

ON THE LACK OF WIDESPREAD BOTTOM SIMULATING REFLECTORS IN THE MEDITERRANEAN BASIN

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The purpose of this study was to calculate the depth of the base of Methane Hydrate Stability Zone (**MHSZ**) as function of temperature, pressure and salinity and the base's depth anomaly induced from a salinity variation.

Two areas of the Mediterranean basin are compared, the eastern and the western part. Those basins, Alboran-Balearic, and the Levantine one has been chosen cause they represent geodynamic end members of the Mediterranean sea.

In this presentation, each of the numerical and graphical slide is anticipated by a text slide.

Natural Gas Hydrates (NGH) are solid compounds composed by 85% of water and 15% of a natural gas (Sloan et al, 1998). The major quantity of NGH are composed by CH_4 so they are called Methane Hydrate (MH).

The water molecules (host) form a cage structure with empty spaces inside each cage that is filled with a gas molecule (guest), *figure 1* and *2*.

The amount of methane hydrate created is defined by *equation 1*.

These compounds have the same mechanical and rheological properties of ice.

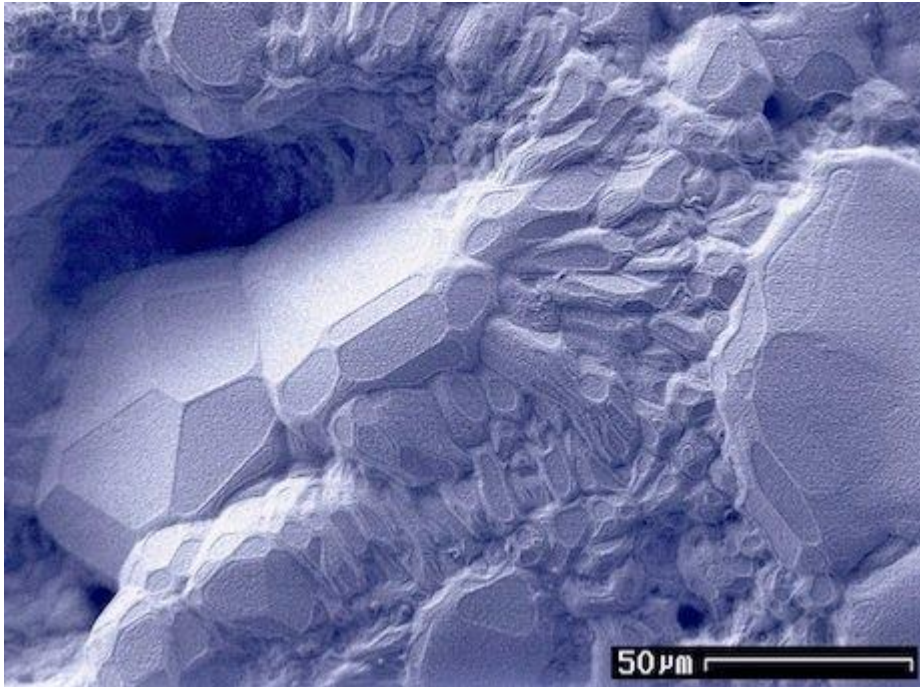


Figure 1
Methane hydrate crystals – cryogenic SEM images
Source: L. Stern / USGS

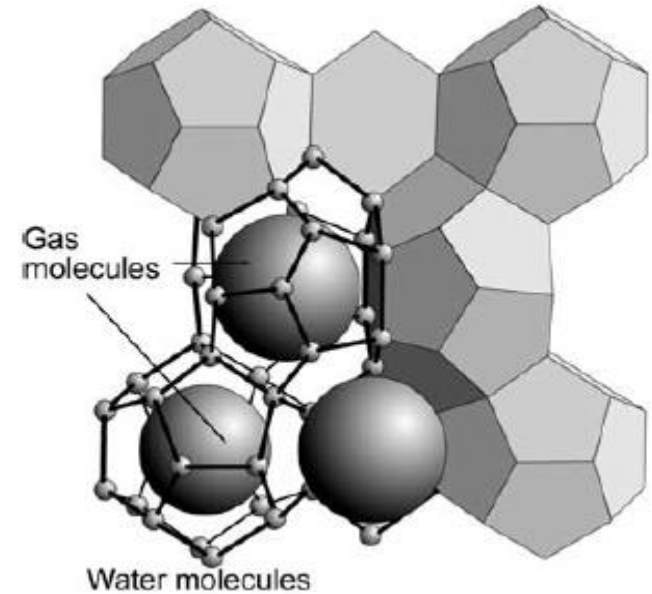
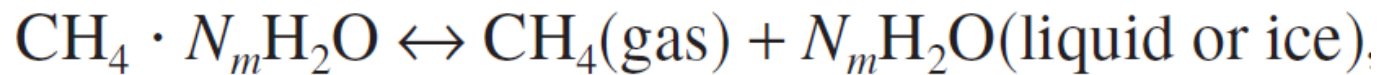


Figure 2
Gas Hydrate of structure I.
Bohrmann & Torres, 2006



Equation 1

N is the hydration number and 'm' indicates methane – Moridis 2014

Understanding the stability conditions is necessary to define depth and thickness of Methane Hydrate Stability Zone (MHSZ). Typically MH are stable at low temperature and high pressure, but chemical composition of the gas and salinity of interstitial water are influencing factors too (*figure 3*).

