Methane Hydrates as a Tertiary Methane Source in the Transylvanian Basin*

Z. Unger[1,2], D. LeClair[2], and I. Györfi[3]

Search and Discovery Article #11307 (2020)**
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[1]ELTE-SEK-Laboratory of the Instruments, Szombathely, Hungary (zunger@shpbv.eu)
[2]Oil&Gas Development, Central Kft., Budapest, Hungary
[3]RomGaz, Târgu Mureș, Romania

Abstract

The Transylvanian Basin as a back arc and a piggyback basin has a thick lithosphere. In this so-called cold basin, there are salt deposits over which biogenic gas was trapped (Krézsek et al 2010). The rate of the generated gas related to the rock volume of this post-salt basin strongly exceeds the average. This allows for the presumption that this methane could have multiple sources. Besides the well-known biodegradation of the organic matter from the sedimentary sequence we supposed to have a secondary methane source from the ancient Deep Hypersaline Anoxic Basins (DHAB), where considerable amount of methane was produced by bacteria (MedRIFF 1995, Unger & LeClair 2017, 2018). Huge quantities of dissolved methane get through these DHAB surfaces into normal salty sea water. This methane output originating from the brines was measured by MedRIFF (1995) and published by Karisiddaiah (2000), proving an occurrence of daily methane output. The question is this: where do the escaping methane molecules migrate? Since in a cold basin, the dissolved methane will be frozen and caught by water molecule clathrates, forming methane hydrates (MH). These methane hydrates can be preserved for geological time on the bottom of the basin, where further methane hydrates could accumulate, adding to the previously frozen ones in the course of basin filling Late Badenian to Late Sarmatian. Once the volcanic activity started in the East Carpathian, the geothermal gradient increased, and the methane hydrates started to dissociate.

$$1m^3 \text{ of MH yields } 0.8m^3 \text{ freshwater and } 164m^3\ CH_4$$

This is an endothermic process triggering considerable volume increase and creating overpressure zone. Due to this pressure, methane starts migrating to the current reservoirs and traps. The freshwater generated by dissociation dilutes the reservoir water, reducing its initial salinity (120-200g/l). Such diluted reservoir water (7-12g/l) has frequent occurrence in the Transylvanian Basin; it is mostly characteristic of deep reservoirs related to gas fields such as Grebenișu de Câmpie-Dobra, Păingeni, Corunca, Filitelnic, etc. Our deduction is this: besides the primary and the secondary methane sources, we face a tertiary methane source and the origin of this is from methane hydrates.

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Methane Hydrates as a

Tertiary Methane Source

in the Transylvanian Basin

by

Zoltán UNGER, David LeCLAIR, István GYŐRFI

ELTE – Savaria Campus - O&GD Central Ltd. - RomGaz

Szombathely – Budapest – Târgu Mureș

Hungary – Romania

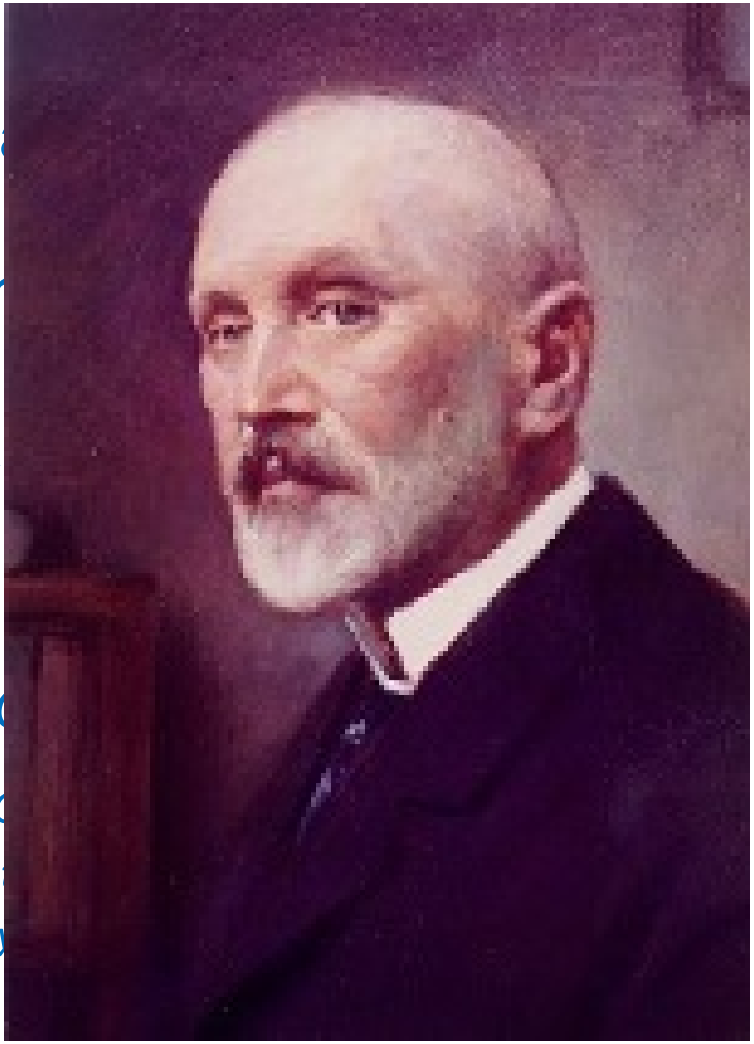
"Theories do not have to be true, just good”

[Roland Eötvös]

Methane Hydr

Tertiary Methan

in the Transylva



by

Zoltán UNGER, David Le

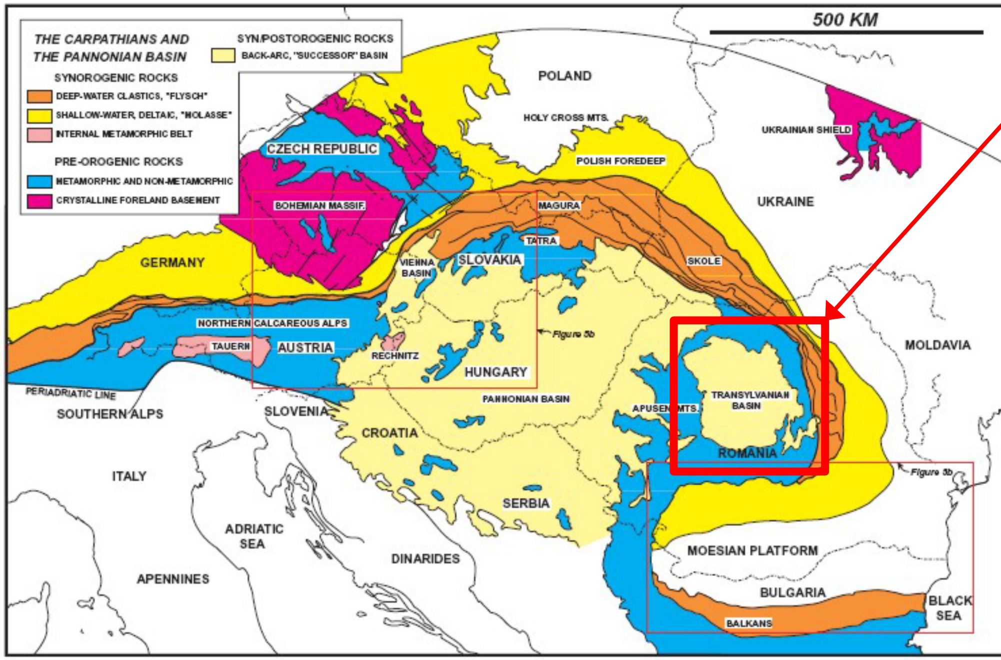
ELTE – Savaria Campus - O&

Szombathely – Budapest

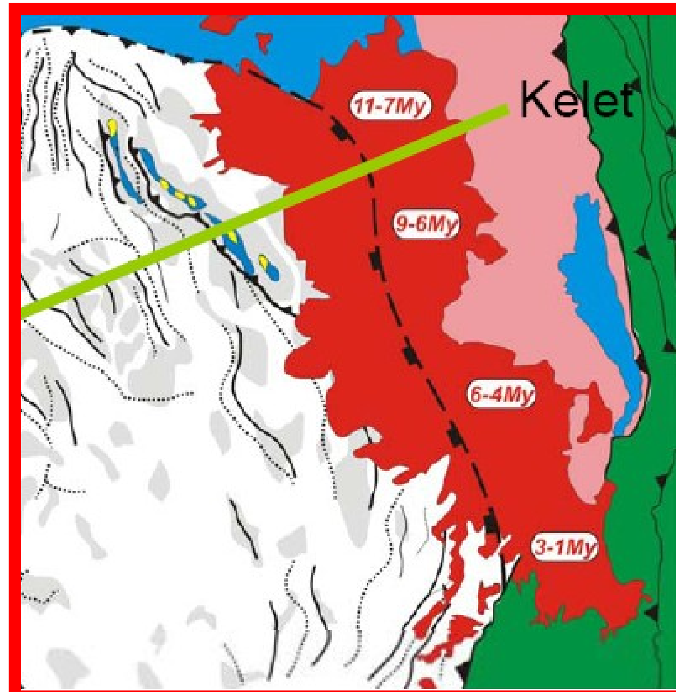
Hungary

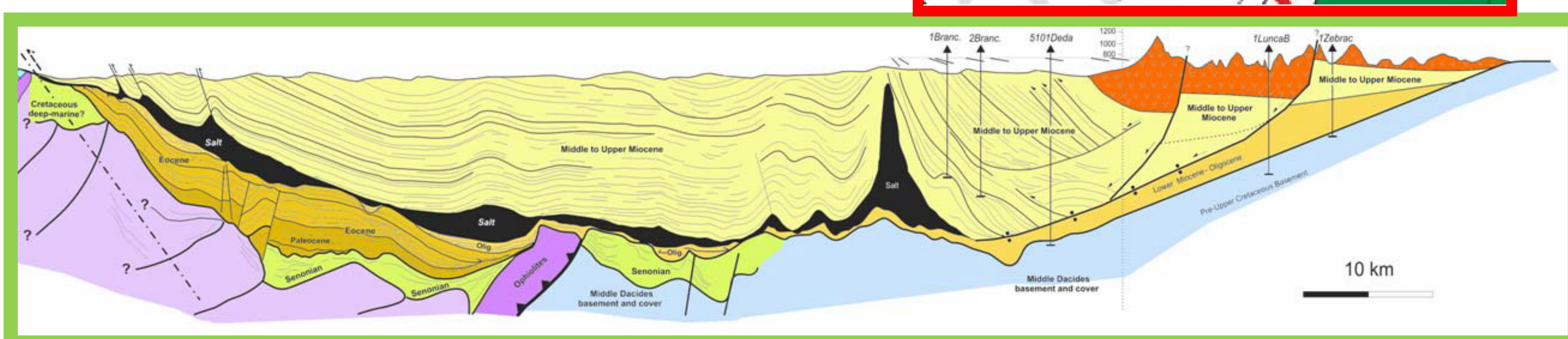
UNESCO Memory of the World: 2016 **Year of Eötvös in Hungary: 2019**

