The Effect of Rapid Changes in Pressure, Temperature and Salinity Conditions on Methane Dissolution and Implication for the Volume of Accumulated Gas*

Constantin Sandu[1] and Marek Kacewicz[2]

Search and Discovery Article #51289 (2016)**
Posted August 29, 2016

*Adapted from oral presentation given at AAPG 2016 Annual Convention and Exhibition, Calgary, Alberta, Canada, June 19-22, 2016

[1]Osha Liang LLP, Houston Texas, United States (ctin_sandu@outlook.com.)
[2]Earth Sciences, Chevron, Pearland, Texas, United States

Abstract

Formation of giant biogenic or mixed biogenic / thermogenic gas accumulations require several processes occurring in an order that maximizes volume of trapped hydrocarbons. They are: generation of large quantities of gas, development of efficient focusing mechanisms, and rapid formation of efficient shallow seals. During these processes a large quantity of gas is dissolved in formation water and rapid change of pressure / temperature conditions or salinity can lead to exsolution of gas. This study demonstrates that volumes of gas temporarily trapped in water may represent a significant contribution to large commercial accumulations. Several synthetic basin models designed to study the effects of erosion and sea level drop on accumulated gas volumes were built using Petromod®. Simulation results demonstrate that the amount of gas dissolved in water was significantly reduced after a rapid sea level drop. Up to 70 bcf of free gas per square kilometer of fetch area was added to the trap when the water level dropped by 1000 m as compared to the nominal case scenario where sea level was kept constant. In the case when water drop was followed by 500 m of erosion only 33 bcf/km^2 of free gas was added to the system compared to the nominal case. This means that rapid sea level drop added two times more of free gas to the trap than if sea level drop was followed by erosion. These findings can be further applied to explain volumetrics of known commercial accumulations of biogenic gas in general. An example is the Miocene discoveries in the Levantine Basin of Eastern Mediterranean, which is believed to be of mostly biogenic origin. Conventional petroleum systems modeling based on biogenic gas generation kinetics failed to explain the large amounts of gas accumulated in the fields. Computed volumes were way below the reported 19 tcf of gas. Similar to the experiments on our synthetic models, the missing volumes could be explained by favorable conditions created by rapid sea level drop during the Messinian event, leading to gas release out of formation water and subsequent focused migration. Various paleo pockmarks observed on seismic slices in the pre-salt section provide further evidence of rapid changes of hydrocarbon phase/volume, intensified migration and "catastrophic" creation of large gas escape features on the Late Miocene seafloor.

Selected References

Duan, Z., N. Møller, J. Greenberg, and J.H. Weare, 1992, The Prediction of Methane Solubility in Natural Waters to High Ionic Strength from

0 to 250 C and from 0 to 1600 Bar: Geochimica et Cosmochimica Acta, v. 56/4, p. 1451-1460.

Haq, B.U., J. Hardenbol, and P.R. Vail, 1987, Chronology of Fluctuating Sea Levels since the Triassic: Science, v. 235/4793, p. 1156-1167.

Lazar, M., U. Schattner, and M. Reshef, 2012, The Great Escape: An Intra-Messinian Gas System in the Eastern Mediterranean: Geophysical Research Letters, v. 39/20, 13 p. doi: 10.1029/2012GL053484

Marlow L, K. Kornpihl, and C.G.S.C. Kendall, 2011, 2-D Basin Modeling Study of Petroleum Systems in the Levantine Basin, Eastern Mediterranean: GeoArabia, v. 16/2, p. 17-42.

Peace, D.G., T. Stieglitz, and R. Spoors, 2012, Imaging New Opportunities and Play Concepts in the Adriatic Sea and Levantine Basin; Petroleum Geoscience, v. 18/4, p. 405-416.

Railsback, L.B., 2011, Petroleum Geoscience and Subsurface Geology: Department of Geology, University of Georgia, Athens, Georgia. http://www.gly.uga.edu/railsback/PGSG/PGSGmain.html, Website accessed August 2016.

The effect of rapid changes in pressure, temperature and salinity conditions on methane dissolution and implication for the volume of accumulated gas

Constantin Sandu [1]
Marek Kacewicz [2]

