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Investigation of Miocene Methane Hydrate Generation Potential in the Transylvanian Basin, Romania

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ABSTRACT

In geology we often revise theoretical models; upon finding new evidence, such as the discovery of methane hydrates, the initial model will be challenged immediately. Hereby the authors put forward two postulates: 1) There is a third, previously unexplored source of methane in the Transylvanian Basin, based on a new theoretical approach on methane hydrate formation; 2) The dissociation of methane hydrates creates a strong chlorinity anomaly. Based on a recent analogy with the Black Sea basin model, we apply our statements to the Transylvanian Basin. Using direct and indirect indicators and the published system tract analysis, we claim that there are substantial grounds to believe that this model of methane hydrate formation applies to the Miocene Transylvanian Basin. Due to the increase of the geothermal gradient as a result of the volcanic activity from the Eastern Carpathians, the clathrates dissociated into methane and freshwater. This process of dilution resulted in a chlorinity anomaly that can be spotted in the formation waters of several gas fields from the Transylvanian Basin.

1. Introduction

The Transylvanian Basin (TB, Romania) is situated in the eastern part of the Carpathian Basin (Figure 1) between the Eastern Carpathian and Apuseni Mountains, and between the Southern Carpathian and Maramureş Mountains. As an important hydrocarbon province, it has been the target of constant exploration in the last century.

It was the potential of discovering potassium salt (sylvine) that attracted the geologists to this region^[1] - and indeed, they found dry gas.

The complicated geological build and evolution of the Transylvanian Basin is well documented in several recent publications^[2-8].

The Transylvanian Miocene sedimentary basin, with its

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thick lithosphere^[7], was part of the Central Paratethys and is regarded as a cold piggyback basin. This contrasts with the Pannonian Basin, with its thin lithosphere and elevated thermic gradient.

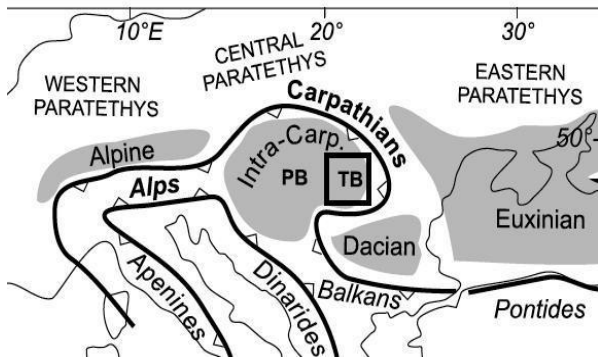


Figure 1. Location of the Transylvanian Basin - Romania

The Transylvanian Basin hosts important gas reserves in the post-salt deposits with characteristic salt tectonics, studied by several researchers^[2-5,7-11]. The origin of the pure methane reserves is a matter of standing debate, since the sheer amount of methane and the volume of methane production suggests the presence of a secondary gas source, in addition to the classical biogenic source^[17].

The industrial gas reserves were discovered by the Kissármás-2 new-field wildcat, although the drilling was initially designed for sylvine exploration^[1]. This was the starting point of the exploration for the most important biogenic gas province (99% methane) from the Carpathian Basin, which still continues to produce gas. As a rough estimate: 30-35 TCF gas was produced from 90 fields in the last 100 years^[18]. Being the focus of research efforts, the basin has undergone intensive exploration in the last few decades in order to understand the hydrocarbon system. Various interpretations and analyses were run and published by several research groups, confirming that the Transylvanian Basin is a mature basin. One of the main results came from Krézsek Cs., Filipescu S., Silye L., Matento L., Coltoi O. etc. and co-authors^[2-5,7-11].

The post salt deposits contain the traps, mostly 4-way closures related to the salt-cored folds^[19]. The reservoirs are composed of Late Badenian to Late Sarmatian siliciclastic deposits with good porosity (~20%) and permeability (<1 D) sealed by argillaceous intercalation.

The biogenic gases are primarily considered to originate in low quality transgressive deep marine shales with TOC ~1%, in which the organic material is thermally immature^[15,20].