Transylvanian Basin in Romania



Krézsek&Bally 2008; Krézsek 2010





Salt and Methane Origin in the Transylvanian Basin

Two models exist for the origin of salt in Transylvania:

1. ***Classical evaporation*** *(Achenius, i.e. Kara Bugas bay example)*
2. ***Deep Hypersaline Anoxic Basin*** *(Unger&LeClair 2018)*

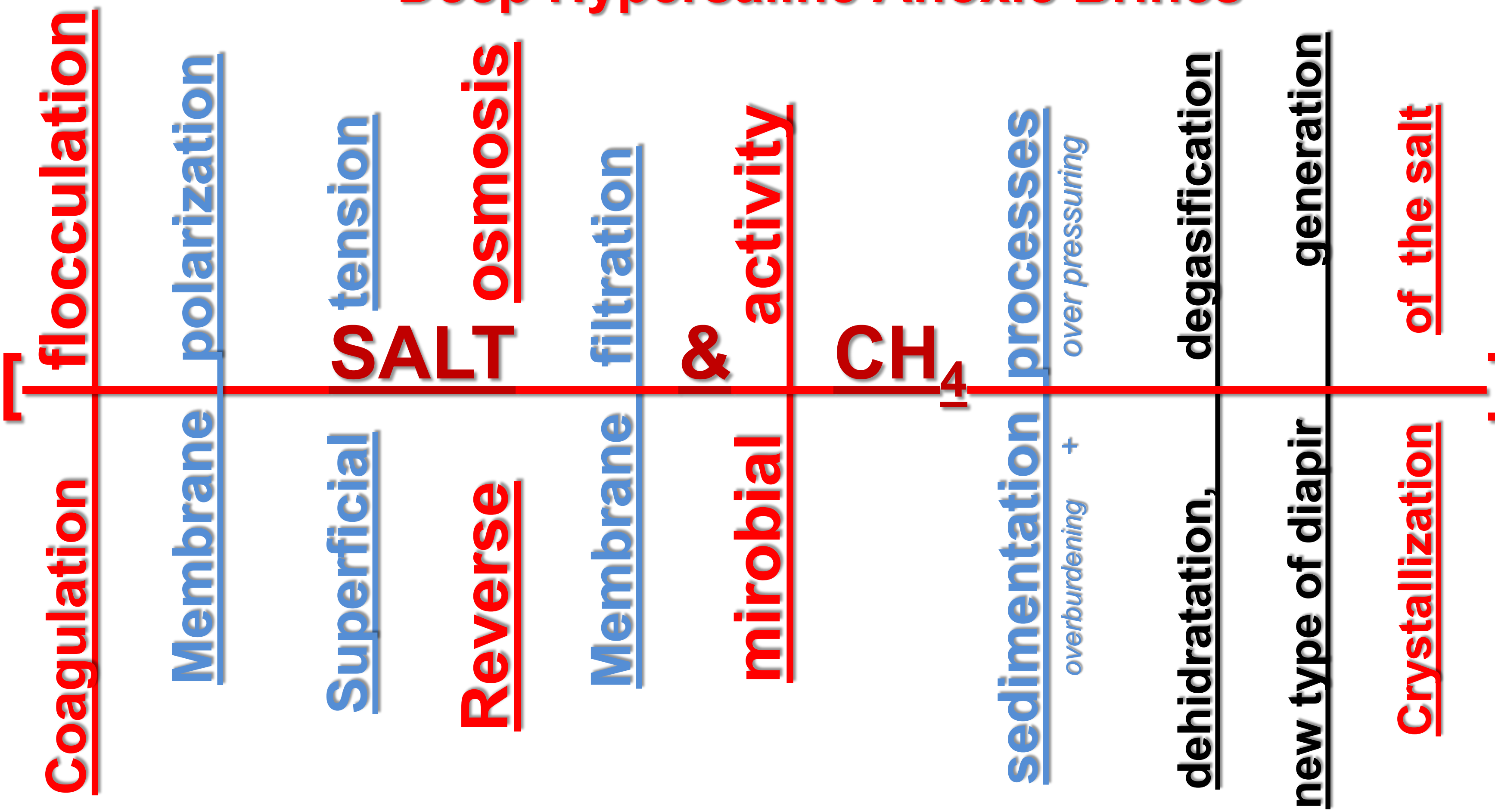
Two theories are present for the generation of biogenic methane of the Transylvanian Basin:

1. **Bacterial degradation of the organic material within the deposited sediments (classical biogenic)**

2. **Parallel salt and methane generation from Deep Hypersaline Anoxic Basins *(Unger&LeClair 2018)***

Salt and Methane Origin in the Transylvanian Basin

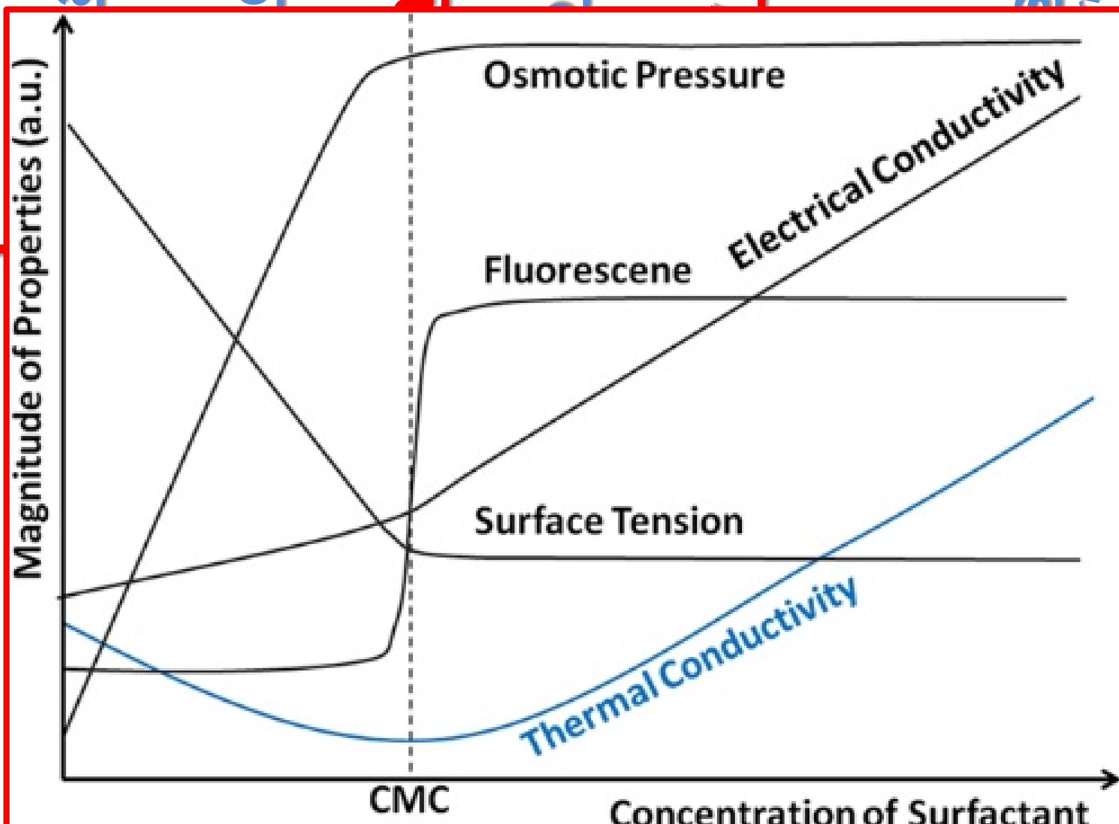
Deep Hypersaline Anoxic Brines



in GEOLOGICAL TIME SCALE

Deep Hypersaline Anoxic Brines

[flocculation / coagulation



degasification / dehidratation,

generation / new type of diapir

of the salt / Crystallization]

in GEOLOGICAL TIME SCALE

Salt and Methane Origin from TrB

If methane content of current DHABs

continues to be confirmed (Karisiddaiah [2000] and M. Yakimov et.al. [2013]),

then substantial volumes of biogenic methane are likely trapped in buried brines

~40 mg/L

Since acetate decomposes into: $CH_3–COOH^- = CH_4 + CO_2$

an additional source for yielding methane in the brine

~500µmol/L = **~30mg/L** is available;

Totally the aggregated methane concentration tend to **~70mg/L** in buried brine.

As a consequence:

these brines can serve as secondary sources for biogenic hydrocarbons!