June 2016

1- OshaLiang LLC
2- Chevron ETC

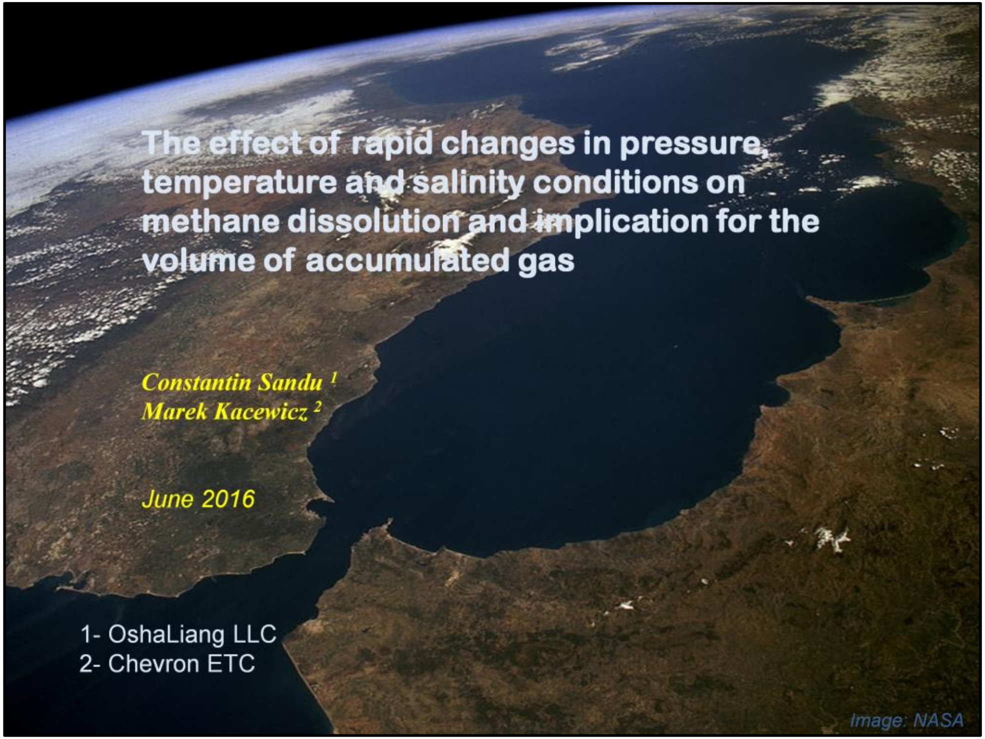
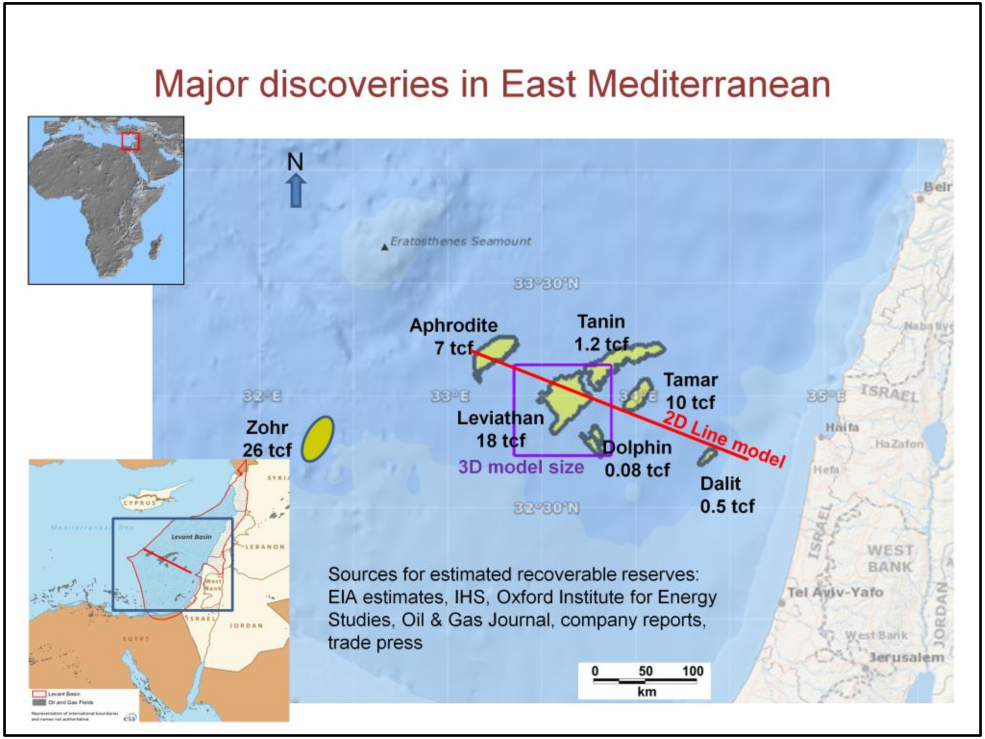
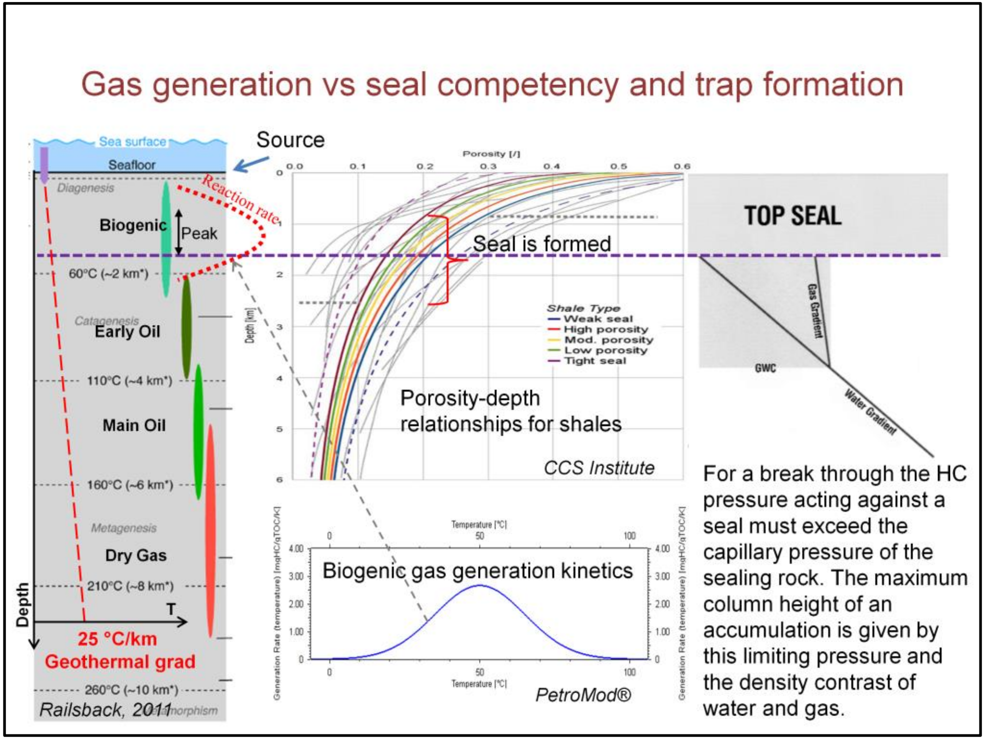