Deep Hypersaline Anoxic Brines (DHABs) are considered to be a second source of Transylvanian biogenic methane, which could be formed in the Middle Miocene,

representing analogies for the present Mediterranean DHAB^[6,17]. These brines can have ~70 mg/L biogenic methane^[21].

In the present article the authors outline a possible third methane source for the Transylvanian gas reserves. We consider that the methane hydrate research of the current Black Sea basin^[12,13] provides a perfect analogy with methane hydrate generation during the Miocene in the Transylvanian Basin.

2. Methods and Materials

Examining some of the special literature records with a critical eye, we describe a theoretical approach to the existence of a potential third source of methane in the Transylvanian Basin. This idea is supported by the formation waters of the Badenian gas reservoirs.

2.1 The Origin of Methane in the Transylvanian Basin

The Transylvanian Basin has a thick lithosphere, and it is considered a so-called cold sedimentary basin with huge salt deposits. The filling deposits of the post-salt basin solely trapped biogenic dry gas^[4], but the volume of gas generated strongly exceeds the expected average. As a recent analogy, the Black Sea basin contains an elevated amount of dissolved methane: 96 Tg. This is 2.4-6 times larger than the global annual geological methane contribution to the atmosphere^[14]. In the last more than ten years, the increasing number of gas flux measurements puts the methane emissions between 30-76 Tg/y^[22], which is roughly the same range as the dissolved gas mentioned above.

These make the (formerly sedimentary) Transylvanian Basin and the Black Sea basin an interesting and attractive target to explore the origin of gas accumulation.

Crânganu & Deming's thermal modelling of the Transylvanian Basin^[15] proves that the oil window is under the salt horizon; as a result, the methane trapped in the post-salt reservoirs can have exclusively biogenic origins. It is obvious that low heat flow (average 45 mW/m²) means immature post-salt deposits^[15].

This potential origin will be confirmed when recent isotopic measurements become available^[4]. Similar isotopic measurements have shown that the hydrates in the Black Sea have microbial origin, with methane $\delta^{13}\text{C}$ values of -84‰ to -70‰ and concentrations of 99.1%-99.9%^[16]. We expect similar values for the Transylvanian Basin's gas isotopic analysis.

This allows for the presumption that the local methane could have multiple sources^[17]. Besides the well-known,

classical biodegradation of organic matter from the post-salt sedimentary sequence, we suppose the existence of a secondary methane source. These are the ancient Deep Hypersaline Anoxic Basins (DHAB) from the Middle Miocene in the Transylvanian Basin, where a considerable amount of methane could be produced by bacteria [6,23].

A modern analogy for such DHABs has recently been described in several places around the globe; one of the first being the Mediterranean Range [24]. An important feature of these layered brines is that they host methane generated by bacteria [25]. Methane in these brines can amount to ~70 mg/L concentration [21]. Similar ancient brines can be considered secondary methane sources for sedimentary basins, i.e. the Miocene Transylvanian Basin [17].

2.2 Recent Methane Hydrate Facies - Analogies for the Miocene Transylvanian Basin

In earlier decades the American and Asian methane hydrates represented the focus of hydrate exploration, but Minsull et al. [13] recently edited a review about the methane hydrate potential of Europe. They defined (direct and indirect) hydrate indicators in order to delineate a restricted exploration acreage, and the drilling cores subsequently proved the existence of methane hydrate. One such successful area of exploration was the Black Sea basin.

If we look for the current methane hydrate generation facies, the perfect analogy for the Transylvanian Basin is the Black Sea. This theory is supported by Radu & Sandu [26], who published an article on gas hydrate stability (GHS) in the Black Sea. Figure 2 depicts the methane hydrate stability zones based on drillings in the seafloor sediments. This figure explains how the temperature and phase curves outline two GH stability zones: one between 400 m-770 m, and the second between 1,000 m-1,600 m. According to the above mentioned authors, more than 10 methane hydrate horizons are documented in the sedimentary deposits between 400 m-800m under the seafloor. This idea is also supported by Zander et al. [12], examining a seismic cross section to highlight the characteristic bottom simulator reflectors (BSR) in the offshore regions of the Danube Delta. Furthermore, Vassilev & Dimitrov [27] propose that 91% of the seafloor is within the range of the gas hydrate stability zone.