Methane Hydrates

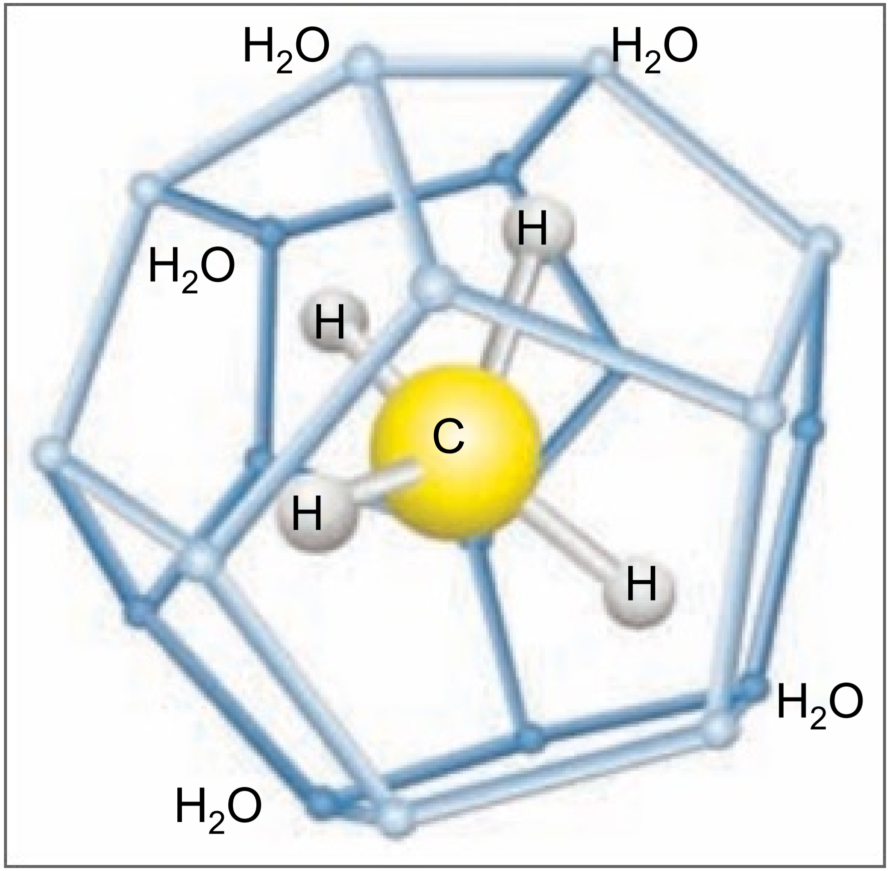
Well known, from the frozen pipelines

Definition of Hydrates

Methane hydrates are METHANE CLATHRATES
– stable compounds of methane and water

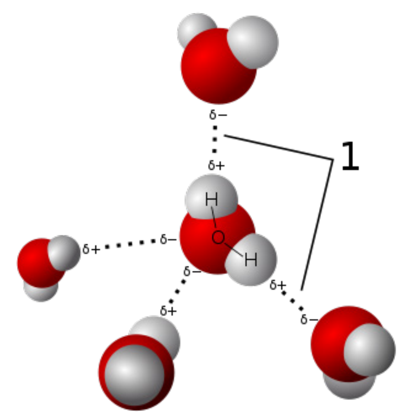
Chemistry of Methane Hydrates

Methane hydrates are the METHANE CLATHRATES

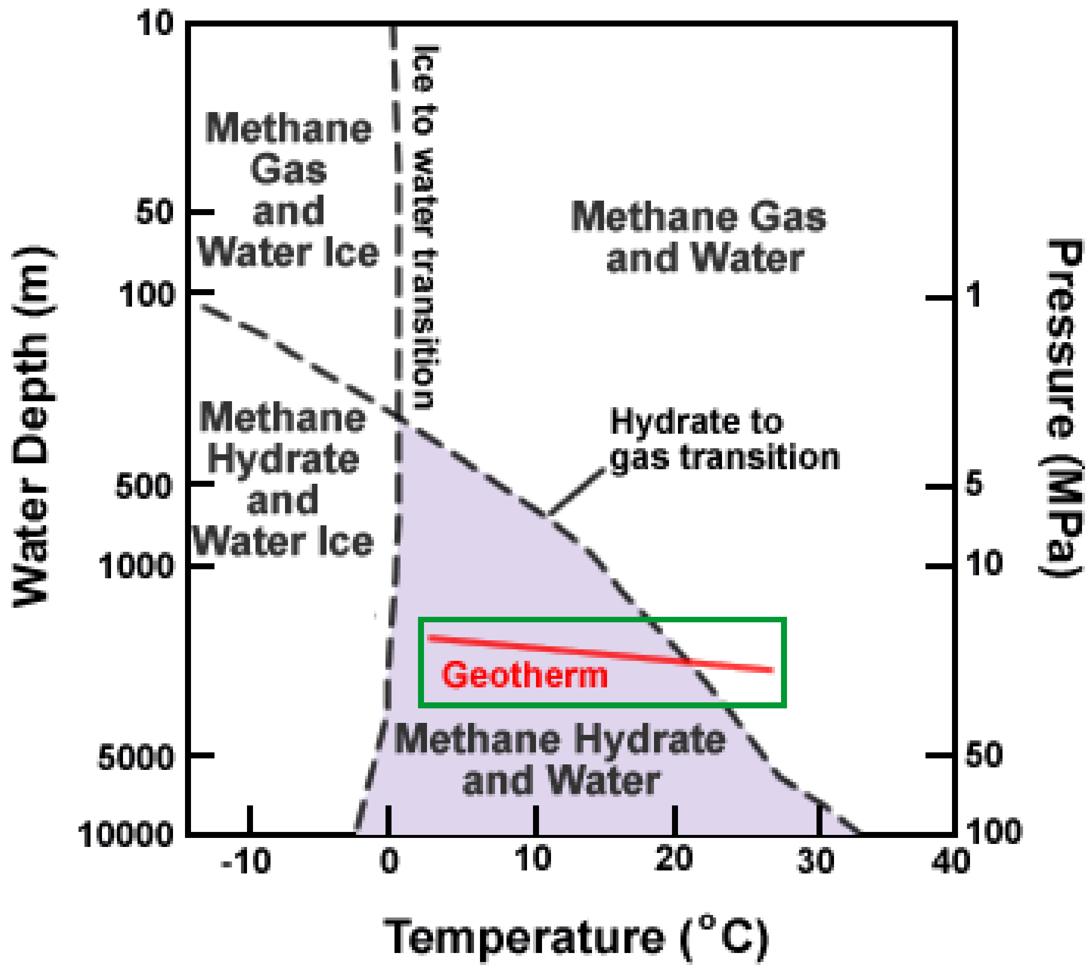


Methane clathrates are composed of several water molecules which trap methane and form a stable mass

Certain temperature and pressure conditions



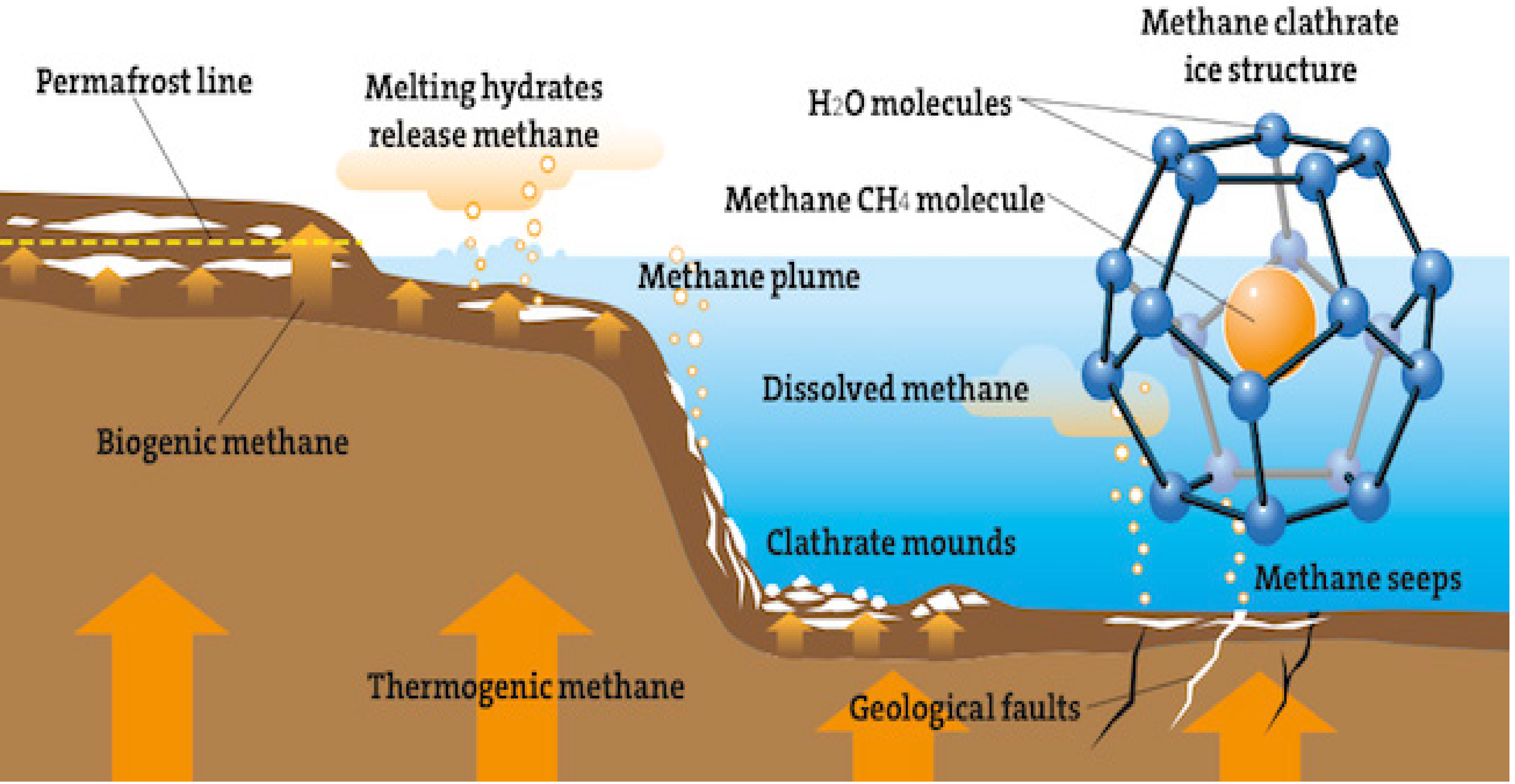
The Water Phase Diagram



Clathrates are the results of thermodynamic laws

Hydrate Facies

Transylvanian Basin water depth during Middle Miocene was up to 3000 m



All this because of ➔

Clathrates occurrences on the Earth

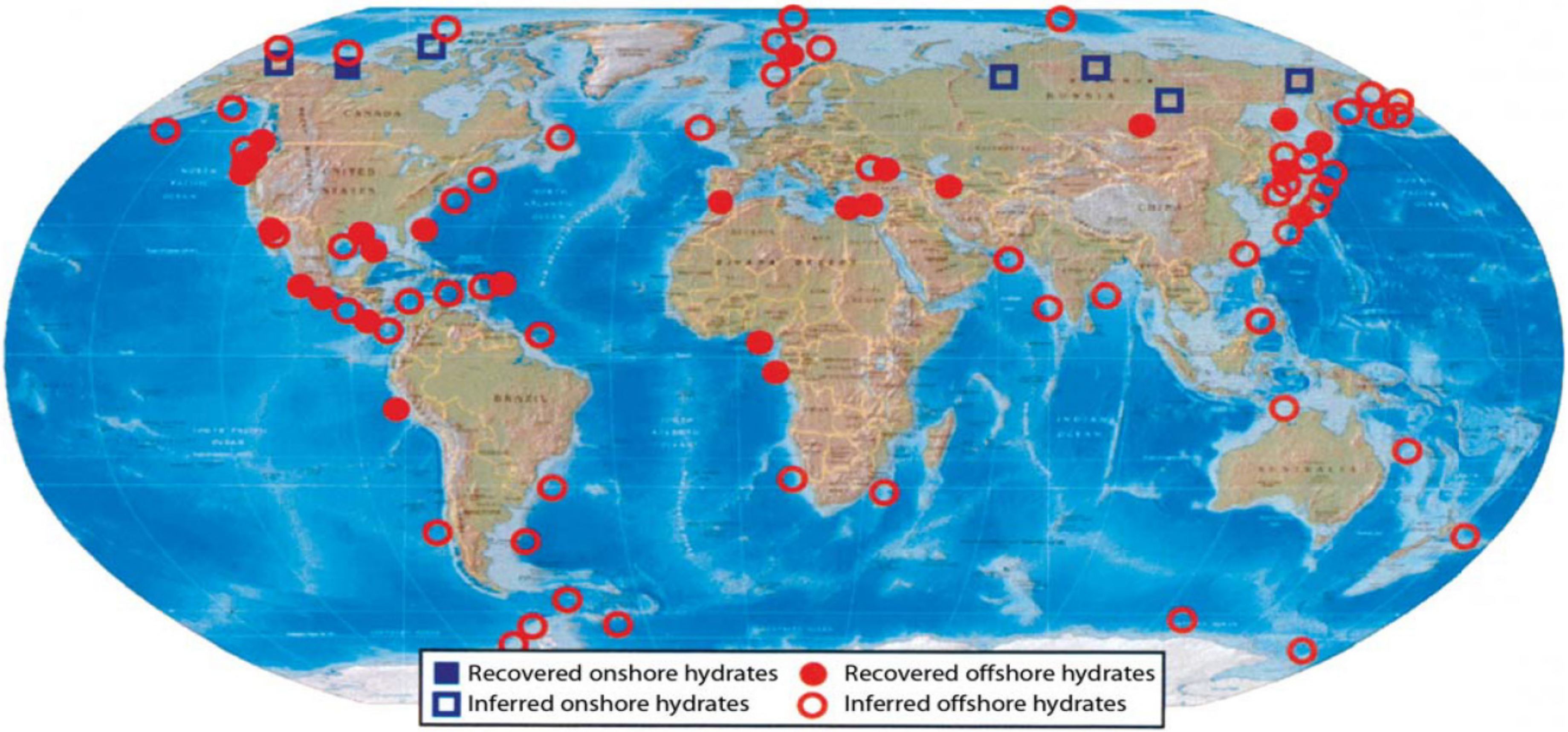


Figure 2. World map with documented and inferred gas hydrate occurrences. Inferred gas hydrate occurrences are based primarily on the presence of a seismic reflection known as the Bottom-Simulating Reflection (BSR), velocity amplitude peculiarities on seismic records, well-log signatures indicative of the presence of gas hydrate, and freshening of pore waters in cores. Samples were recovered using research submersibles, remotely operated vehicles (ROVs), grab samplers, dredges, piston coring, and coring during DSDP, ODP, and IODP operations. Data from Kvenvolden and Lorenson (2001) and updated by Milkov (2005). Reprinted from Doyle et al. (2004).