Image: NASA



Presenter's notes:

- The Levantine Basin in the Eastern Mediterranean
- Discovery of major gas fields in the pre-salt sequences (Miocene)
- Information on whether the gas in these new discoveries is of biogenic or thermogenic have strategic implications :
    - if the gas is thermogenic, then the chance of deeper thermogenic oil potential could be reduced or even excluded
    - while biogenic gas would leave an opportunity open for deeper thermogenic systems which could include oil
- Publicly available knowledge disclose that gas that has been discovered is of biogenic origin
- Approximate line of the 2D model and size of the 3D synthetic model



Presenter's notes:

- Big accumulations needs significant generation and timely trapping mechanism
- Generation
  - Biogenic methane is generated by microbial processes at low temperature and shallow depth
  - For a 25 C/km gradient the generation windows will look like these: biogenic is shallow
  - Moreover, substrate is dissolved components -> they tend to diffuse and migrate up
  - The process is more complex but for simplification a simple kinetics based exclusively on temperature was used in simulations
  - Petromod model: standard thermally controlled biogenic kinetics with 50C peak and 80C cutoff - used as reference for testing
- Trapping
  - The competency of the seal depends on many factors but are closely related to porosity
  - In normally consolidated shales typical trends in porosity loss look like these
  - Generally accepted about max 20% porosity to have a good seal: 1000-2000 m depth
- How is then possible to have big biogenic accumulations? Dissolved gas may contribute partially

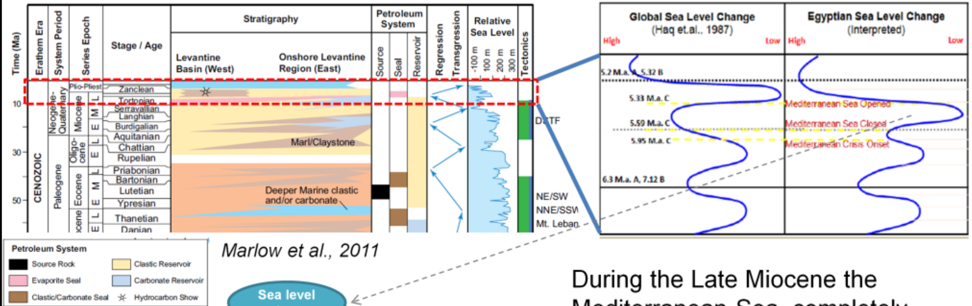
Objectives and methods

- Understand the processes and quantify the contribution of dissolved gas component to a gas accumulation when rapid changes in PTS condition occur in the basin.
    - General assessment of an area subjected to rapid changes in PT conditions: Levant basin 2D basin modeling application.
    - Quantitative assessment of an idealized basin where rapid changes in PT conditions are simulated: Synthetic 3D basin model.
    - Independent calculation to asses the effect of salinity: Numeric implementation of methane solubility.