The existence of a MHSZ is a requirement for MH formation, and that at least a part of MHSZ thickness coincides with an appropriate reservoir is necessary for MH preservation. If the GHSZ falls in the water column the MH can properly form but, due to its density lower than water, it will rise to minor depth and, reached the upper limit of MHSZ, it will dissociate.

$$T_s = \left[\frac{1}{T_w} - \frac{n_H \Delta H^f}{\Delta H^0} \left(\frac{1}{273.15} - \frac{1}{T_{fs}} \right) \right]^{-1}$$

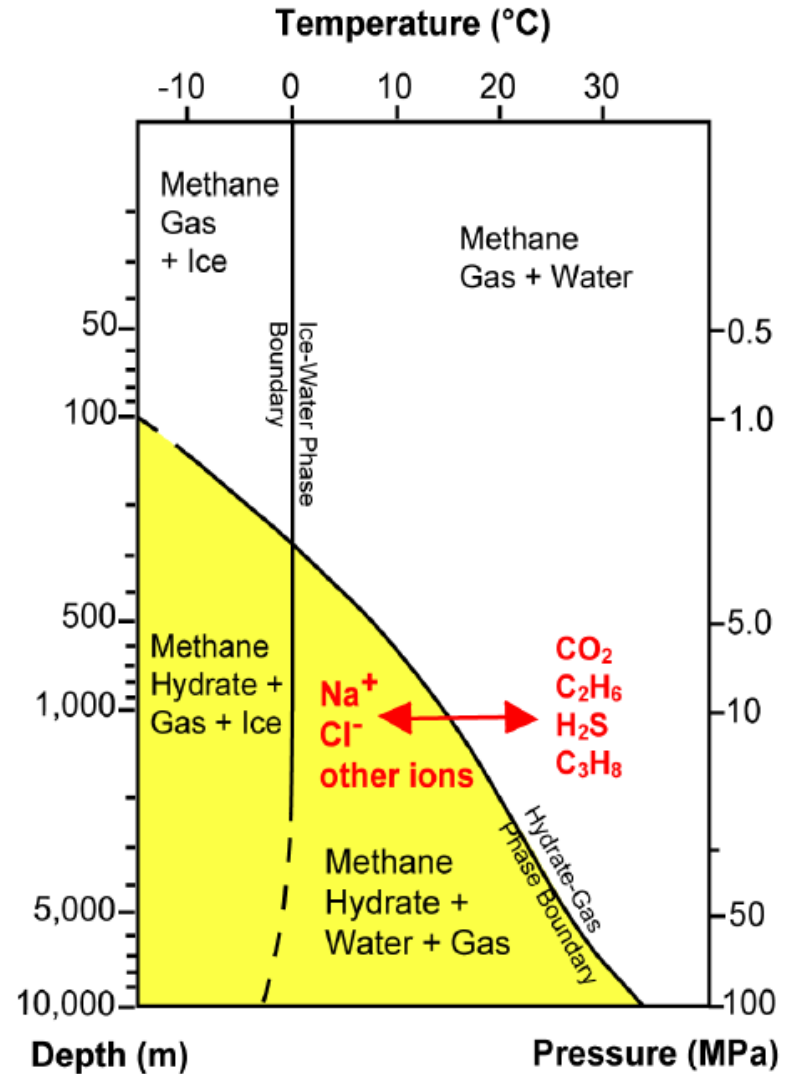
Equation 2 -

The dissociation temperature function of salinity

Moridis, 2014

Figure 3- Phase diagram of Methane Hydrate. Yellow area represents the stability field.

Bohrmann & Torres (2006)



As a consequence of Messinian Salinity Crisis (MSC) approximately 6 millions years ago large and thick deposits of evaporites were deposited in the Mediterranean basin.

The eastern part of Mediterranean sea has thicker sedimentary cover and an older and colder lithosphere than the western part. This is reflected in a large difference between the geothermal gradient of the two areas.

21 sites within the areas of interest have been selected from DSDP and ODP drilling expeditions. Their location is shown in *figures 4 and 5*.