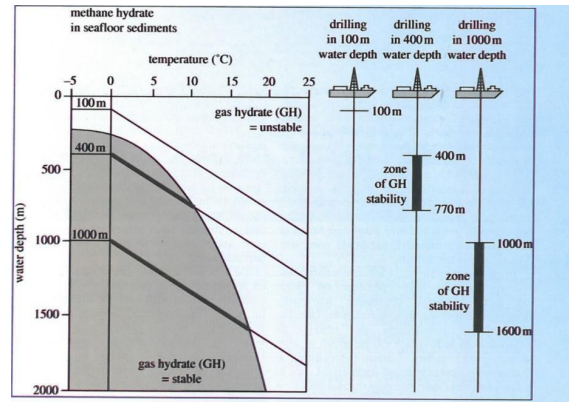


Figure 2. Hydrate formation and stability zones in the Black Sea basin

(after Radu Gh. & Sandu V., 2015)

Based on the system tract analysis for the Miocene sedimentary Transylvanian Basin by Krézsek et al. [4], it was shown that gas hydrate stability zone started at ~400 m seawater depth in deep lacustrine environments, at least up until the Sarmatian age. As a consequence, the probability of methane hydrate formation was high over a relatively long period, approximately ~4 MA.

If we apply Minsull's direct and indirect hydrate indicators [13] to the Miocene Transylvanian Basin, we find several overlaps with the actual Black Sea basin indicators. We are aware that the identification of similar Miocene direct indicators is troublesome; however, it is known that gas seepages and chlorinity anomalies are present as indirect indicators. From among the indirect indicators, we highlight the subsurface escape structures and gas escapes of mud volcanoes active in our days (Figure 3) [28].

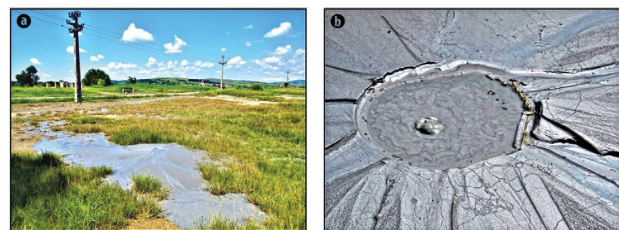


Figure 3. An active mud volcano at Homoród, with a well-expressed flat cone, small crater and mud flows: (a) general view, (b) detail of the cone

(Photo by Silviu Rădan courtesy to Seghedi et al. [28])

We overlaid the mud volcano database on a lineament map generated from the digital terrain model [29]. The distribution of the mud volcano structures shows a perfect overlap on the lineaments of the Transylvanian Basin (Figure 4) [30].

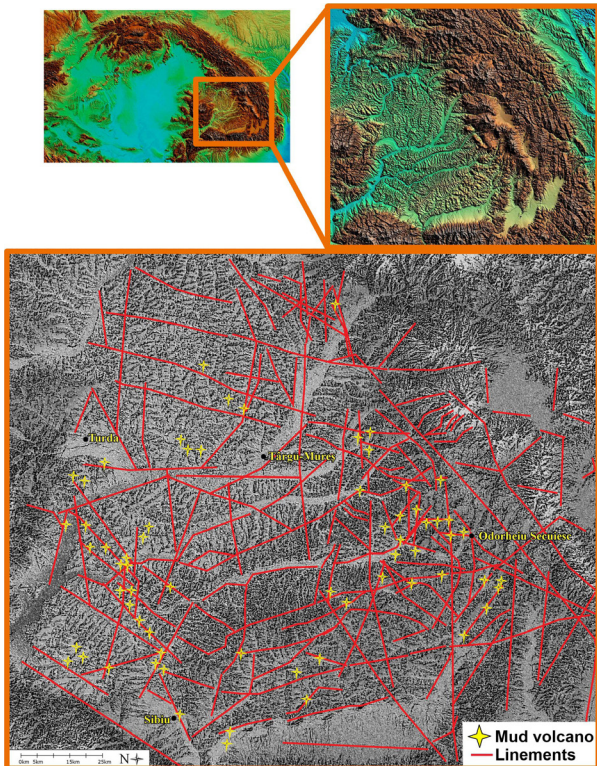


Figure 4. Relationship between mud volcanoes and lineaments^[29]

In 2010 Spulber et al. measured 27 gas flux sites out of the 73 documented mud volcanoes in the Transylvanian Basin, and extrapolated that the methane output could be up to 680 t/year^[31].