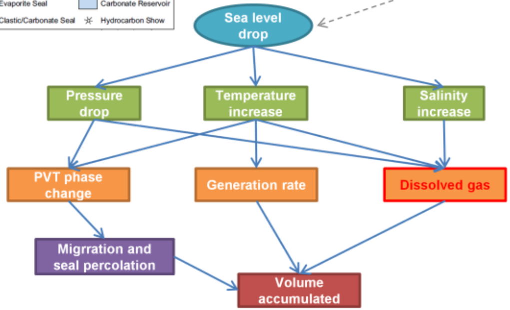
Presenter's notes:

- Understand the processes and quantify the contribution of dissolved gas
- 2D basin modeling of a real example basin
- Volumetric assessment using a synthetic basin model
- Numeric model to asses the effect of salinity

The Messinian Salinity Crisis



Marlow et al., 2011



During the Late Miocene the Mediterranean Sea, completely evaporates resulting in:

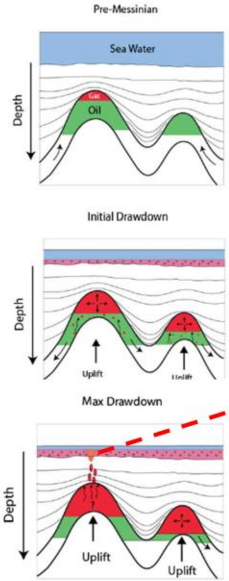
- Pressure drop at surface that propagated deep into the subsurface
- Temperature increase at surface, propagated into the subsurface (attenuation with depth)
- About 2 km of salt deposition

Presenter's notes:

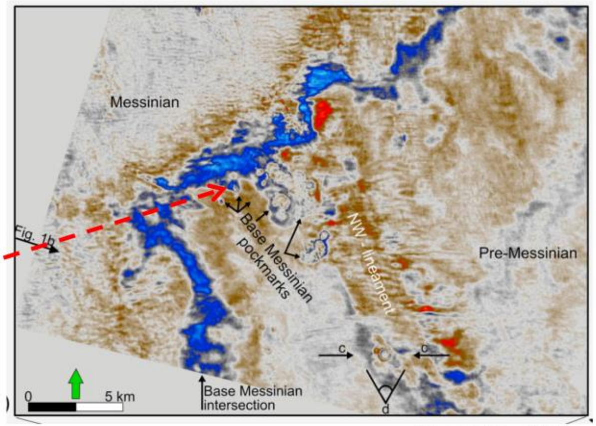
- Brief geologic history:
  - Remnant of the Neo-Tethys Ocean.
  - Permo-Trias rifting and marine transgression deposited the first shallow water carbonate.
  - Jurassic, post-rift subsidence led to deep water pelagic sedimentation.
  - Late Cretaceous subduction in the Taurides Arc.
  - Platform area during the Late Oligocene–Early Miocene.
  - Miocene filled with the coarse clastic basin floor fan sediments.
- Messinian event: Brief interval with Mediterranean desiccation and sea level drop
- Mediterranean sea level curve is out of phase with the global curve due to rebalance of water in the global ocean
- PTS changes and consequences for volume accumulated
- Interest for the contribution of dissolved gas: once out of solution it has higher mobility and move up

Geophysical evidences of the effect of the rapid sea level drop

A number of features like giant pockmarks and bright spots, discovered in 2-D and 3-D seismic data provide evidence for continuous gas emission throughout the Messinian.



(Fraser et al., 2011)

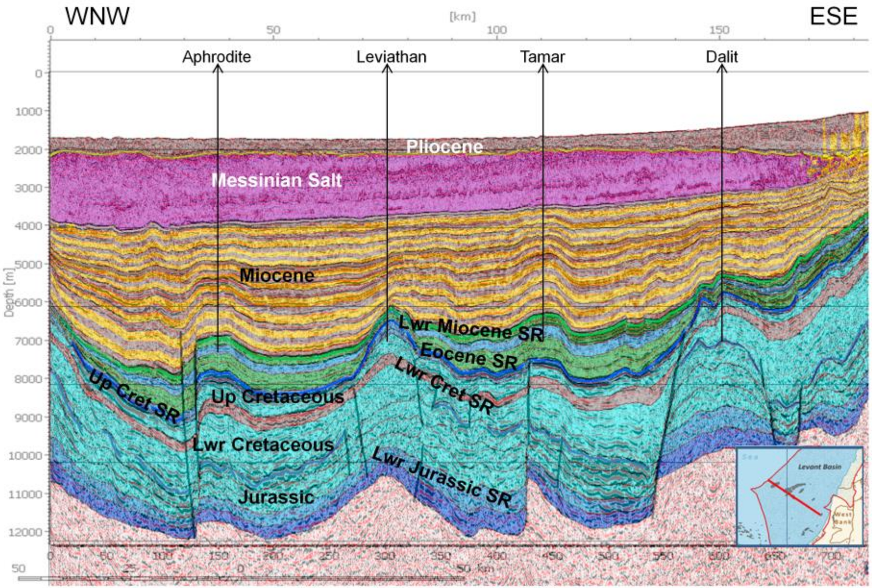


(Lazar et al., 2012)

Presenter's notes:

- When PVT in preexisting reservoir changes then phase composition changes
- Degasification can have same effect
- New high-resolution 3-D pre-stack depth migrated seismic reflection data show evidence for gas outflow stemming from pre-Messinian sources