ODP				
LEG	SITE	HOLE		
160	967	A		
	968	A		
	966	A	D	E
	965	A		
161	975	B	C	
	976	B	C	D
	977	A		
	978	A		
	979	A		

DSDP				
LEG	SITE	HOLE		
42	376			
	375			
	371			
	372			
13	121			

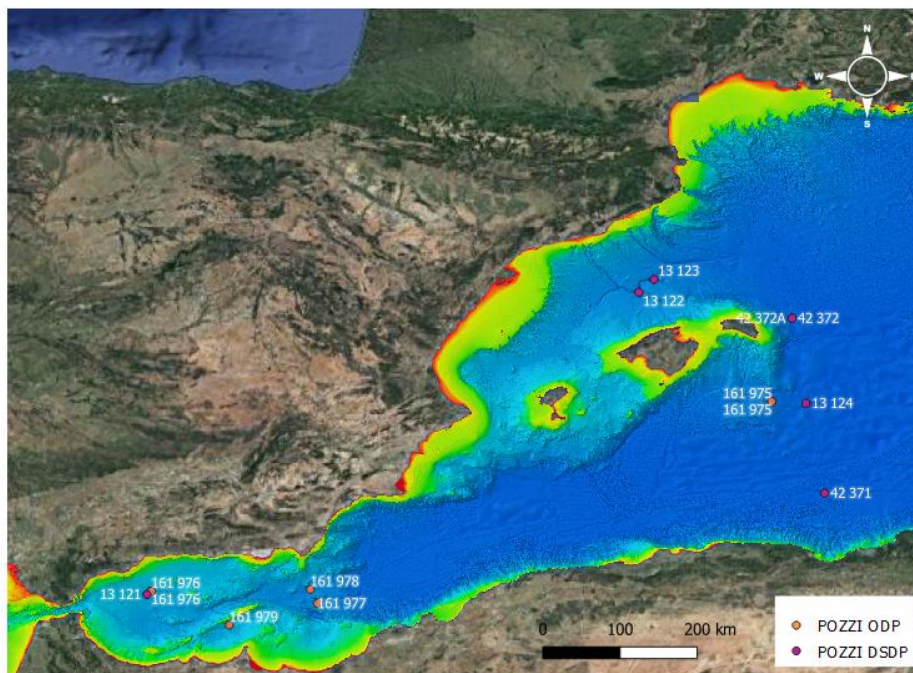


Figure 4

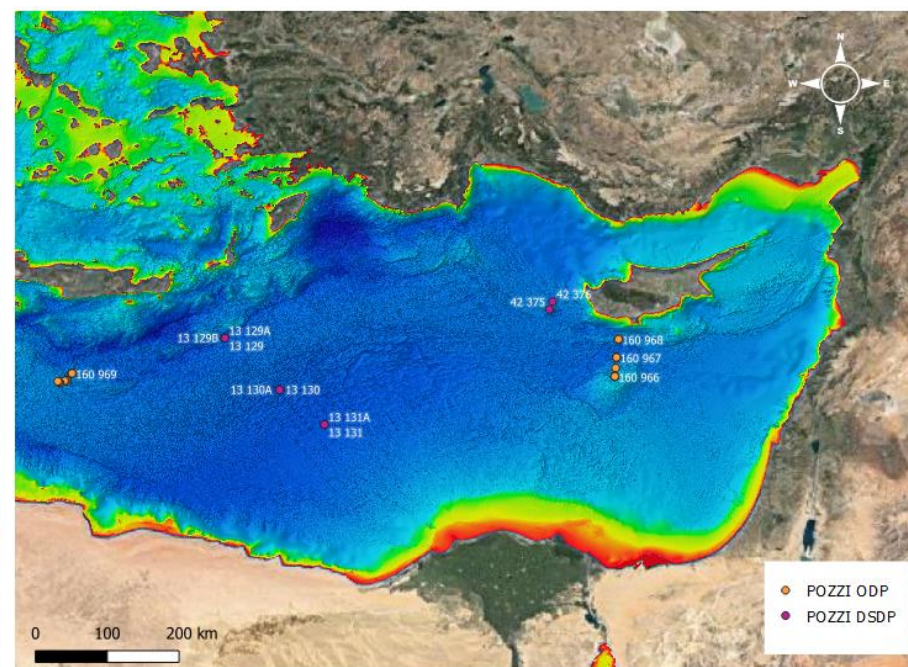


Figure 5

From all the sites considered we extracted available data of pore-water salinity, and available information on bottom water temperature and expected geothermal gradient.

With an algorithm in C++ language, we calculated the hydrostatic pressure in each sampled point and starting from Moridis' equation (equation 3) the stability pressure of MH.

The stability pressure in each point is defined as the minimum pressure with specific boundary conditions of temperature and salinity so that methane hydrates are stable.

Input data:

- Salinity (ppm)
- Temperature (°K)
- Bathymetry (m)

$$P = e^{(-C(1)+C(2)*T-C(3)*(T^2)+C(4)*(T^3)-C(5)*(T^4)+C(6)*(T^5))}$$

c(1)=1.94138504464560d5

c(2)=3.31018213397926d3

c(3)=2.25540264493806d1

c(4)=7.67559117787059d-2

c(5)=1.30465829788791d-4

c(6)=8.86065316687571d-8

Equation 3
Moridis (2014)

Output data:

- Hydrostatic pressure (MPa)
- Stability pressure (MPa)

In the following slides we illustrate one example of the results obtained for all sites.

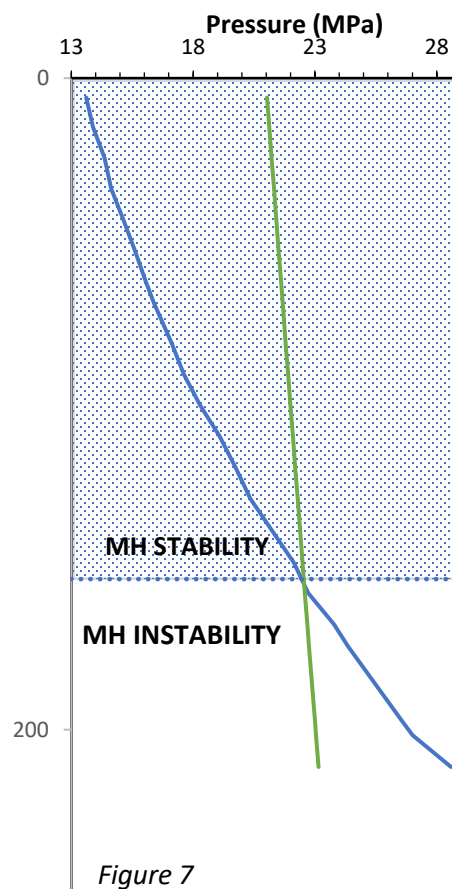
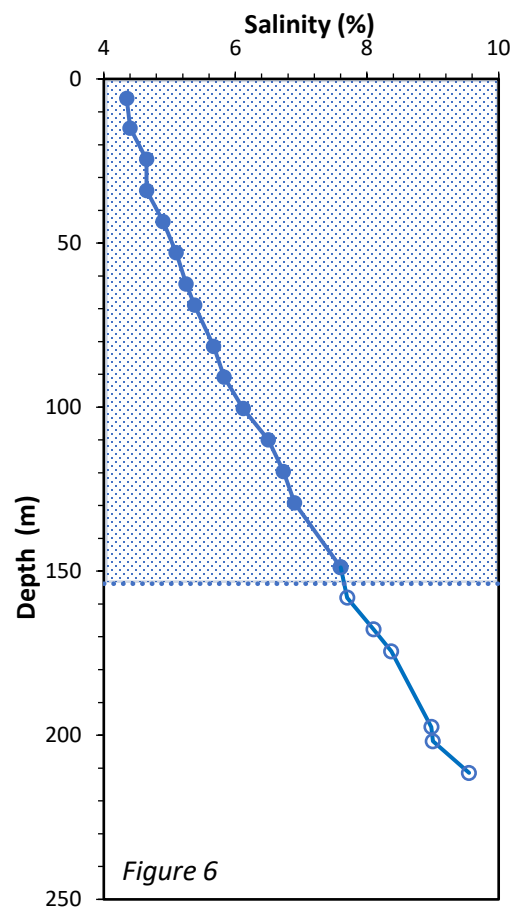
Figure 6 represents the salinity function with depth; *figure 7* represents stability and hydrostatic pressures as a function of depth. The dotted area is the calculated MHSZ.