These indirect indicators represent arguments for the existence of Miocene methane hydrates.

The huge trapped methane reserves lead us to presume that methane in the Transylvanian Basin might have multiple sources^[17].

Up until now the classic sedimentary deposit sequence, rich in organic matter, has been considered the primary and sole source of biogenic methane in the Transylvanian Basin. However, recent analogies have shown that ancient DHABs can be considered as a secondary source, with biogenic methane concentrations as high as ~70 mg/L^[21,25].

We propose that dissociated methane hydrates can be regarded as a third source of methane, formed in the deep lacustrine environments from the Middle Badenian up until the Late Sarmatian age.

2.3 Miocene Methane Hydrates Formed in the Transylvanian Basin

As mentioned above, the methane component of methane hydrates can originate from DHABs, as well as from the normal bacterial degradation of organic matter. Under the appropriate marine thermodynamic conditions,

the escaped methane molecules can be caught in hydrate cages.

In the case of the actual deep hypersaline anoxic brines in the Mediterranean Range it was shown (and even measured) that the brines produce a methane output^[24] (Figure 5).



Figure 5. Measuring the daily methane output with a mobile mass spectrometer

(courtesy to MedRIFF 1995)

In Table 1, Yakimov et al.^[21] compiled the average chemical composition of the Medee Lake brine from the Mediterranean Basin. The layered brine has varying build-up and composition structure, and it clearly shows the methane content and salinity (blue lines), as well as the daily methane production MPR (red line).

This is a possible analogy for the methane output from the ancient brines (DHAB) within the Miocene Transylvanian Basin. Without making quantitative assumptions (which would require further detailed modelling and analysis), we can state that it is highly probable that considerable methane output was released from the Miocene brines in the Transylvanian Basin^[6].

2.4 Theoretical Approach for Methane Hydrate Formation in the Transylvanian Basin

Based on the actual methane output from the brines and using these as an analogy for the ancient brines from geological times, the question emerges naturally: what is happening with the escaping methane molecules?

In accordance with the thermodynamic potential, in a cold basin the escaped methane molecules will be frozen and caught by water molecule clathrates, forming methane hydrates (MH). The salty seawater presents an obstacle in this process. Figure 6 shows methane hydrate stability in a coordinate system, depicting temperature versus pressure in the presence of NaCl. The different colours correspond to increasing rates of salinity concentration from 1 mol to 5 mol.

Table 1. Average chemical composition of the Medee Lake brine

Parameters	Brine L1 2,940 m	Brine L2 2,975 m	Brine L3 3,010 m	Brine L4 3,102 m
Density, kg dm ⁻³	1.19	1.21	1.22	1.22
Temperature, °C	14.45	14.73	15.32	15.44
Salinity	304	314	325	345
Na ⁺	4,022	4,110	4,165	4,178
Cl ⁻	4,684	4,833	4,830	5,259
Mg ²⁺	603	630	773	788
K ⁺	331	363	462	471
Ca ²⁺	2.4	2.6	3.0	2.8
SO ₄ ²⁻	140.4	146	166.9	201
HS ⁻	0.67	0.93	0.97	1.64
Br ⁻	49.0	53.3	62.6	65.3
H ₃ BO ₃	1.9	2.0	2.2	2.3
NH ₄ ⁺	2.31	2.27	2.45	2.35
Li ⁺ μmol L ⁻¹	149	160	166	163
CH ₄ μmol L ⁻¹	18.0 ± 3.1	70.3 ± 2.3	24.1 ± 3.3	13.9 ± 1.4
Acetate μmol L ⁻¹	132 ± 21	539 ± 42	508 ± 37	n.d.
GB nmol L ⁻¹	170 ± 9	n.d.	44 ± 7	0*
MPR, μmol L ⁻¹ day ⁻¹	2.1 ± 0.2	3.1 ± 0.4	1.5 ± 0.6	0.5 ± 0.4

*The values correspond to the glycine betaine concentration found in the sediments collected at the depth of 3,105 m.