Clathrates occurrences offshore

depth, thickness, dissociation pressure tempperature

OFFSHORE GAS-HYDRATE DEPOSITS

Table 1

Location	Water depth, m	Gas-hydrate layers, m	Depth to BSR, m	Pressure drop required for dissociation, bar	Gas-hydrate temperature, °C.
Nankai-1	945	1,141-1,210	1,210	45	11
Mississippi Canyon	1,330	1,365-1,470	—	115	7
Blake Ridge-1	2,790	2,990-3,220	3,220	200	11
Guatemala-2	1,720	1,870-2,120	—	125	9.5
Mexico-1	1,770	1,950-2,170	2,540	125	7
Mexico-3	1,950	2,050-2,212	2,750	130	7.2
Guatemala-3	2,000	2,450-2,500	2,500	27	18
Black Sea	2,020	2,030-2,040	—	160	4.0
Guatemala-1	2,400	2,750-2,800	—	125	15.6
Bush Hill	2,420	2,440-2,480	—	95	4
Japan Sea	2,600	2,600-2,650	2,650	95	17
Mexico-2	2,900	3,000-3,077	3,700	250	5.2
Costa Rica	3,100	3,400-3,439	—	260	10
Blake Ridge-2	3,500	3,600-3,700	3,700	20	22
Peru-Chile-2	3,900	3,950-4,000	4,300	305	10
Nankai-2	4,700	4,800-4,870	—	415	4
Peru-Chile-1	5,070	5,200-5,260	5,700	430	6.5

Note: BSR—bottom-simulating reflector

Clathrates Occurrences Onshore

Jamal-Nyenyec Region,

close to

Bovanenkovszkoje gas field
(Siberia)

2016
a **Jamal-** and **Gidan peninsula**
Siberia

DHAB Brine Characteristics

Table 1 | Average chemical composition of the *Medee* Lake brines. All concentrations in mmol kg^{-1} unless otherwise stated. Reported geochemical values are mean ± 5% (n = 6) obtained during 2010–2012 years unless otherwise stated. Abbreviations used: GB, glycine betaine; MPR, methane production rates; n.d., not determined

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_3BO_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

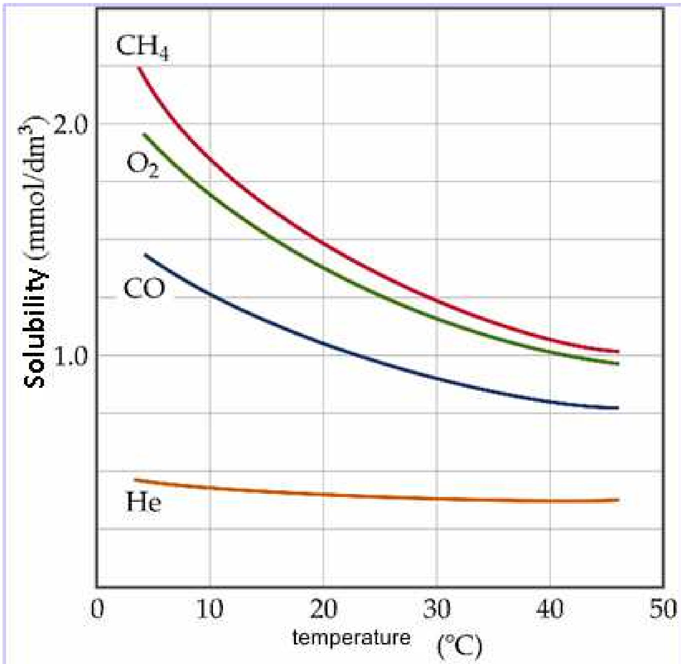
*The values correspond to the glycine betaine concentration found in the sediments collected at the depth of 3,105 m.

Daily methane production: MPR, um/L/day (red line)

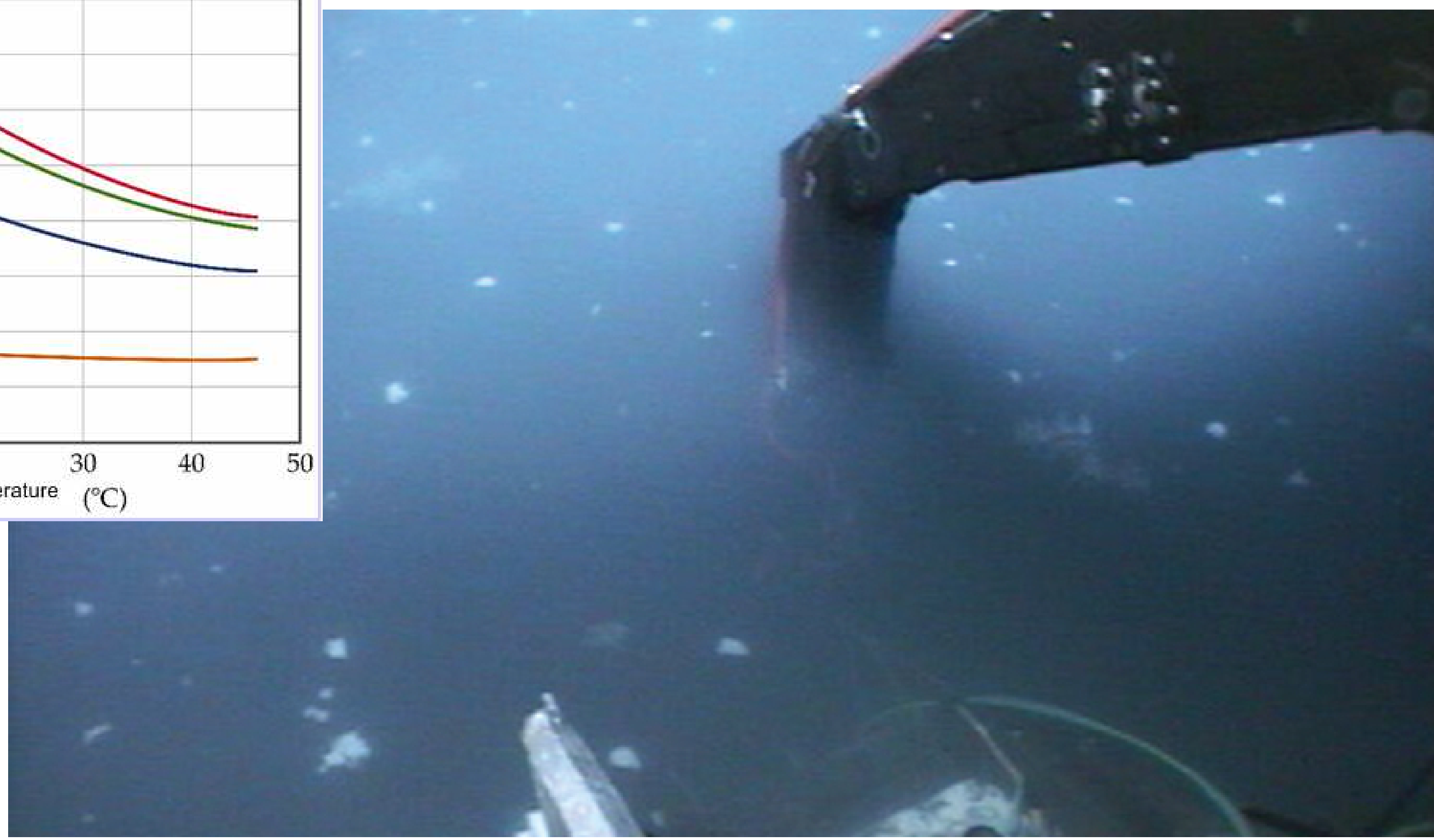
M. Yakimov et.al. [2013]

Methane output from the brine

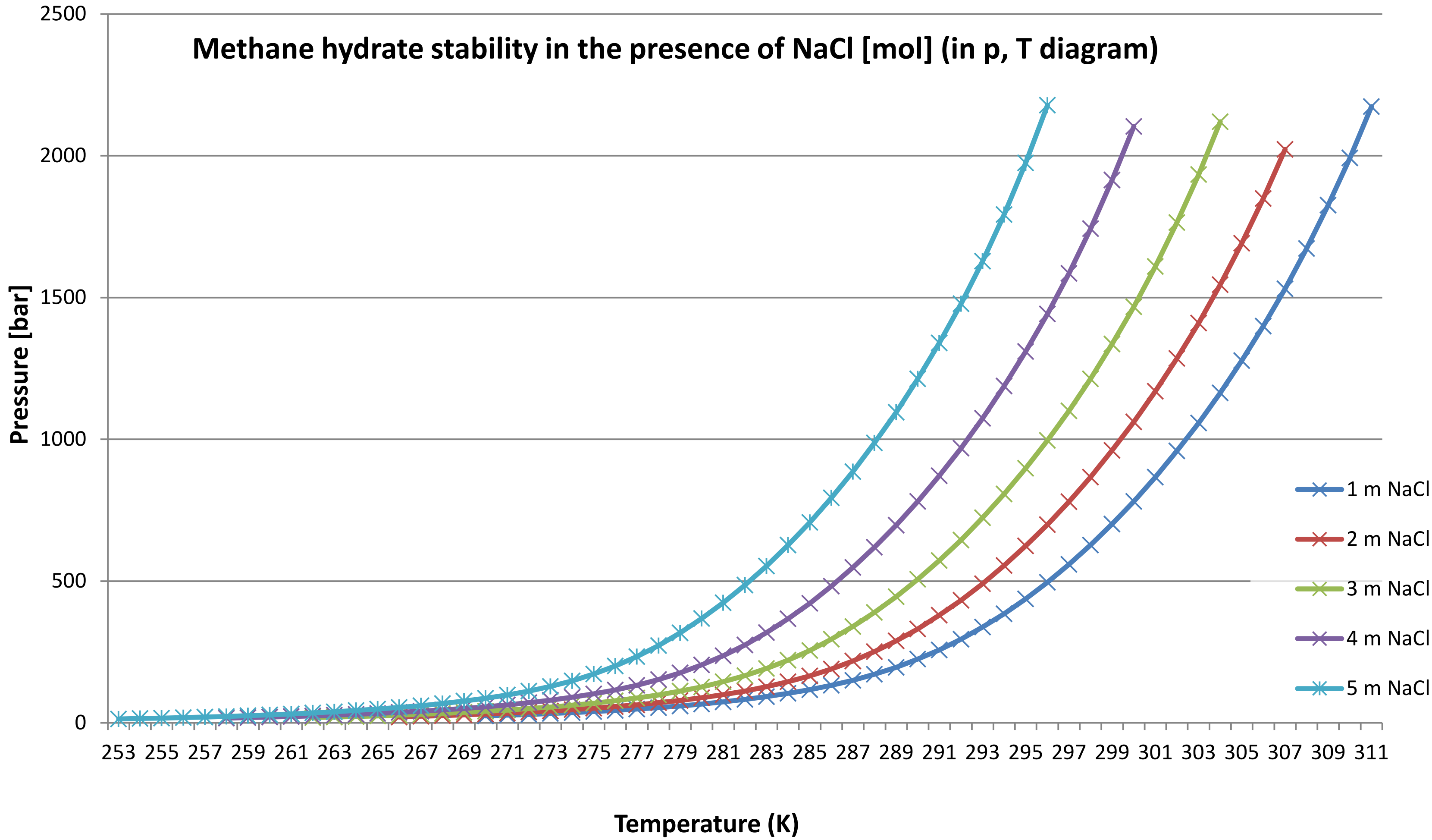
diffusive methane flux 1.1 mol /m^2 /yr
advective methane fluxes of up to 2 mol /m^2 /yr