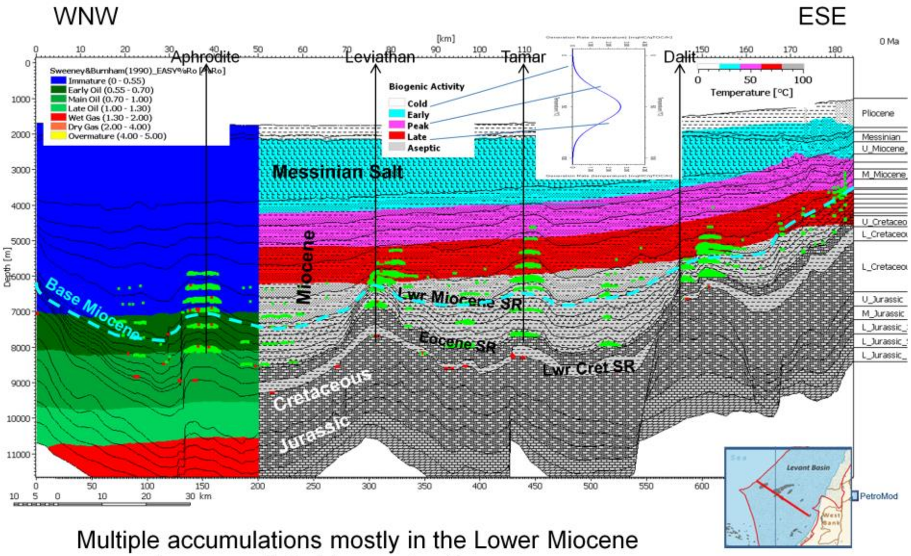
2D Model



Seismic data from Peace et al. 2012

Presenter's notes: Petromod 2D basin model for qualitative estimate of dissolved gas content evolution
The stratigraphic structure of the Levant Basin presents sequences of carbonate and siliciclastic deposits both from deep and shallow water environments.
PS elements

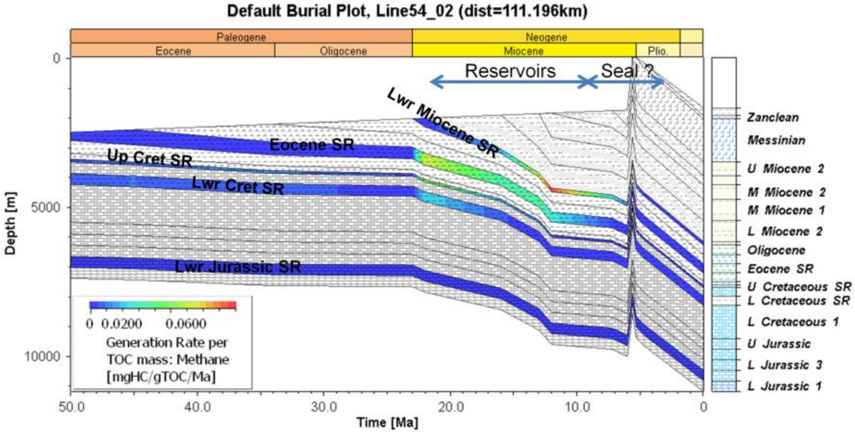
Biogenic maturity at present day



Multiple accumulations mostly in the Lower Miocene reservoirs as predicted by most authors.

Presenter's notes: Results of BM showing methane accumulation at present
Simulation using biogenic kinetics and dissolved methane component
Pseudo maturity zones for biogenic methane and comparison with Vitrinite scale

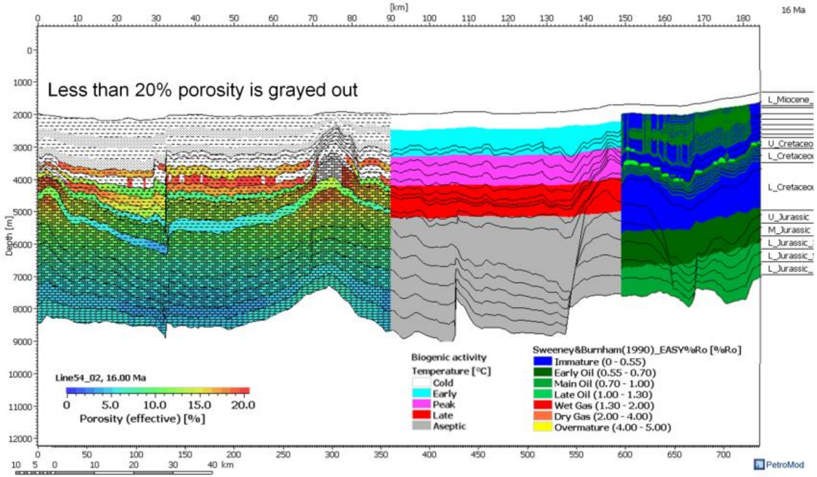
Burial and source generation history



All SR were mostly active during early Miocene ahead of the sea level drop.
Accumulations are therefore supplied mostly by post-generated gas.

