, the trapping of the HC-gas–N_2 fluid, filling the uppermost reservoirs at Répcelak is supposed to postdate that of the CO_2 fluid. Additionally, if the HC-gas–N_2 fluid was generated in some OM-rich Silurian metasediments, re-heated by the basaltic intrusions, it had to reach the traps shortly after the CO_2.

On the other hand, the Middle Miocene strata, including the source rocks, entered the oil window in the late Miocene (Csizmeg et al. 2012), at about 8–7 My ago. Hence the generation and migration of the low maturity oils corresponding to the oil traces obviously preceded the liberation of the CO_2 fluid from the 5 to 4.2 My old Pliocene basaltic intrusive bodies. Hence it seems to be logical to suppose that the trapping of these oils took place earlier than that of the CO_2.

It is not known up to what degree the trap volumes available were filled with oil before the trapping of the CO_2 fluid in the early Pliocene. The absence of oil fields, despite the availability of mature source rocks and important traps, is an intriguing question for the approximately 80-year-old petroleum exploration of the Danube Basin. Massive replacement of the oil trapped in the Répcelak and Mihályi structures by the later arriving CO_2 fluid would be at least partly a reasonable answer for this. Such a massive replacement of the oil would not be a surprise; in the oil industry the use of CO_2 for enhancing oil recovery is a common practice.

This scenario would also explain the presence of methane and early-moderately mature light fluid hydrocarbons in the CO_2-rich gases in a non-named accumulation of the Mihályi High, reported by Koncz and Etler (1994). According to our interpretation, they would represent oil-associated gases and oil components, added into the mixing/replacing CO_2.

It is worth mentioning that traces of crude oil are also reported from the Schorngraben (S. Permian Basin, Germany) and Montmiral (SE Basin, France) CO_2 deposits (Pearce et al. 2004).

It is quite possible that the accumulation of CO_2 was a relatively short process at Répcelak and Mihályi. According to Weinlich et al. (1999) the Bublák mofetta, the most intense of the mofettas active in the western Eger rift (Czech Republic), sourced by a cooling intrusive body present in the subcontinental mantle, is delivering CO_2 into the atmosphere at a rate of 28 m^3/h. Supposing such a rate of trapping, about 20 and 25 ky would have been necessary for the accumulation of the approximately 5.5 and 7 Md m^3 CO_2 gas at Répcelak and Mihályi (Fig. 3), respectively.

It is possible that at Répcelak the CO_2 charge was not sufficient to fill entirely the middle reservoirs and was exhausted without reaching the uppermost ones. But one cannot exclude that at the time of arrival of the CO_2 fluid the trapping capacity of the upper reservoirs were smaller than at the time of arrival of the HC-gas–N_2 fluid because of the less advanced sealing.

It cannot be excluded that the scenario outlined here works also for other multistacked gas accumulations enriched in both CO_2 and N_2.

Conclusions

The vertical change of the gas composition in the Répcelak accumulation reflects in-reservoir mixing of a mantle-related CO_2 fluid and a metasedimentary HC-gas–N_2 fluid.

The HC-gas–N_2 fluid was generated either in the deepest part of the basin or in re-heated Silurian metasediments, rich in organic matter.

Oil traces present in both accumulations are linked to two source rocks of likely Middle Miocene age. One of them was deposited in anoxic, the other in oxic conditions. An anoxic source rock is present east of Répcelak.

Oil first entered the reservoirs of the two accumulations during the Late Miocene. It was followed by the CO_2 fluid during the Pliocene. The CO_2 fluid filled the bulk of the trap volumes of both accumulations, mixing with the previously arrived oil and likely replacing an unknown part of it. Finally the HC-gas-N_2 fluid arrived, filling mostly the uppermost reservoirs at Répcelak.

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References

Árkai, P., Z. Horváth, M. Tóth 1987: Regional metamorphism of the East Alpine type Paleozoic basement, Little Plain, W-Hungary: mineral assemblages, illite crystallinity – b_0 and coal rank data. – Acta Geologica Hungarica, 30, pp. 153–175.

Badics, B., I.Vető 2012: Source rocks and petroleum systems in the Hungarian part of the Pannonian Basin: The potential for shale gas and shale oil plays. – Marine and Petroleum Geology, 31, pp. 53–69.

Balázs, E. 1971: A Kisalföld medencealjzatának ópaleozóos kőzetei (The basement Paleozoic rocks of the Little Plain). – MÁFI Évi Jelentése 1969-ről, pp. 659–673.