MEDRIFF Consortium 1995

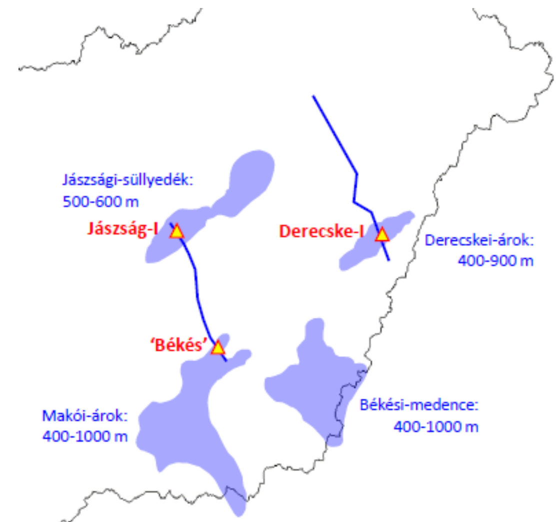


NaCl Depresses Clathrate Formation



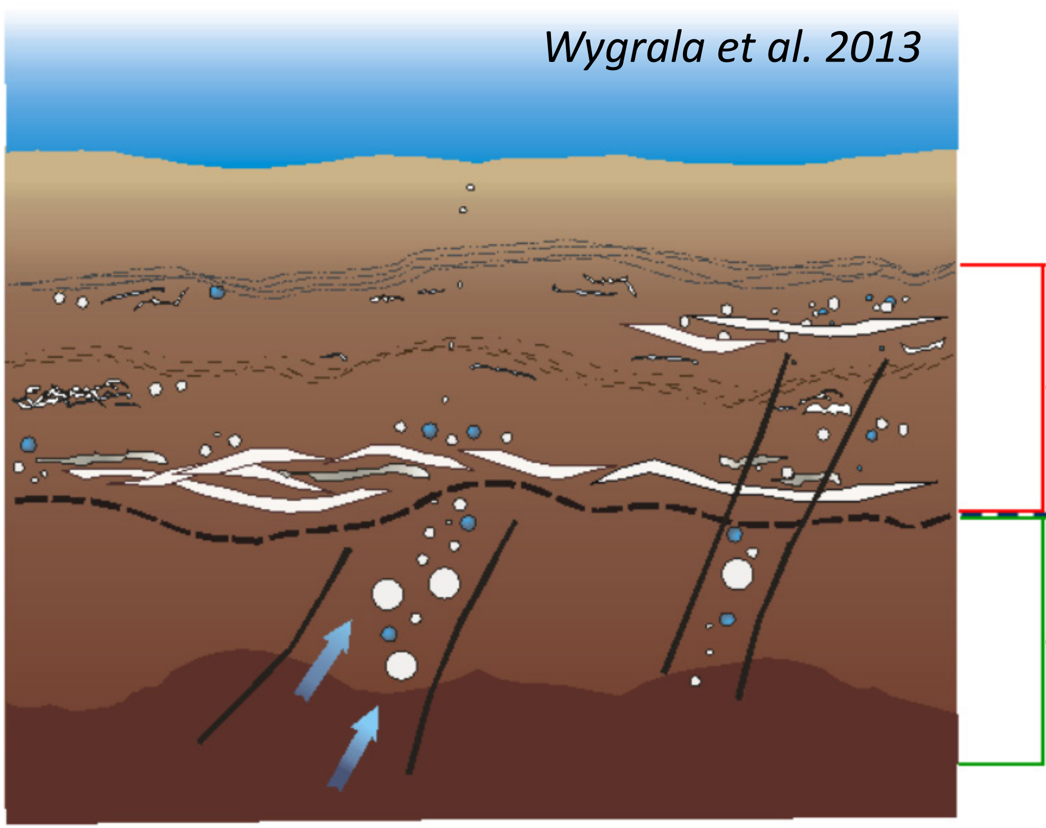
Gas Hydrate Generation Theorized in the East Pannonian Basin

HaroldZsófia, BalázsAttila, BarthaAttila, SzalayÁrpád (2018)



Bérczi I. 1988, Horváth F. 2005, Balázs A. 2013

Gas Hydrate Stability Zone (GHSZ)



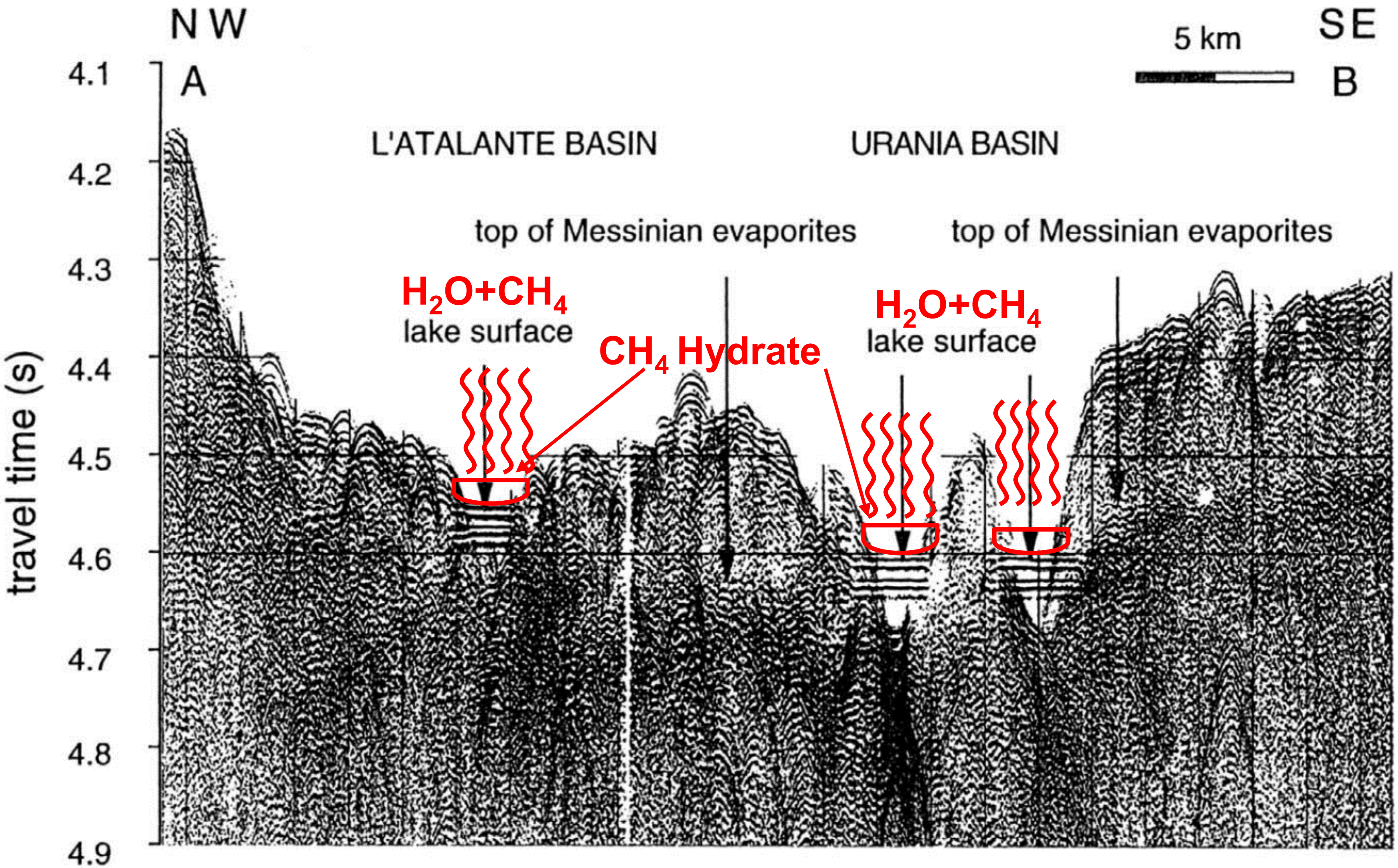
Biogenic Gas Generation and Hydrate Formation