When the MHSZ base was not reached using the available data, values have been extrapolated using a linear function for hydrostatic pressure and a logarithmic function for the stability pressure.

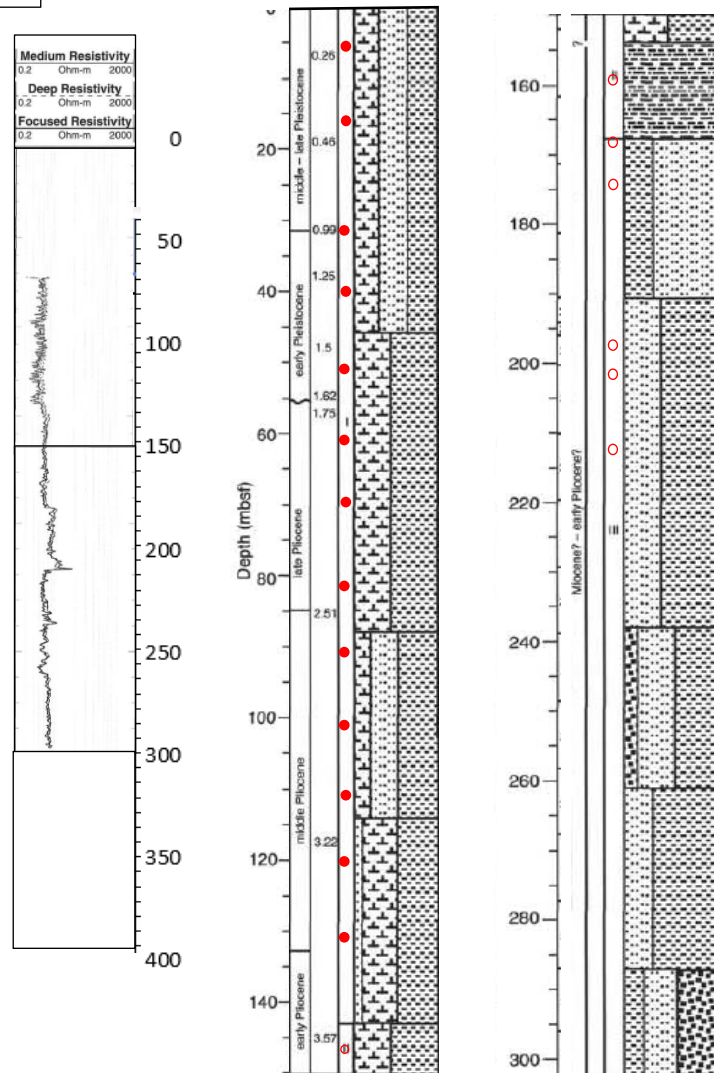
Once we defined the MHSZ for each site, resistivity data were analysed to look for anomalies that could be induced from MH presence. No relevant anomalies have been observed.

ODP 160_968_A

Bathymetry: 2067 m
Geothermal gradient: 15.74 °C/Km
Seafloor temperature: 13.6 °C



 MHSZ



Salt in interstitial water is an inhibiting factor due to the stronger affinity that water has to ions instead of hydrate structure. The effect that salinity has in the hydrate stability is quantified in the change of the equilibrium dissociation temperature at a given pressure (equation 2).

To evaluate the effect of salinity on the dept of the MHSZ base, the estimate of stability pressure has been made with a virtual salinity of 38.5 ‰, approximately the seafloor one, and as a consequence a new base depth of MHSZ has been calculated (*Table 1, yellow column*).

-  MHSZ base with real salinity data
-  MHSZ base with virtual salinity of **38.5 ‰**
-  MHSZ base falling in seafloor sediments

	Leg	Site	Hole	Bathymetry (m)	Geothermal gradient (°C/km)	MHSZ base depth (m) at real salinity	MHSZ base depth (m) at constant salinity	Number of sampled point for each well
EASTERN MED. SEA								
	160	966	A	926	25.06	-196.74	/	3
	160	966	D	926	25.06	-147.36	/	8
	160	966	E	926	25.06	-149.8	-119.1	3
	160	967	A	2553	22.13	201.36	257.17	14
	160	968	A	1961	15.74	153.84	290.25	21
	42	375		1849	25.93	82.95	88.996	2
	160	965	A	1506	24.21	57.7	56.891	2
	42	376		2107	26.06	153.04	154.493	6
WESTERN MED. SEA	161	976	B	1108	72.1	-23.04	-28.019	19
	13	121		1147	72.38	-12.97	/	3
	161	976	C	1108	73.69	-10.73	/	5
	161	976	D	1107	72.11	-16.62	/	18
	161	979	A	1062	105.19	-39.63	/	23
	161	975	C	2415	67.45	81.81	81.554	7
	161	975	B	2415	67.45	85.52	85.172	9
	42	371		2795	83.42	71.87	86.909	6
	42	372		2657	79.52	54.5	62.131	10
	161	977	A	1984	86.27	43.48	41.893	23
	161	978	A	1929	87.79	23.023	293.485	15