Presenter's notes: Source generation activity: generation overlap with reservoir deposition
How was regarding seal?

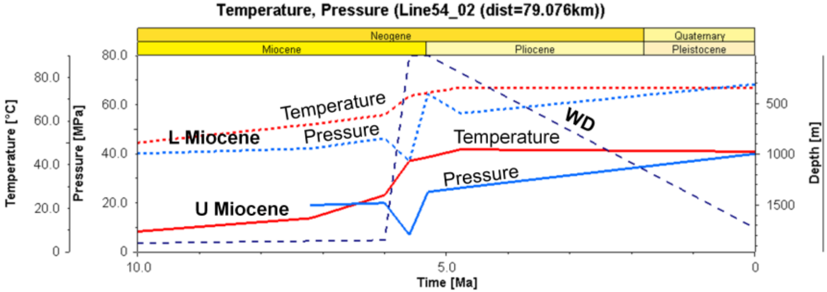
Seal formation vs source activity (16 Ma)

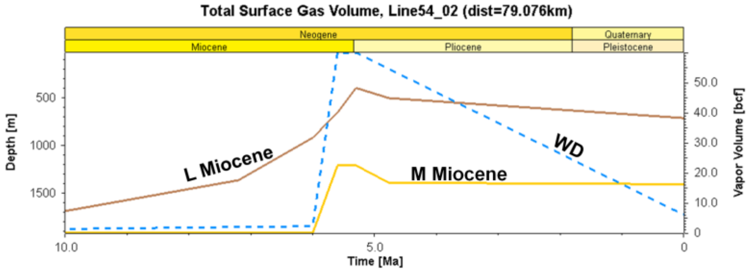


The gas generation window partially overlap with a zone situated above the 20% threshold porosity level required for probable competent seal.

Presenter’s notes: Section during Early Miocene showing the relation between generation window and seal formation
If we consider the 20% porosity threshold then gas generation windows peak just before seal is there
Different story will be if conventional kinetics will be used

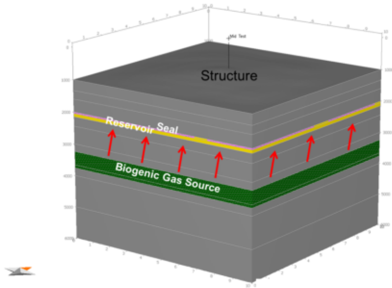
Effect of SL drop on various parameters at Leviathan location

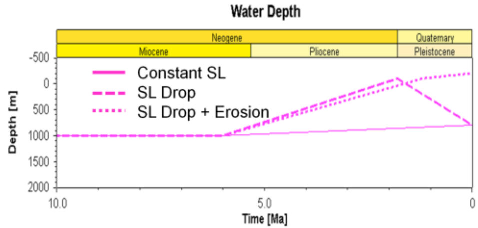




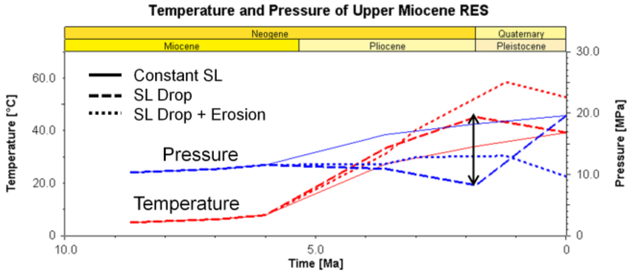
Presenter's notes: T, P evolutions for L and U Miocene during SL drop
Attenuation effect with depth visible
Gas is not accumulating steady, bumped up by the propagating effects of the SL drop

Synthetic 3D Basin Model



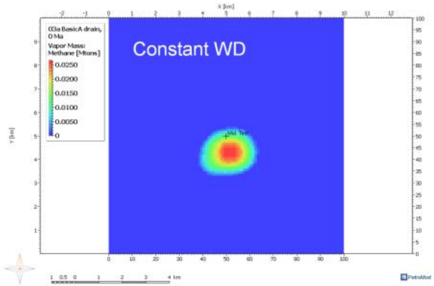


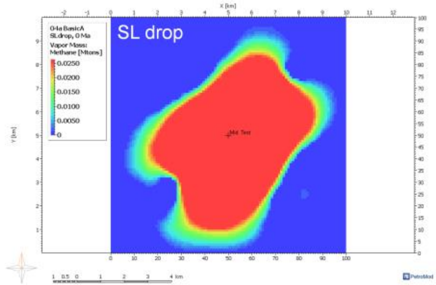
Three scenarios were simulated using a synthetic 3 D basin model in order to estimate the volumes of gas dissolved and accumulated

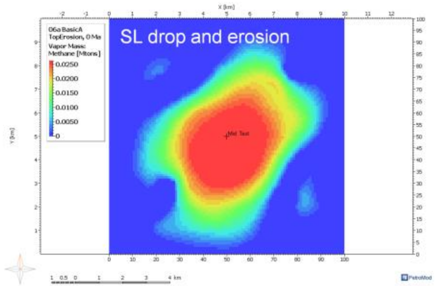


Presenter's notes: 3D synthetic model built to quantify the effect of SL drop on dissolved gas
100x100 km block
Same kinetics and dissolved gas run
Three scenarios simulated
The size of accumulation is given by the magnitude of the deviation of P,T condition down and up resp.