BSR: Bottom Simulating Reflector

Gas Generation

Mediterranean Sea DHABs as a Modern Analogy

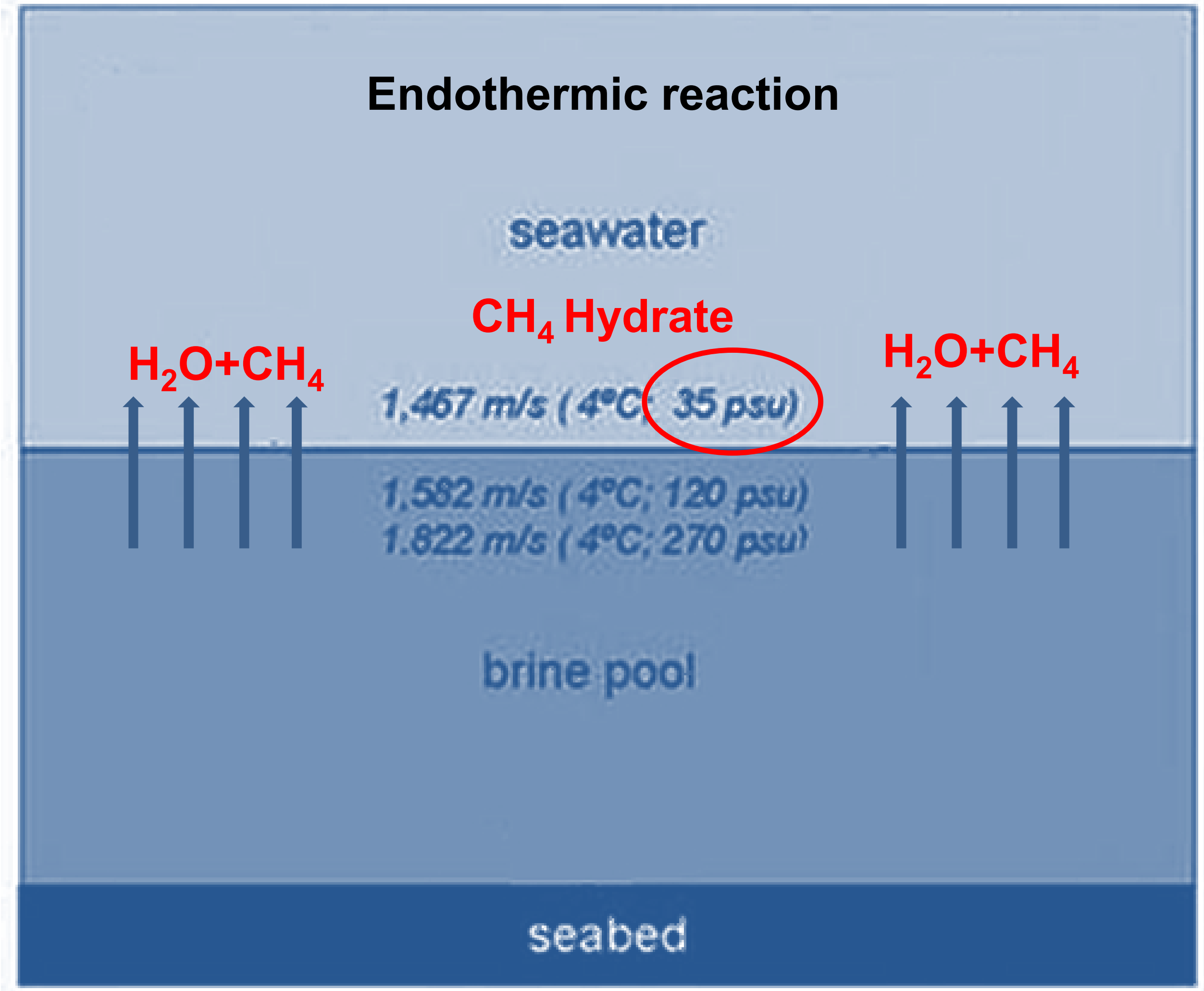
L'Atalante and Urania Basins analogy for the former Transylvanian Sea
Sonar Line from Bottom of the Mediterranean Sea



DHAB Hydrate Formation

In the Deep Med DHAB, hydrate formation is inhibited by the high salinity of the DHAB below the interface.

Hydrates are theorized to occur above the interface, **in the less saline water**.



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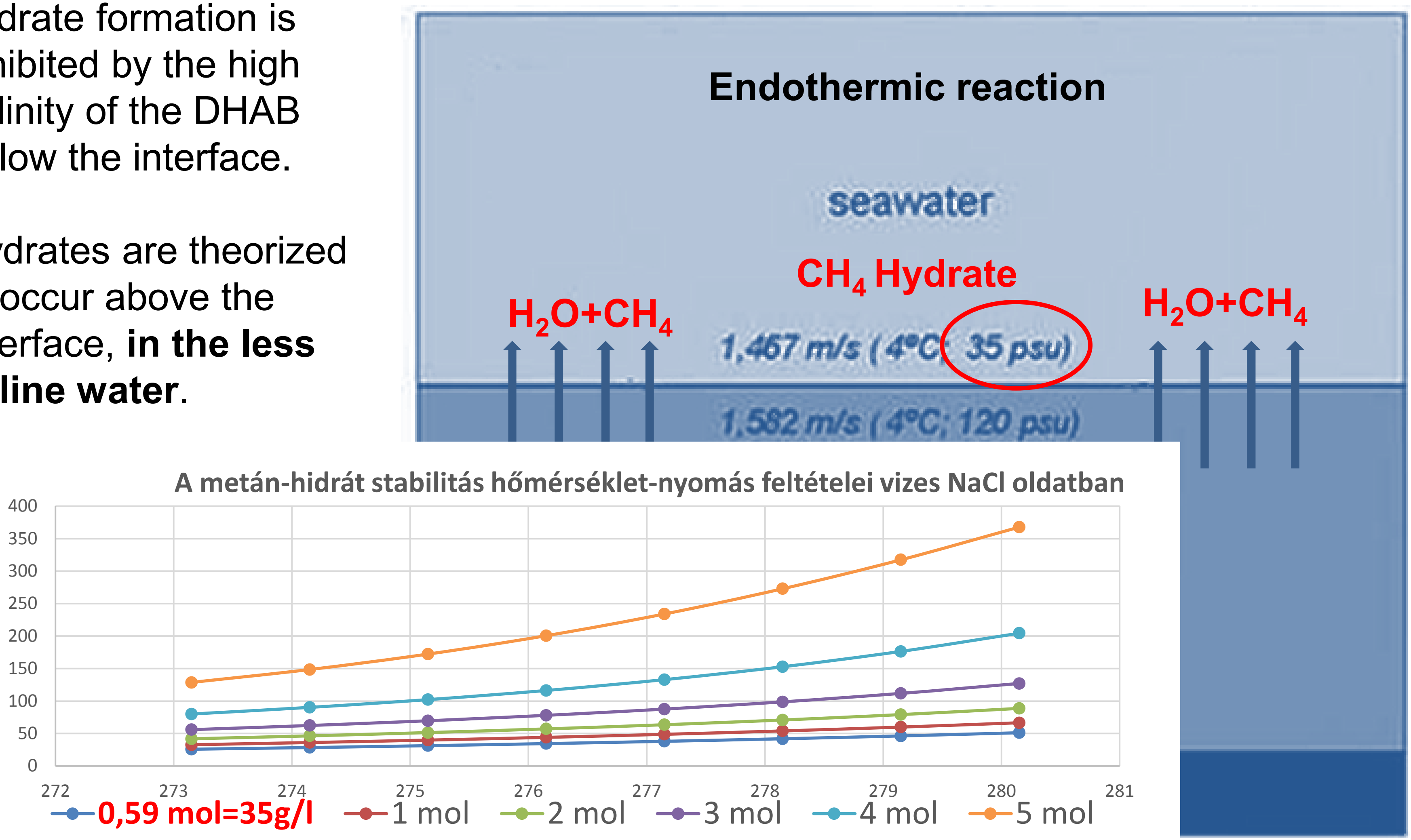
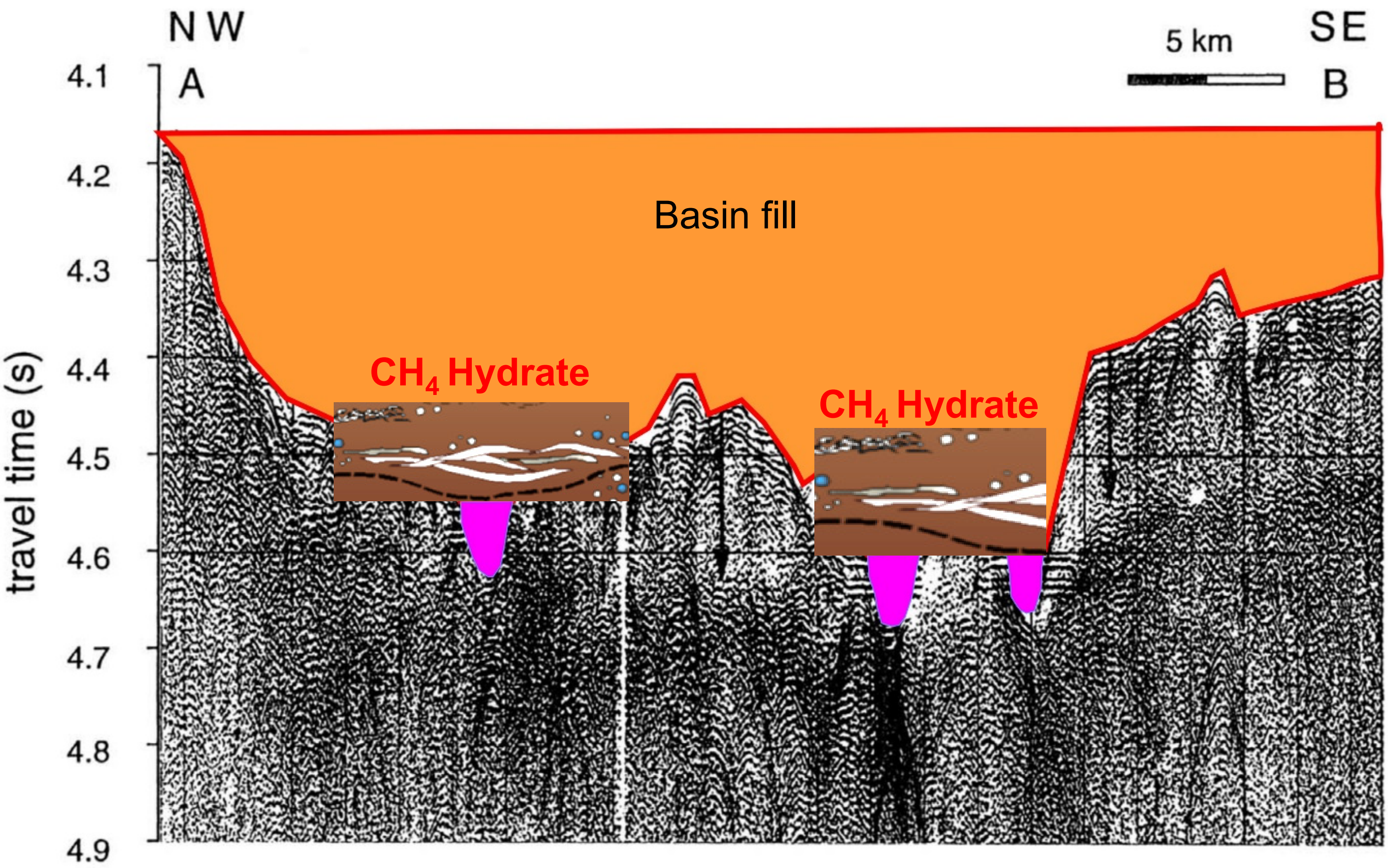


Transylvanian Basin
Gas Hydrate Formation



Black Sea as a Modern Analogy for the Ancient Pannonian Basin

Forum

identificării acumulărilor naturale de hidrați de gaze. Conform datelor făcute publice, la cercetarea și crearea complexului hidroacustic au luat parte savanții din Irkutsk, Moscova, Sankt-Petersburg. Complexul a fost testat cu succes pe Lacul Baikal; acesta se poate scufunda la o adâncime de până la 1,6 km, are capacitatea să studieze profilul rocilor sedimentare de pe fundul lacului, morfologia, să măsoare temperatura, conductivitatea electrică, să evalueze conținutul de metan. În cazul unor concluzii pozitive din partea celor mai importanți experți specialiști în acest domeniu din alte state, producția de roboți-exploratori va putea fi realizată pe viitor la scară industrială.