Table 1

We analysed the difference in expected MHSZ base depth between the ‘real salinity’ case and the virtual salinity (sea bottom salinity) case. Such difference is highly variable. In all cases removing the MHSZ base moves deeper when the the effect of salinity is removed (*figures 8, 9*).

This phenomenon reflects a thinning of the MHSZ when the effect of high salinity interstitial water is considered.

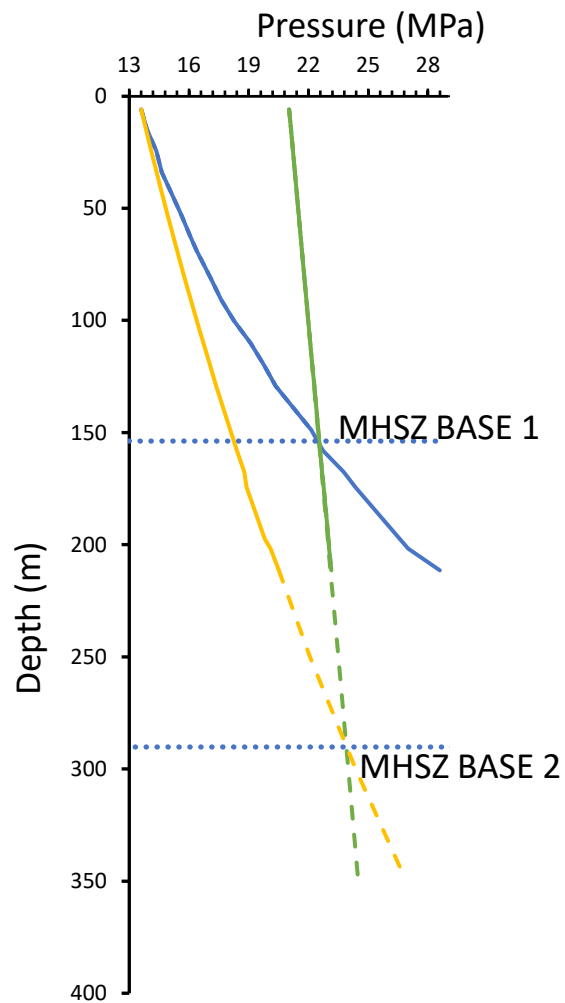
ODP 160 968 A
Eastern Med.

Figure 8

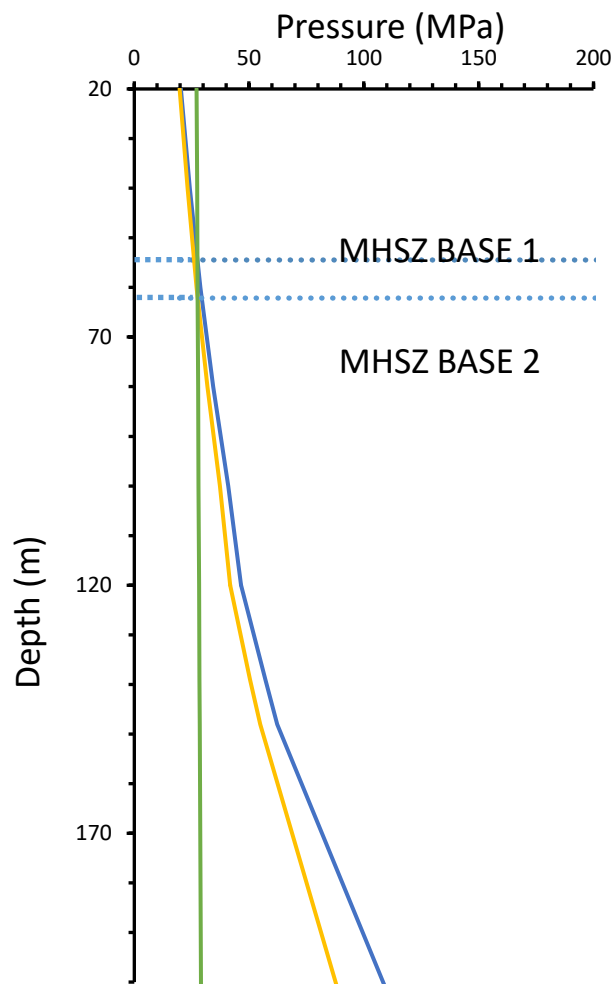
ODP 42 372
Western Med.

Figure 9

- Hydrostatic pressure
- Stability pressure with real salinity data
- Stability pressure with virtual salinity data

The results from all sites are plotted in a two-dimensional graph where the MHSZ base depth is x-axis, (zero set at the seafloor) and bathymetry is the y-axis.

The left part of the graphs contains the MHSZ base that falls in the water column, the right part in the seafloor sediments.

In the right part, two groups of points, one for the western and one for the eastern Mediterranean, reflect the different geothermal gradient of the two basins. Both groups are split into 2 sub-groups representing the MHSZ base position at real and virtual salinity. The extrapolated line to the zero depth of the MHSZ identifies approximately 1130 m as the minimum water depth for which at least partially MHSZ falls in the seafloor sediments.