Accumulation on Upper Miocene Reservoir



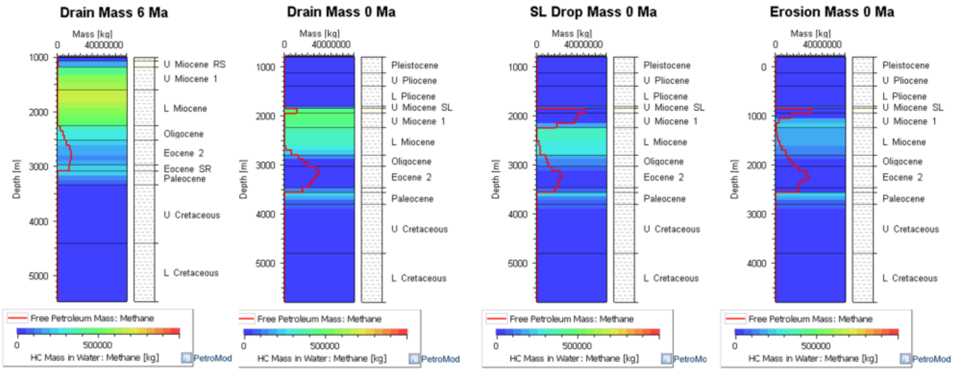




The scenario of sea level drop produces the highest mass of methane accumulated in model reservoir.

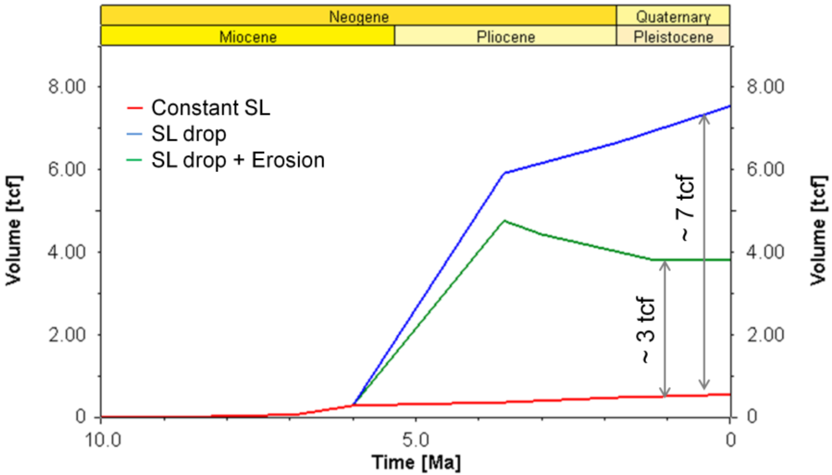
Presenter's notes: Maximum accumulation occur for SL drop scenario.

Final phase partition for methane



Presenter's notes: Illustration of the effect of the SL drop on the three scenarios

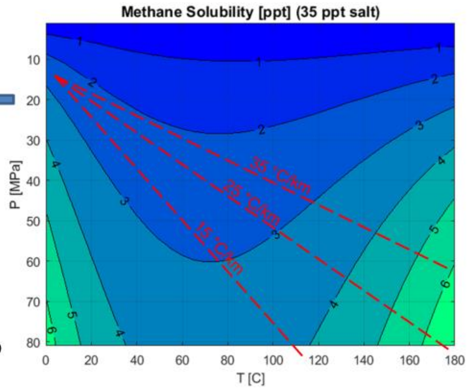
Reservoir accumulation history



Presenter's notes: Result of simulations: Calculations over the entire layer
Source generation: enhanced when higher temperature
Expulsion: low when less generated, high when high generated and less compaction
Migration balance: measure of efficiency – lost to surface
Migration loss:
Accumulation in reservoir: high for SL drop

The prediction of methane solubility in natural waters

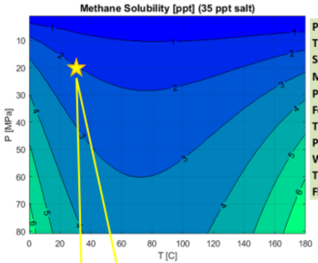
Pressure	20	*MPa*
Temperature	33.7	*C*
Salinity	35	*g/kg*
Methane Solubility	1.98E+00	*g/kg*
Porosity	31	*%*
Fetch Area	100	*km^2*
Thickness	1000	*m*
Pore Volume	3.10E+10	*m^3*
Water Density	1035	*kg/m^3*
Total Dissolved CH4	6.35E+10	*kg*
Flashed Volume	3129.45	*bcf*



- Model of *Duan et al., 1992* was numerically implemented in *Matlab* program.
- Methane solubilities in aqueous solutions are determined by the balance of its chemical potentials in the liquid phase and in the gas phase.
- These can be written in terms of fugacity in the vapor phase and activity in the liquid phase
- The fugacity coefficient of CH_4 in the vapor phase is calculated from the equation of state for pure CH_4.
- Model tested against experimental data.