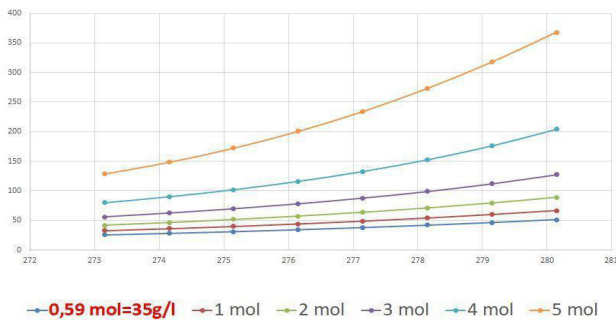


Figure 6. Methane hydrate stability in the presence of NaCl [mol] (P-T diagram)

The lowest curve (dark blue) shows a seawater concentration of 35 mg/L = 0.59 mol. The diagram demonstrates that methane hydrate stability is more sensitive to temperature than to pressure in normal seawater. The curve is almost parallel to the temperature axis. The importance of this is highlighted when the freshwater output from the brines^[6] dilutes the normal seawater concentration. This will immediately facilitate the formation of methane hydrate, i.e. water freezing together with the methane. Figure 7 sketches out the process:

- (1) The brine pool releases fresh water and dissolved methane into the normal seawater^[6];
- (2) This will dilute the seawater, reducing the salt concentration to levels under 35 mg/L=0.59 mol, which eliminates the obstacle (salty water) to form methane hydrate;
- (3) Due to the thermodynamic potential, the methane

hydrate freezes.

This process of methane hydrate generation can be repeated for as long as methane production is active and the thermodynamic conditions stay unchanged. The ice clathrates can be preserved for geological times on the bottom of the basin in the gas hydrate stability zone, where further methane hydrates could accumulate as the basin fills up. In the case of the Transylvanian Basin this took place on the deep lacustrine facies from the Late Badenian to the Late Sarmatian period.

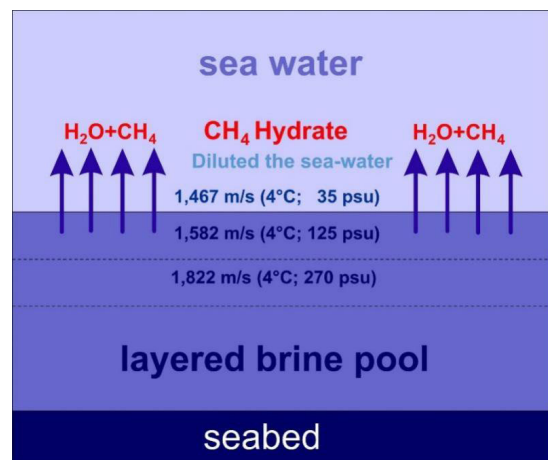


Figure 7. The interface process between seawater and brine: beyond a certain pressure and at a certain temperature, the brine releases water and methane into normal seawater. This dilutes seawater and facilitates methane hydrate generation.

(MedRIFF 1995 figure amended by the authors)

3. Discussion

3.1 Recent Chlorinity Anomalies Generated by Ancient Methane Hydrates

Once the volcanic activity started in the Eastern Carpathian, the regional geothermal gradient increased, and the trapped methane hydrates started to dissociate. It is also well known that: 1 m³ MH yields 0.8 m³ freshwater and 164 m³ CH₄ [32].

This process triggers considerable volume increase and creates an overpressure zone. Due to this pressure, methane starts migrating to the reservoirs and traps. The melted freshwater generated by dissociation dilutes the reservoir water, reducing its initial salinity. Consequently, the chlorinity anomaly indicator is present.