Extrapolated lines of the group points in the right are virtual and forced to pass through the intercept defined at 1130 m.

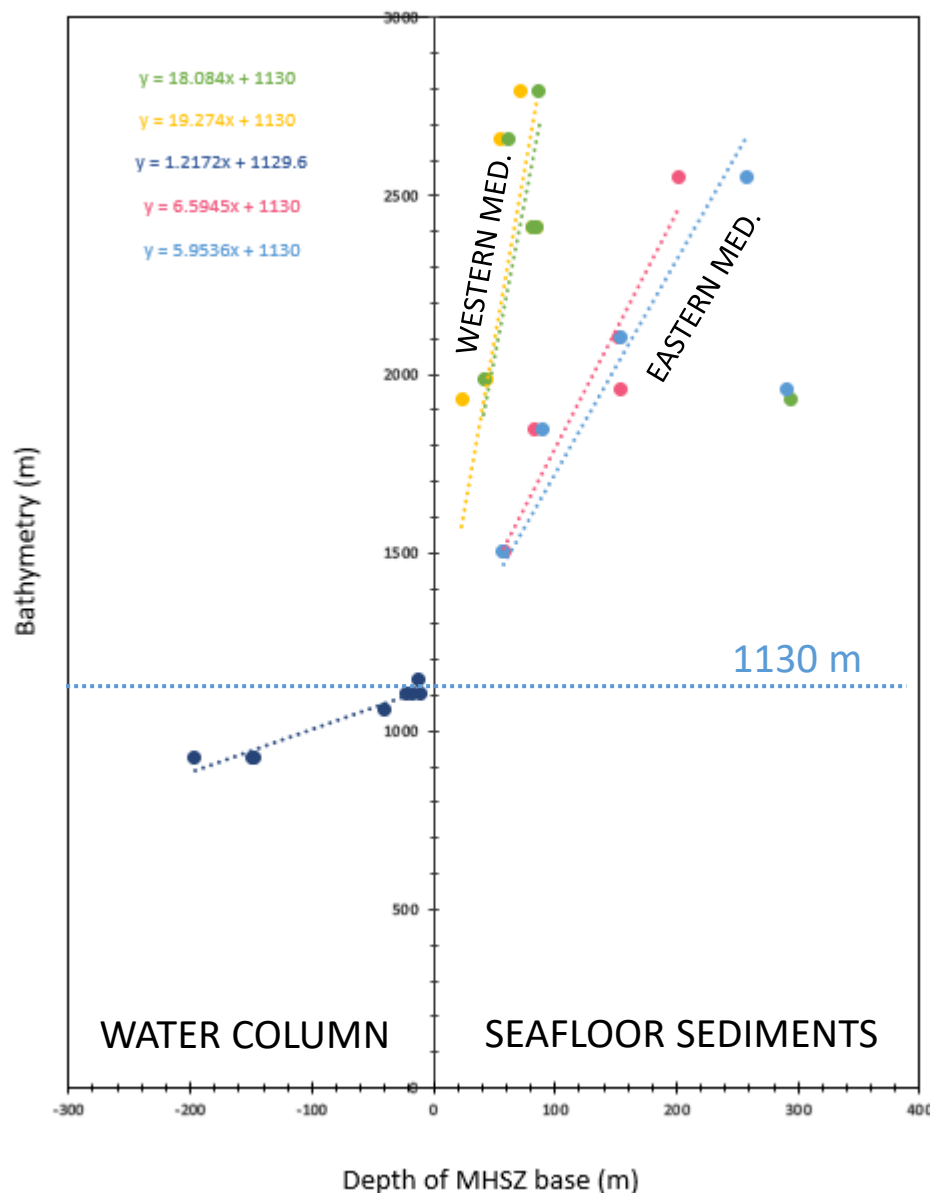
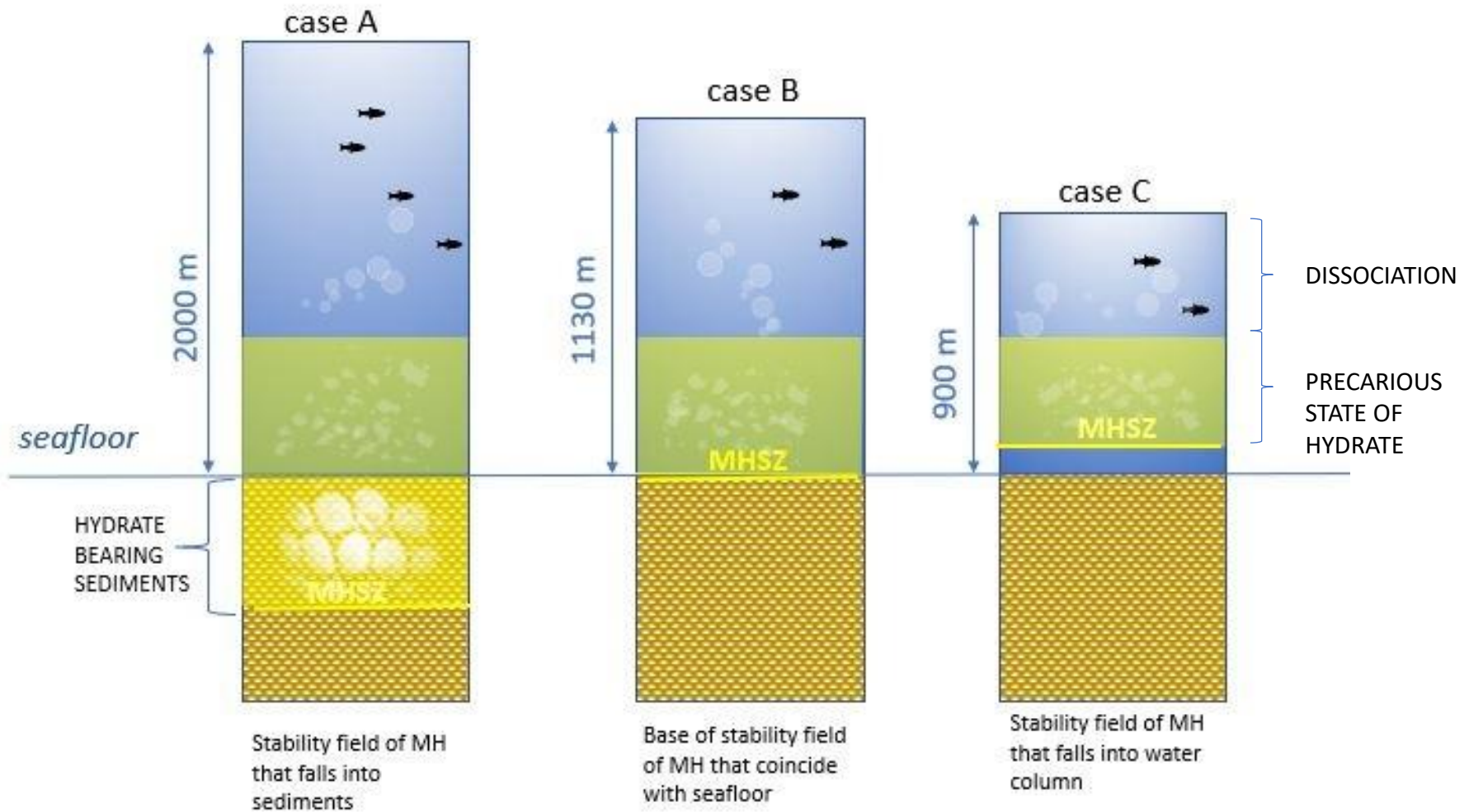