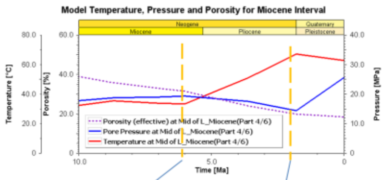
Presenter's notes: Numeric model implemented to calculate the effect of P, T changes but also salinity
Calculate CH4 Sol f(T,P,cNaCl)
Gradients shown
Probabilistic model in future development

Salinity effect



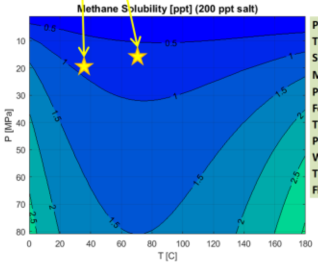
Pressure	20	MPa
Temperature	33.7	C
Salinity	35	g/kg
Methane Solubility	1.98E+00	g/kg
Porosity	31	%
Fetch Area	100	km^2
Thickness	1000	m
Pore Volume	3.10E+10	m^3
Water Density	1035	kg/m^3
Total Dissolved CH4	6.35E+10	kg
Flashed Volume	3129.45	bcf

3D model extraction



1393 bcf

1967 bcf



Isolated

Pressure	20	MPa
Temperature	33.7	C
Salinity	200	g/kg
Methane Solubility	9.47E-01	g/kg
Porosity	31	%
Fetch Area	100	km^2
Thickness	1000	m
Pore Volume	3.10E+10	m^3
Water Density	1200	kg/m^3
Total Dissolved CH4	3.52E+10	kg
Flashed Volume	1736.19	bcf

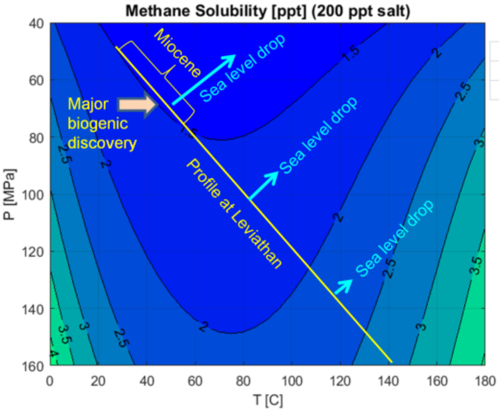
Coupled with P,T

Pressure	14.4	MPa
Temperature	67	C
Salinity	200	g/kg
Methane Solubility	6.34E-01	g/kg
Porosity	31	%
Fetch Area	100	km^2
Thickness	1000	m
Pore Volume	3.10E+10	m^3
Water Density	1200	kg/m^3
Total Dissolved CH4	2.36E+10	kg
Flashed Volume	1162.37	bcf

An increase in salinity from 35 ‰ to 200 ‰ reduces the solubility of methane to almost half.

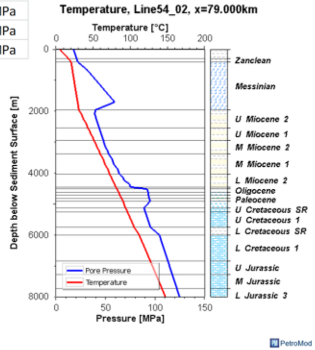
Presenter’s notes: Calculations when transition from one condition to other

Risk study application



30	C	53	MPa
60	C	77	MPa
141	C	162	MPa

Leviathan



The pressure temperature profile at Leviathan location reaches a minimum solubility zone over a location corresponding to Mid Miocene interval. A rapid sea level drop would determine a reduction of the solubility having the highest gradient along Miocene section. Major discoveries of biogenic gas accumulations have been found in about the same interval.

Presenter's notes: More gas out of solution when higher solubility gradient

Conclusions

- Volumes of gas temporarily trapped in water may represent a significant contribution to large commercial accumulations when rapid change of pressure / temperature conditions or salinity occurs.
- Simulation results on a idealized model showed that overall up to 70 bcf of free gas per square kilometer of fetch area was added to the trap when the water level dropped by 1000 m as compared to the case where sea level was kept constant. In the case when water drop was followed by 500 m of erosion only 33 bcf/km^2 of free gas was added to the system compared to the nominal case.
- These findings can be further applied to explain volumetrics of known commercial accumulations of biogenic gas in general like is the case of Miocene discoveries in the Levantine basin of Eastern Mediterranean following on a study that may involve a 3D basin modeling of the area.