Balázs, E. 1975: A kisalföldi medence paleozóos képződményei (The Paleozoic Formations of the Little Plain basin). – Földtani Kutatás, 18, pp. 17–25.

Balogh, K., Á. Jámbor, Z. Partényi, L. Ravaszné Baranyai, G. Solti 1982: A dunántúli bazaltok K/Ar radiometrikus kora (K/Ar radiogenic age of Transdanubian basalts). – MÁFI Évi Jelentése 1980-ról, pp. 243–259. (In Hungarian with English summary.)

Balogh, K., E. Árva-Sós, Z. Pécskay, L. Ravasz-Baranyai 1986: K/Ar dating of post-Sarmatian alkali basaltic rocks in Hungary. – Acta Mineralogica et Petrographica, Szeged, 28, pp. 75–94.
Borsy, Z., K. Balogh, M. Kozák, Z. Pécskay 1986: Újabb adatok a Tapolcai-medence fejlődéstörténetéhez (Contributions to the evolution of the Tapolca-basin, Hungary). – Acta Geographica Debrecina, 23, pp. 79–104. (In Hungarian with English abstract.)
Boudou, J.P., A. Schimmelmann, M. Ader, M. Mastalerz, M. Sebilo, L. Gengembre 2008: Organic nitrogen chemistry during low-grade metamorphism. – Geochimica et Cosmochimica Acta, 72, pp. 1199–1221.
Clayton, J.L., C.W. Spencer, I. Koncz, Á. Szalay 1990: Origin and migration of hydrocarbon gases and carbon dioxide, Békés Basin, southeastern Hungary. – Organic Geochemistry, 15, pp. 233–247.
Cornides, I., N. Takaoka, K. Nagao, S. Matsuo 1986: Contribution of mantle-derived gases to subsurface gases in a tectonically quiescent area, the Carpathian Basin, Hungary revealed by noble gas measurements. – Geochemical Journal, 20, pp. 119–125.
Csizmeg, J., B. Márton, Á. Szalay, I. Vető, M. Peffer, G. Varga, Gy. Pogácsás 2012: Neogene hydrocarbon potential and inert gas risk in the Hungarian part of the Danube basin – 29th IAS Meeting of Sedimentology, Sedimentology in the Heart of the Alps, Schladming, Austria, p. 343
Didyk, B.M., B.R.T. Simoneit, S.C. Brassel, G. Eglington 1978: Organic geochemical indicators of paleoenvironmental conditions of sedimentation. – Nature, 272, pp. 216–222.
Franko, O., D. Vass, J. Francu, M. Král, M. Pereszlényi, J. Milicka 1992: First occurrence of oil in the Slovak part of the Danube basin. – Mineralia slovaca, 24, pp. 453–460. (In Slovakian.)
Fülöp, J. 1990: Magyarország geológiája, Paleozoikum I. (Geology of Hungary, Paleozoic I.) – Hungarian Geological Institute, pp. 74–97.
Gerling, P., E. Idiz, G. Everlien, E. Sohns 1997: New aspects on the origin of nitrogen in natural gas in Northern Germany. – Geologisches Jahrbuch, Reihe D, 103, pp. 65–84.
Gulyás, Á. (Ed.), J. Kiss 2006: Magnetic dZ anomaly map of Hungary. – Eötvös Loránd Geophysical Institute of Hungary
Haas, J., T. Budai, L. Csontos, L. Fodor, Gy. Konrád 2010: Pre-Cenozoic geological map of Hungary, 1:500 000 – Hungarian Geological Institute.
Harangi, Sz., O. Vaselli, S. Tonarini, Cs. Szabó, R. Harangi, N. Coradossi 1995: Petrogenesis of Neogene extension-related alkaline volcanic rocks of the Little Hungarian Plain Volcanic Field (Western Hungary). – Acta Vulcanologica, 7, pp. 173–187.
Hatalyák, P., P. Zahuczki, G. Wittmann, I. Berkes, G. Németh 2011: Discovery of the Nagykőrös-South gas field (Hungary) and its production possibilities. – MOL Szakmai-Tudományos Közlemények, 2011, pp. 74–80.
Hrušecký, I. 1999: Central Part of the Danube Basin in Slovakia: Geophysical and Geological Model in Regard to Hydrocarbon Prospection. – EGRSE Special Issue VI.1., pp. 2–55.
Juhász, Gy. 1991: Lithostratigraphical and sedimentological framework of the Pannonian (s.l.) sedimentary sequence in the Hungarian Plain (Alföld), Eastern Hungary. – Acta Geologica Hungarica, 34, pp. 53–72.
Koncz, I. 1983: The stable carbon isotope composition of the hydrocarbon and carbon dioxide components of Hungarian natural gases. – Acta Mineralogica-Petrographica, Szeged. 26, pp. 33–49.
Koncz, I., O. Etler 1994: Origin of oil and gas occurrences in the Pliocene sediments of the Pannonian Basin. – Organic Geochemistry, 21, pp. 1069–1080.
Kőrössy, L. 1989: A dráva-medencei kőolaj- és földgázkutatás földtani eredménye (Hydrocarbon geology of the Drava Basin in Hungary). – Általános Földtani Szemle, 24, pp. 3–122. (In Hungarian with English abstract.)
Kovać, M., R. Synak, K. Fordinál, P. Joniak, Cs. Tóth, R. Vojtko, A. Nagy, I. Baráth, J. Maglay, J. Minár 2011: Late Miocene and Pliocene history of the Danube Basin: inferred from development of depositional systems and timing of sedimentary facies changes. – Geologica Carpathica, 62, pp. 519–534.