Figure 10- depth of MHSZ base function of Bathymetry

The relationship between depth of MHSZ and bathymetry in the previous graph is similar for the Western and Eastern Mediterranean Basins, reflecting a rather similar structure of the water column.

1130 m is identified as the water depth below which MHSZ falls in the water column and beyond which MHSZ falls into seafloor sediments. Only in the second case, MH can potentially be preserved.

The top of MHSZ falls in the water column at approximately at the same depth in all sites



Noticeably, the difference between the real and virtual MHSZ base is smaller in the Western than in the Eastern Mediterranean.

This effect is due to different effect that salinity and temperature have on the MHSZ base depth. Because temperature is the major influencing factor, in the western Mediterranean, where the geothermal gradient is up to three times higher than that of the eastern part, the effect of salinity is less appreciated.

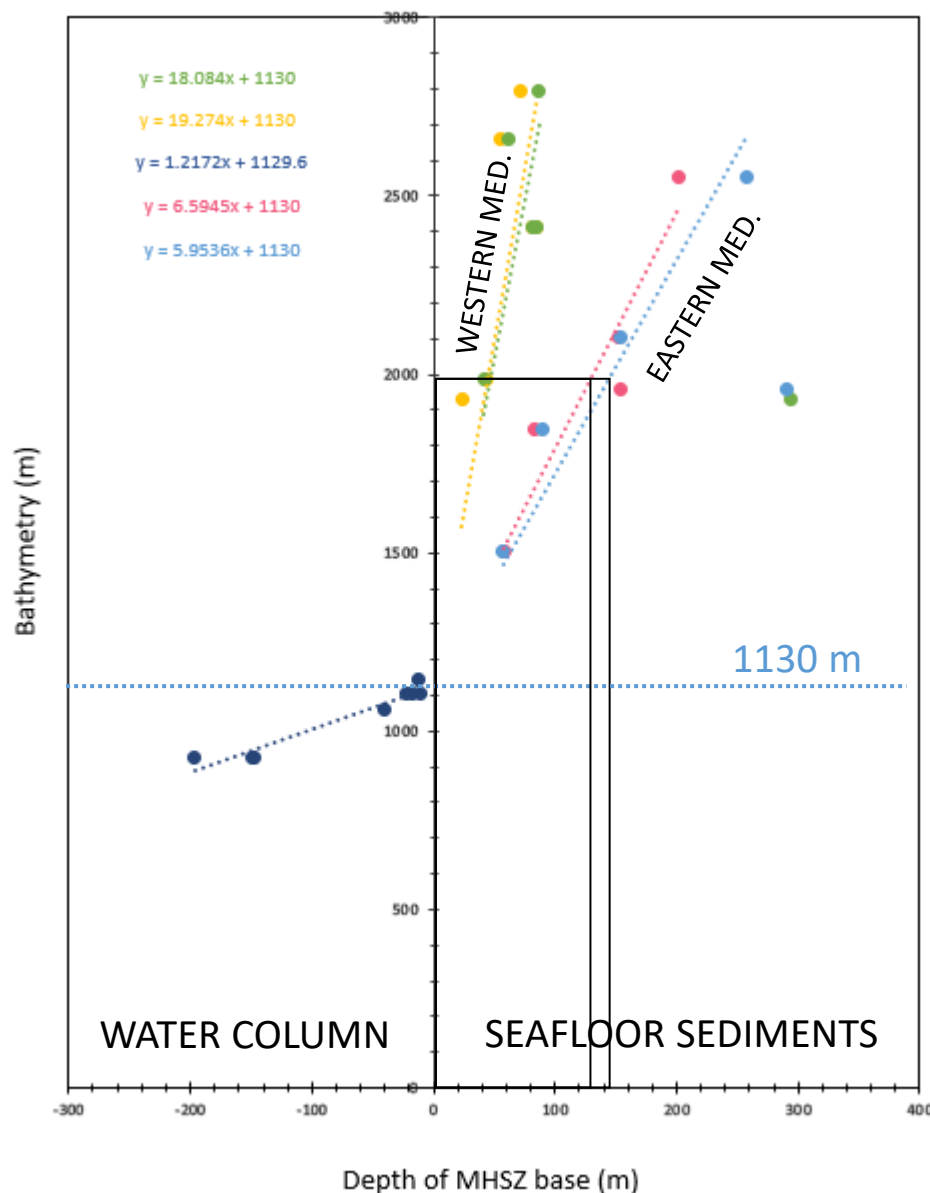


Figura - profondità del campo di stabilità degli idrati di metano in funzione della batimetria

Biogenic methane productions was analysed in all sites.

Biogenic methane is produced by methanogenic archaea. Their metabolism is compatible only with an anoxic environment where even the oxygen contained in sulphate ions has been reduced (*figure 10*).

‘The Methane production zone’ starts where ‘sulphate reduction zone’ ends.

By analysing ion sulphate concentration in interstitial water we found that for more than an half of the sites methane production zone is not reached. In some cases this is due to the high concentration of sulphate ions due to upward diffusion of ions from evaporitic deposits.

Only in 2 sites, in the Alboran basin, the methane production zone intersects at least partially the MHSZ (*table 2*).