În general, cele mai noi tehnologii privind prospecțiunile și valorificările hidraților de

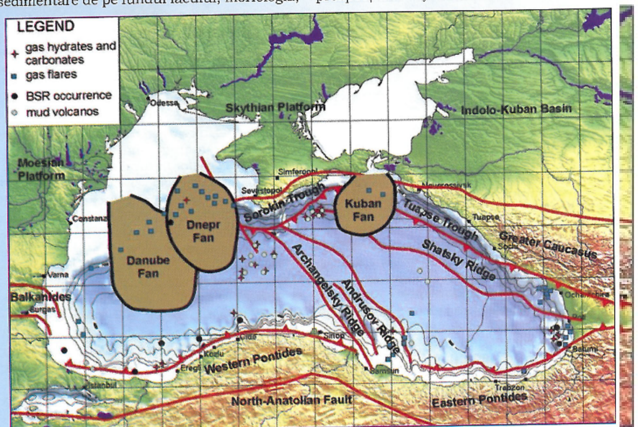


Figura nr. 1: Localizarea hidraților de metan în bazinul Mării Negre.

metan apar atât în domeniul invențiilor destinate căutării acestora, cât și în cel al producției directe. Astfel, de curând, a fost propusă o nouă tehnologie care se adresează domeniului de producție a gazelor, în special de extracție a gazelor din cristalohidrați. Tehnologia se bazează pe scăderea locală de presiune prin aplicarea dispozitivelor hidrodinamice cavitaționale speciale, care sunt caracterizate printr-un consum minim de energie, ceea ce face soluționarea unei astfel de probleme eficientă din punct de vedere economic.

În prezent, sunt intens cercetate tehnologiile de producție a metanului din hidrați de gaz, în special utilizând metodele moderne de intensificare a proceselor tehnologice (adaosuri de agenți surfactanți, care accelerează transferul de căldură și masă; utilizarea nano-prafurilor hidrofobe; acțiune acustică de diapazoane diferite, chiar și obținerea de hidrați în unde de șoc).

Cercetările condițiilor de formare, d stabilitate și ale proprietăților hidrațilo de metan în condiții naturale permit s prognozăm cu fermitate prezența acestora î diferite regiuni de pe uscat, în oceanele planet și în special pe fundul Mării Negre. Confor investigațiilor seismice din Marea Neagră, a fost depistate anomalii, care demonstreaz prezența hidraților de gaz (*Figura nr. 1*). Astf de porțiuni sunt cunoscute în depresiunea d vest a Mării Negre, zone anticlinale de barier pe ridicarea structurală Palass, în curbu Sorokino, proeminența din Anapa, la poale versantului continental caucazian.

Resursele de metan în zăcămintele c criohidrați din apropierea malului sud al Crimeei sunt evaluate la 20-25 trilioar metri cubi, iar cantitatea de metan în toa Marea Neagră, conform evaluărilor Academi de Științe din Ucraina dar în special datori rezultatelor forării și analizării eșantioanel solului de pe fundul mării în peste 400 c

carote, este de 100 trilioane metri cubi. Exploatarea zăcămintelor hidraților de gaze poate fi la fel de rentabilă ca și exploatarea unor zăcăminte mari de gaze convenționale. Costurile de producție a metanului din hidrați de gaze din Marea Neagră pot fi cel mult de 54 USD pentru 1000 de metri cubi de combustibil.

În Marea Neagră sunt depistate peste zece zăcăminte de hidrați de gaz în straturile superioare ale depunerilor marine, la un interval de depunere de 0,6-2,85 m (pe versantul continental, pe ridicarea structurală Palass). În unele regiuni ale Mării Negre, la adâncimi de 300-1000 m, sunt descoperite zăcămintele de metan sub formă de criohidrați, iar grosimea stratului acestora fluctuează între 400-800 m sub fundul mării. Limita de jos a existenței hidraților de metan și hidrogen sulfurat depinde de adâncimea mării și de mărimea gradientului termic în secțiunea rocilor (*Figura nr. 2*).

Din *Figura nr. 2* rezultă că hidrații sunt

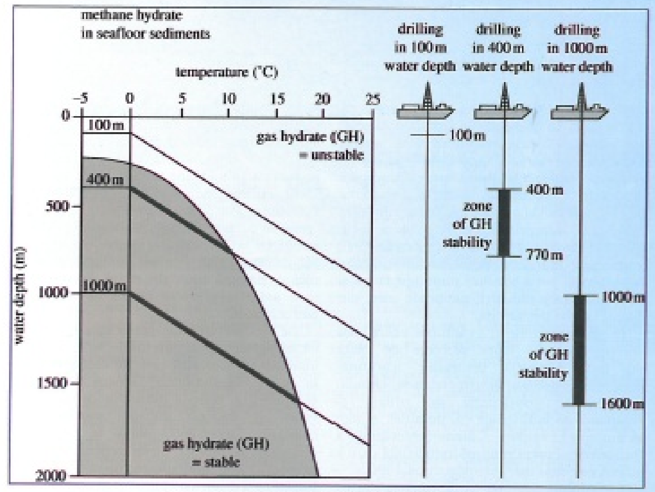


Figura nr. 2: Zona de stabilitate a criohidraților.

situați preponderent în zonele de adâncime, pe fundul marin, în condiții de saturare cu hidrogen sulfurat la anumite presiuni și temperaturi. Astfel, aceste aspecte trebuie neapărat luate în calcul în alegerea metodelor tehnologice de extracție a hidraților de metan din bazinul Mării Negre.

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(continuare în nr. viitor)

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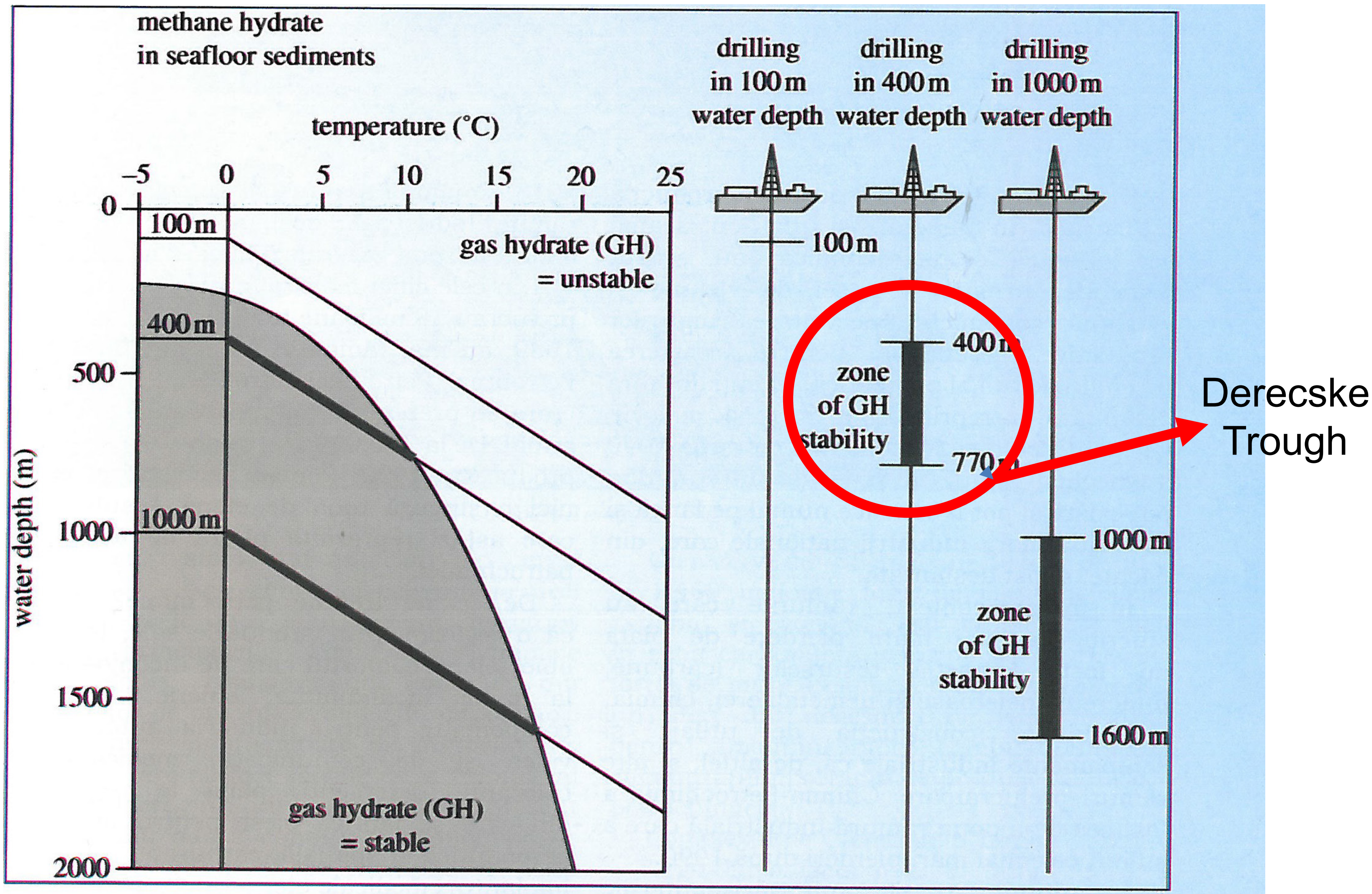
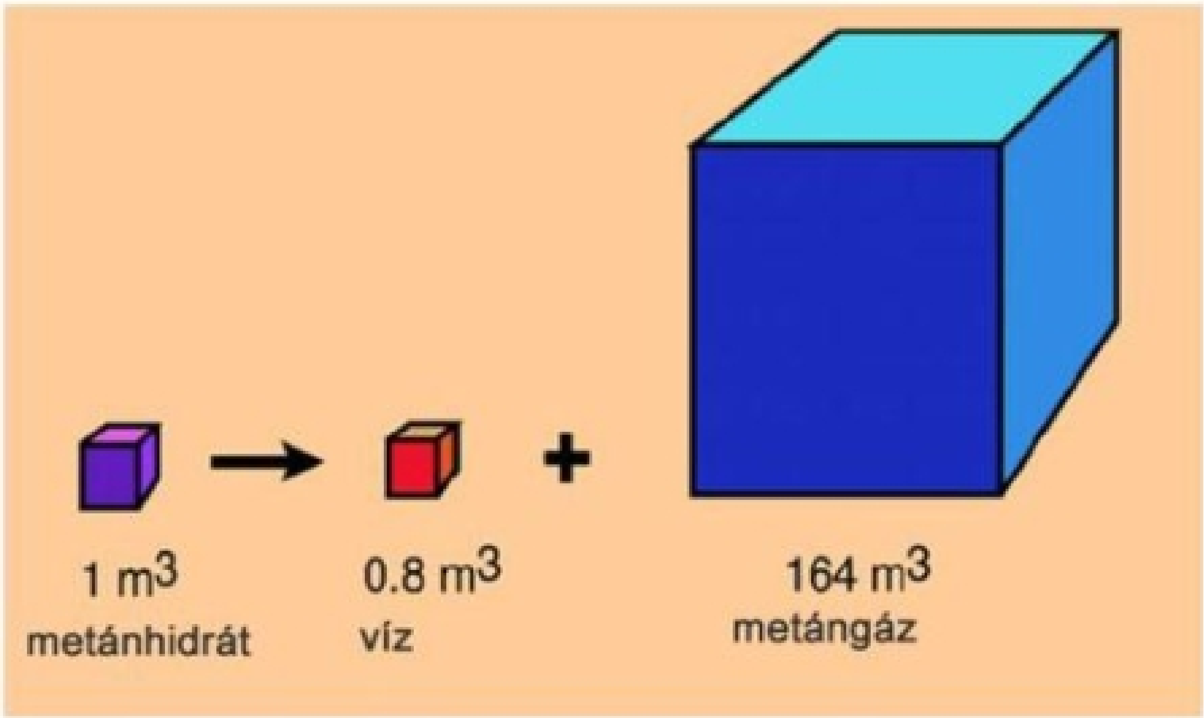
Black Sea as a Modern Analogy for the Ancient Pannonian Basin

Report on Hydrate Formation and Stability in the Black Sea



Radu Gh.&Sandu V.(2015) Monitorul de Petrol si Gaze, XIV,nr.2 (156), pp.2-5.