Krooss, B., L. Friberg, Y. Gensterblum, J. Hollenstein, D. Prinz, R. Littke 2005: Investigation of the pyrolytic liberation of molecular nitrogen from Palaeozoic sedimentary rocks. – International Journal of Earth Sciences, 94, pp. 1023–1038.
Krupskij, Y.Z. 1992: Zakarpatsskij progib – nova gazonosna oblast' Ukraini. – Geologicheski Zhurnal, 1992, pp. 70–75. (In Ukrainian.)
Ladwein, H.W. 1988: Organic geochemistry of the Vienna Basin: model for hydrocarbon generation in overthrust belts. – AAPG Bull., 72, pp. 586–599.
Lenkey, L., P. Dövényi, F. Horváth, S.A.P.L. Cloething 2002: Geothermics of the Pannonian basin and its bearing on the neotectonics. – EGU Stephan Mueller Special Publication Series, 3, pp. 29–40.
Littke, R., B. Krooss, E. Idiz, J. Frielingsdorf 1995: Molecular nitrogen in natural gas accumulations: generation from sedimentary organic matter at high temperatures. – AAPG Bulletin, 79, pp. 410–430.
Magyar, I., D.H. Geary, P. Müller 1999: Paleogeographic evolution of the Late Miocene Lake Pannon in Central Europe. – Paleogeography, Paleoclimatology, Paleoecology, 147, pp. 151–167.
Magyar, I., M. Lantos, K. Ujszászi, L. Kordos 2007: Magnetostratigraphic, seismic and biostratigraphic correlations of the Upper Miocene sediments in the northwestern Pannonian Basin System. – Geologica Carpathica, 58, pp. 277–290.
Magyar, I., D. Radivojevič, O. Sztanó, R. Synak, K. Ujszászi, M. Pócsik 2012: Progradation of the paleo-Danube shelf margin across the Pannonian Basin during the Late Miocene and Early Pliocene. – Global and Planetary Change, 103, pp. 168–173.
Maros, Gy., V. Maigut, R. Barczikayné Szeiler, L. Fodor, L. Gyalog, Zs. Kercsmár, Á. Magyari, L. Orosz, K. Palotás, I. Selmeczi, A. Uhrin, Zs. Vikor, B. Atzenhofer, R. Berka, M. Bottig, A. Brüstle, C. Hörfarter, G. Schubert, J. Weilbold, I. Baráth, K. Fordinál, B. Kronome, J. Maglay, A. Nagy, B. Jelen, H. Rifelj, I. Rižnar, M. Trajanova 2011: Pre-Cenozoic model horizon grid for Supra-Regional Area. – Transenergy, Geological and Geophysical Institute of Hungary, State Geological Institute of Dionyz Stur, Geological Survey of Austria, Geological Survey of Slovenia.
Mattick, R.E., P.G. Teleki, R.L. Phillips, J.L. Clayton, Gy. Dávid, Gy. Pogácsás, B. Bardócz, E. Simon 1996: Structure, Stratigraphy, and Petroleum Geology of the Little Plain Basin, Northwestern Hungary. – AAPG Bulletin, 80, pp. 1780–1800.
Mészáros, L. 1970: Report on exploration of the Mihályi occurrence. – MBFH Open File Report No T 8721. (In Hungarian.)
Mészáros, L. 1979: Report on exploration of the Mihályi-Répcelak occurrences – MBFH Open File Report No T 18580. (In Hungarian.)
Pearce J., I. Czernichowski-Lauriol, S. Lombardi, S. Brune, A. Nádor, J. Baker, Pauwels, G. Hatziyannis, S. Beaubien, E. Faber 2004: A review of natural CO_2 accumulations in Europe as analogues for geological sequestration. A review of natural CO_2 accumulations in Europe as analogues for geological sequestration. – Geological Society, London, Special Publications, 233, pp. 29–41.
Sachsenhofer, R.F. 1994: Petroleum generation and migration in the Styrian Basin (Pannonian Basin system, Austria): an integrated geochemical and numerical modelling study. – Marine and Petroleum Geology, 11, pp. 684–701.
Sajgó, Cs. 1984: Organic geochemistry of crude oils from south-east Hungary. – In: Schenck, P.A. et al. (Eds): Advances in Organic Geochemistry, Pergamon Press, pp. 569–578.
Sajgó, Cs. 2000: Assessment of generation temperatures of crude oils. – Organic Geochemistry, 31, pp. 1301–1323.
Šarković, M., S. Stanković S. Milosavljević, G. Karović 1992: Petroleum Geology of the Southeast Pannonian Basin – Results, Problems, and Future Exploration Strategy. – In: Spencer, A.M. (Ed.): Generation, Accumulation and Production of Europe's Hydrocarbons II. Spec. Publ. EAPG, No 2, pp. 200–209.
Sherwood Lollar, B., C.J. Ballentine, R.K. O'Nions 1997: The fate of mantle-derived carbon in a continental sedimentary basin: Integration of C/He relationships and stable isotope signatures. – Geochimica et Cosmochimica Acta, 61, pp. 2295–2307.