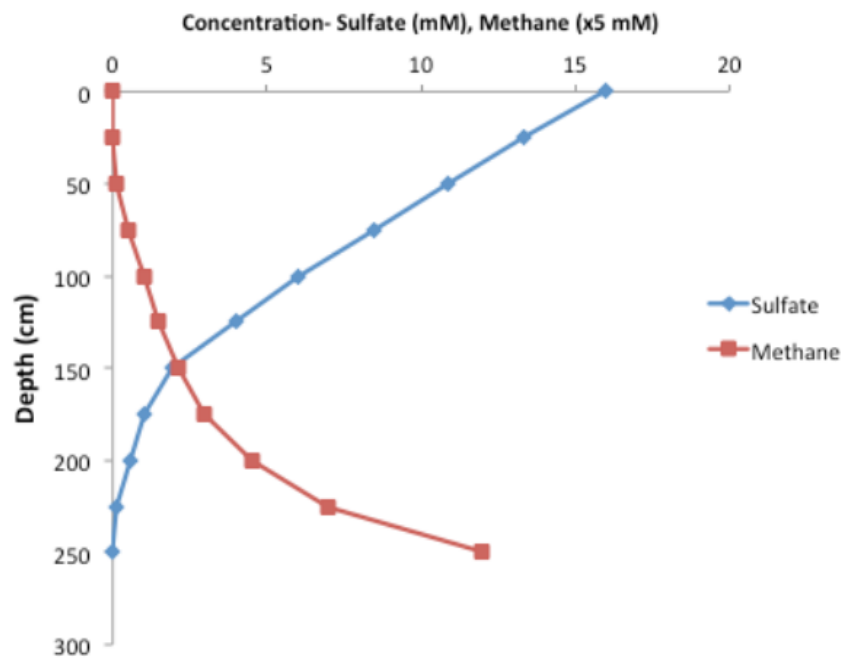


Figure 10 – concentration profile of sulphate and methane. Black Sea. B.B. Jorgensen et al. (2001)

Table 2. Summary table of sites where the methanogenic zone coincides with the stability field

SITE	Sulphate-reduction	Intersection between MHSZ and Sulphate-reduction zone
160_967	○	--
160_968	○	--
160_966	○	--
160_965	○	--
161_975	○	--
161_976	●	No
161_977	●	Yes
161_978	●	Yes
161_979	●	No
13_121	--	--
42_371	--	--
42_372	--	--
42_375	--	--
42_376	--	--

- Ongoing Sulphate-reduction
 ● Depleted Sulphate-reduction

- 1) 1130 m water depth is identified as the **theoretical bathymetric minimum** to for MHSZ existence in Mediterranean sea sediments.
- 2) A **linear trend represents the MHSZ base as a function of bathymetry** for realistic values of interstitial water salinity
- 3) A **MHSZ base's depth anomaly** induced by the positive anomaly of salinity observed in the wells has been identified for all sites.
- 4) Except for sites in Alboran basins where methanogenesis is an active process, the **boundary conditions for biogenic methane production are not an active process** in the MHSZ.

Bohrmann, Gerhard, e Marta E. Torres. «Gas Hydrates in Marine Sediments». In *Marine Geochemistry*, a cura di Horst D. Schulz e Matthias Zabel, 481–512. Berlin/Heidelberg: Springer-Verlag, 2006. https://doi.org/10.1007/3-540-32144-6_14.

Jørgensen, Bo Barker; Weber, Andreas; Zopfi, Jakob (2001-08-01). "Sulfate reduction and anaerobic methane oxidation in Black Sea sediments". *Deep Sea Research Part I: Oceanographic Research Papers*. **48** (9): 2097–2120. [doi:10.1016/S0967-0637\(01\)00007-3](https://doi.org/10.1016/S0967-0637(01)00007-3). ISSN 0967-0637.

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