Methane Hydrate Dissociation

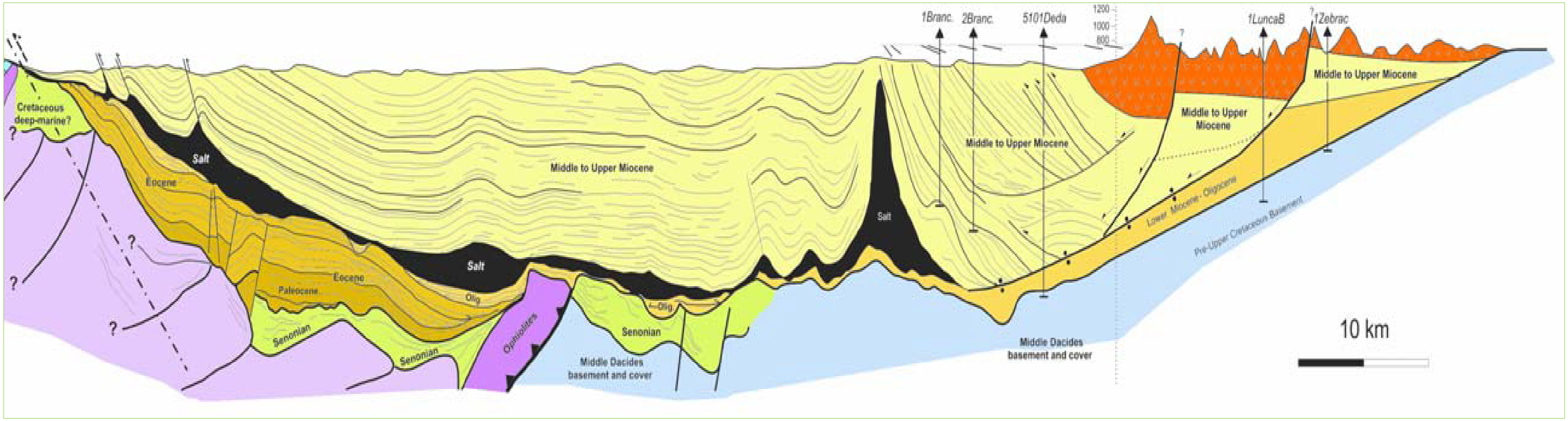


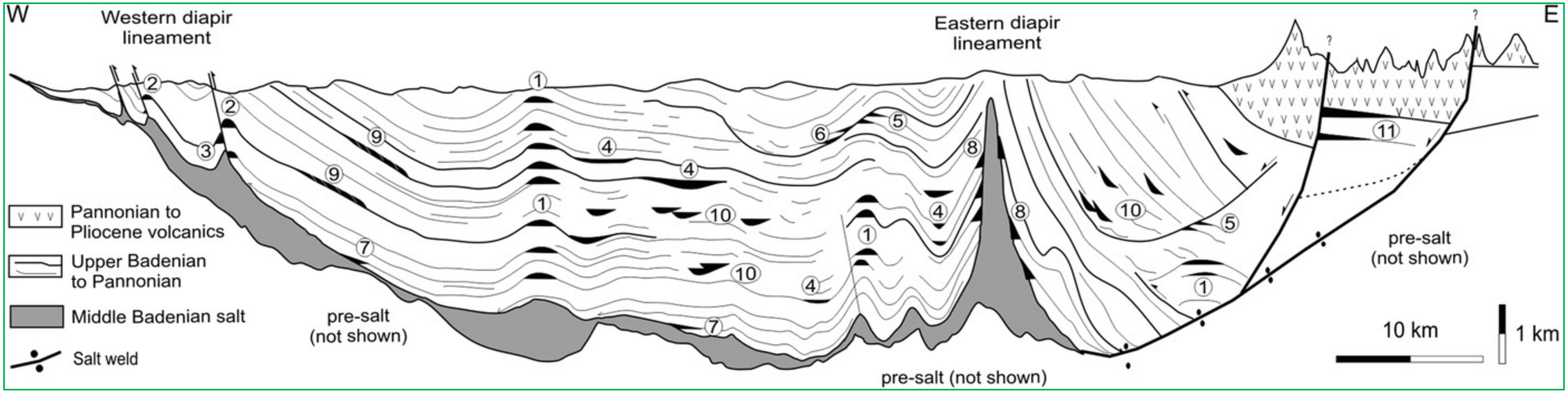
Methane Hydrate Melting => Fresh Water + Methane (exothermic reaction)

Methane hydrate <u>dissociation</u> would happen in the Transylvanian Basin due to the increasing geothermal gradient during East Carpathian volcanism. Afterwards the gas migrated to the sand bodies, resulting in over-pressured reservoirs of methane <u>and sweeter *(less salty)* water in the reservoirs.</u>

Transylvanian Basin traps

[Krézsek 2010]





Post Middle Badenian traps and reservoirs

Sweetener water in the reservoirs in Transylvanian Basin 1-27 *[g/l]*

FIELDS:

Grebenișu de Câmpie
- Depth: 1500-1600m
- ***Salinity: 7-18***

Dobra
- Depth: 1100-1400m
- ***Salinity: 3-15***

Damieni
- Depth: 2200-2500m
- **Salinity: 8-14**

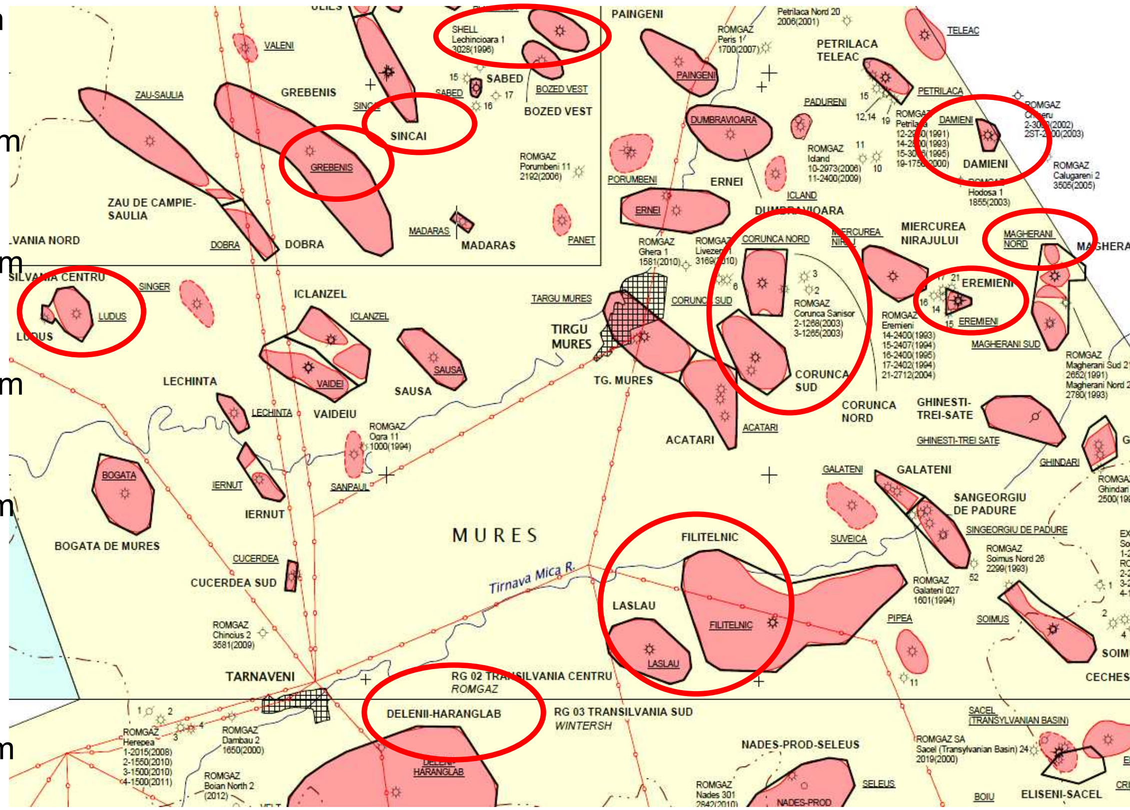
Corunca N
- Depth: 1200-1700m
- ***Salinity:11-22***

Corunca S
- Depth:1500-1700m
- ***Salinity: 9-20***

Eremieni
- Depth:2200m
- ***Salinity: 5-17***

Magherani
- Depth:2400-2500m
- ***Salinity: 7-19***

Filitelnic
- Depth: 2000-2800m
- ***Salinity: 1-13***



Lechinta
- Depth:1800m
- ***Salinity: 5-20***

Ludus
- Depth:700-900m
- ***Salinity: 3-21***

Sincai
- Depth:1400m
- ***Salinity: 7-17***

Laslau Mare
- Depth:2100-2800m
- ***Salinity: 3-15***

Deleni-Haranglab
- Depth:900-1100m
- ***Salinity: 1-27***

Conclusions

Three theories exist for the methane gas generation in the Transylvanian Basin: biodegradation of organic material, generation from ancient brines (DHAB), and from **METHANE HYDRATES**.

1. Methane hydrates could have formed in the Transylvanian Basin from Late Miocene to until end of Sarmatian from methane generation by DHAB

2. Several million years of methane hydrate formation could have been the preserved

3. Dissociation of the methane and water could happen due to the volcanic activity and the resulting increased heat flow

4. The over-pressured reservoirs would be due to the dissociation of the gas from the hydrates and the large increase in the volume of gas and liquid

5. The low salinity of the water from deeper reservoirs could be due to the hydrate dissociation process which creates fresh water

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