Tari, G. 1994: Alpine tectonics of the Pannonian Basin. – PhD dissertation, Rice University, Houston, Texas, 501 p.

Tari, G., F. Horváth 2010: A Dunántúli-középhegység helyzete és eoalpi fejlődéstörténete a Keleti-Alpok takarós rendszerében: egy másfél évtizedes tektonikai modell időszerűsége (Eo-Alpine evolution of the Transdanubian Range in the nappe system of the Eastern Alps: revival of a 15 years old tectonic model) – Bull. of the Hung. Geol. Soc., 140, pp. 483–510.

Thompson, K.F.M. 1979: Light hydrocarbons in subsurface sediments. – Geochimica et Cosmochimica Acta, 43, pp. 657–672.

Uhrin, A. 2011: Lake-level changes and their controlling factors in some sub-basins of the Late Miocene Lake Pannon. – PhD dissertation, Eötvös Loránd University, Budapest, Hungary, 127 p.

Vass, D., M. Pereszlényi, M. Kovac, M. Král 1990: Outline of Danube basin geology. – Földtani Közlöny, 120, pp. 193–214.

Vető, I. 1988: Organic matter of Lower Triassic formations in the Transdanubian Mid-Mountains. Hydrocarbons and migration. – Annals of the Hungarian Geological Institute, 65/2, pp. 323–331. (In Hungarian with English abstract.)

Vető, I. 2005: Indigenous and imported gases in the Pannonian basin system. – Abstracts of the 22nd International Meeting on Organic Geochemistry Seville – Spain. September 12–16, p. 496.

Vető, I., I. Gajdos, K.D. Lőrincz, S. Pap 1997: Origin of nitrogen-rich gases in Eastern Hungary, Pannonian Basin. – 18th Int. Meeting on Org. Geochem., Maastricht, Abstracts, pp. 229–230.

Weinlich, F.H., K. Bräuer, H. Kämpf, G. Strauch, J. Tesar, S.M. Weise 1999: An active subcontinental mantle volatile system in the western Eger rift, Central Europe: Gas flux, isotopic (He, C, and N) and compositional fingerprints. – Geochimica et Cosmochimica Acta, 63, pp. 3653–3671.

Wijbrans, J., K. Németh, U. Martin, K. Balogh 2007: $^{40}Ar/^{39}Ar$ geochronology of Neogene phreatomagmatic volcanism in the western Pannonian Basin, Hungary. – Journal of Volcanology and Geothermal Research, 164, pp. 193–204