In the case of the Transylvanian Basin, the initial reservoir waters of 120-200 g/L salinity will be diluted. This is the reason why formation water reaches salt concentration levels between 7-12 g/L, thus creating a strong chlorinity anomaly. This phenomenon occurs frequently in the Transylvanian Basin (Figure 8) and it is mostly characteristic of deep reservoirs related to gas fields such as:

- Grebenișu de Câmpie (7-18 g/L),
- Dobra (3-15 g/L),
- Corunca North (11-12 g/L),
- Corunca South (9-20 g/L),
- Filitelnic (1-13 g/L),
- Magherani (7-19 g/L),
- Damieni (8-20 g/L),
- Eremieni (5-17 g/L),
- Lechința (5-20 g/L),
- Luduș (3-21 g/L),
- Șincai (7-17 g/L),
- Laslău Mare (3-15 g/L),
- Deleni-Hărănglab (1-27g/L) [33].

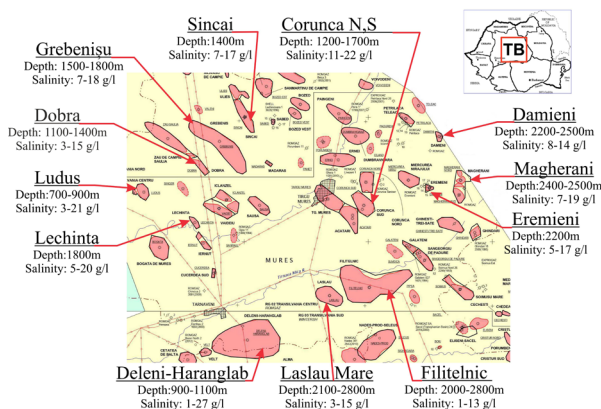


Figure 8. Chlorinity anomalies (g/L) for the dry gas fields in the Transylvanian Basin (Basemap courtesy of IHS)

Our deduction is: besides the primary and secondary methane sources, there is a tertiary methane source: dissociating methane hydrates. The exclusively dry gas (the absence of the thermogenic methane) shows that only biogenic methane was trapped in the reservoirs from those three sources.

4. Conclusions

The authors attempted to draw an analogy between the current methane hydrate occurrence in the Black Sea basin and the possible methane hydrate formation in the Miocene Transylvanian Basin deposits. The analysis of the direct and indirect indicators suggests that all conditions supporting the formation of methane hydrate exist in the Miocene Transylvanian Basin.

The relatively high frequency of active and less active mud volcanoes - as indirect indicators - represent a strong argument for the existence of former methane hydrates.

The methane, generated from the primary (biodegradation) and the secondary (DHAB) sources, was trapped in water clathrates, creating multiple Miocene methane hydrate horizons, similarly to the Black Sea today. According to the water depth, in a cold sedimentary basin (such as the Miocene Transylvanian Basin), the required thermodynamic potential was present for the generation of methane hydrate. This phenomenon lasted from the Middle Miocene until the Late Sarmatian age over a period of ~ 4 MA.

Those methane hydrates could have been preserved for millions of years until the Eastern Carpathian magmatic activity started, when the regional geothermal gradient increased, and the methane hydrate consequently dissociated. This melting yielded free methane, which escaped from the H₂O molecule clathrate cages. The remaining freshwater, now made up of pure H₂O molecules, is responsible for the low salinity of the formation water, i.e. the normal reservoir salinity was diluted by the melted hydrates, creating the chlorinity anomaly. 1 m³ MH yields 0.8 m³ freshwater and 164 m³ CH₄.

This idea is supported by the low salinity concentration (7-12 g/L) of the formation waters of several gas fields in the Transylvanian Basin.

Based on these theoretical considerations we can state that:

1) The dry gas in the Transylvanian Basin can have a tertiary source. The generated gases could have initially been trapped as methane hydrate, just like in the current Black Sea basin.

2) After dissociation the methane migrated into traps formed by salt tectonics, and the resulting melted water

diluted the formation water.

This hypothesis urges us to re-evaluate the origin of methane wherever the salinity level of reservoir waters has dropped, wherever it may be on the globe.

Author Contributions

The authors have the following contribution to this article: Unger: 40%, LeClair: 40%, Györfi: 20%.

Conflict of Interest

The authors have no conflicts of interest.

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