Supplemental Material

DATA AND METHODS

The Moridis' 2014 equation governing methane hydrate stability pressure as function of water temperature and salinity (Moridis, 2014) has been used to calculate whether a state of equilibrium exists between a free gas-seawater mixture and gas hydrate at each point for which temperature and salinity data are available. We simulate the stability of methane because this is the most abundant hydrocarbon gas known in the Mediterranean basin.

Input variables are in situ salinity and temperature. From those parameters, the density of water and the hydrostatic pressure have been calculated. This model has been selected because the input salinity variable is considered in the equation of state, thus allowing effective calculations with variable salinity downhole.

At each point a stability pressure exists or does not exist. Across the boundary between two points identifying the change of equilibrium (top or bottom of the MHSZ) the stability pressure has been linearly interpolated and the equilibrium change is identified with the intersection of the hydrostatic pressure curve with the linear interpolation.

The same model used for the water column was run also from sea level to the total penetration depth of 44 DSDP and ODP boreholes so that both top and bottom of MHSZ were identified.

Mediterranean Water Mass Model

Data

The seafloor of the Mediterranean basin is constrained by a 100x100 m cell resolution EMODNET bathymetric dataset providing an equal resolution hydrostatic pressure field (https://emodnet.eu/en/bathymetry).

3D data of the water column salinity and temperature comes from the free Copernicus Marine Environment Monitoring Service (CMEMS, https://marine.copernicus.eu/). CMEMS is a public model of circulation, thermophysical and chemical characteristics of water masses. The CMEMS product named MEDSEA_MULTIYEAR_PHY_006_004 has been used, providing the re-analysis of the physical state of the Mediterranean Sea, expressed in 3D monthly mean fields of potential temperature and salinity covering the period from 1987 to 2019 in a grid with a horizontal resolution of 1/24° (~4.5 km). The data are available from the surface to the maximum water depth of the Mediterranean organised in 141 vertical levels. To better represent the major variations of thermo-haline properties of the water masses, the thickness of the 141 levels increases from the sea surface seafloor to the sea bottom from metres to hundreds of metres.

The data used for the water mass model are from 1st January 1995, the closest time date to the ODP Legs 160, 161 that provide most of the borehole data.

The Mediterranean water mass model of methane hydrate stability is described by a 3D volume of 142,882 nodes with a horizontal resolution of 1/24° and a variable vertical resolution given by the thickness of the Copernicus depth levels. The Moridis (2014) equation was run for all the vertical steps of each element of the horizontal grid, from the mean sea level height to the seafloor.

Accuracy

The accuracy of the Mediterranean water mass model has been quantified by performing the uncertainty propagation of the input primary variables. One element of the grid for each Mediterranean basin (fig. 1A) has been analysed to better estimate the average error of the model. Uncertainty values are supplied in the Quality Information Document (QUID) section of the product (Supplementary Information Table T2).

The maximum error of the depth of the top of the MHSZ (fig. 1A and Supplementary Information Plates P1 and P2) is 1.45% in the Herodotus-Levantine basin, corresponding to a maximum depth variation of ±19 metres.

Borehole Models

Data

In the subsurface, the input primary variables were pore water salinity and in situ temperature measurements. Of the 46 DSDP/ODP sites drilled in the Mediterranean, salinity values are available for 38 sites (44 holes) (http://deepseadrilling.org/index.html; http://www.odplegacy.org/samples_data/). When absent, in situ temperature values were calculated from the interpolated (Kriging method) geothermal gradients extracted from 'The Global Heat Flow Database' (http://ihfc-iugg.org/). When not available, seafloor temperature and salinity were taken from the *Perseus* database (https://isramar.ocean.org.il/perseus_data/), collecting scientific cruise measurements from the years 80' to the present, when these reached the Mediterranean Deep Water. Otherwise, data was taken from the CMEMS database.

To prioritise, in this case, temperature and salinity measurements instead of values from circulation models such as CMEMS, water column salinity and temperature overlying each well location have been taken from the *Perseus* database. The temperature and salinity measurements of the water column closest to each well location have been extracted and resampled to 1 data value every 2 decibars of depth pressure in the upper 300 m, and 1 data sample every 10 decibars for deeper water.

Accuracy

Also in the case of the boreholes model the accuracy has been quantified by performing the uncertainty propagation of the input primary variables. One borehole in each Mediterranean basin (fig. 1A) has been analysed to better estimate the average error of the model.

Temperature and salinity data in the water column above each site selected from the *Perseus data base* has originated from CTD probes measurements. We assume the instrumental error of the calibrated CTD probes: Temperature ± 0.002°C and Salinity 0.002 ppt, both considered to be negligible for our purpose.

In DSDP and ODP expeditions downhole temperature measurements were collected with the Down-hole Temperature Instrument (DTI) and the ADARA tool respectively, both with an instrumental error of 0.1°C (*31, 32*). Pore water salinity, measured with a Goldberg optical hand-held refractometer, is affected by an instrumental error of 1 % (*33*).

The resulting maximum error of the depth of the base of the MHSZ (Figs. 2 and S1) is 0.43% and is in the Herodotus-Levantine basin, corresponding to a maximum depth variation of +9 and -4 metres.

Model sensitivity to Subsurface Brines

To evaluate the contribution of the pore-water salinity anomaly to the base of MHSZ the model was run for all DSDP and ODP sites also with constant pore water salinity equal to the bottom water salinity, while temperature values were kept unchanged. Therefore, each modelled value of the base of MHSZ is presented as a pair of values, one corresponding to the real in-situ salinity and another corresponding to the virtual salinity equal to the bottom water. The difference between the two is the anomaly induced by the presence of subsurface brines (Fig. 4).

A fully synthetic case has been analysed with the following constraints and seafloor depth 2730 m (representing the abyssal depth of the Western Mediterranean basin):

1. low geothermal gradient: 10°C/km; constant pore water salinity = bottom water salinity: 38.45 ppm.
2. low geothermal gradient: 10°C/km; linear (diffusive) pore water salinity gradient:300 ppm/km.
3. high geothermal gradient: 100°C/km; constant pore water salinity = bottom water salinity: 38.45 ppm.
4. high geothermal gradient: 100°C/km; linear (diffusive) pore water salinity gradient: 300 ppm/km.

Figure S1 Caption

Figure S1. Model results of the subsurface depth of the base of the MHSZ in all boreholes with and without subsurface brines. mbsl=meters below sea level; mbsf=meters below seafloor. The maximum error of the depth of the base of the MHSZ is 0.43% in the Herodotus-Levantine basin, corresponding to a maximum depth variation of +9 and -4 m (see Supplementary Information Data and Methods for details). Abbreviations for Mediterranean sub-basins follow the terminology of figure 1. A) Model results subdivided by geothermal structure of the subsurface. High geothermal gradient basins (blue) versus low geothermal gradient basins (green). Note the marked thicker subsurface MHSZ and larger anomaly induced by subsurface brines in the old, geothermally cold basins of the Eastern Mediterranean. B) Same data as A) indicating the sub-basins with the same colour code as in figure 1. The numerical results are reported in Table S1.

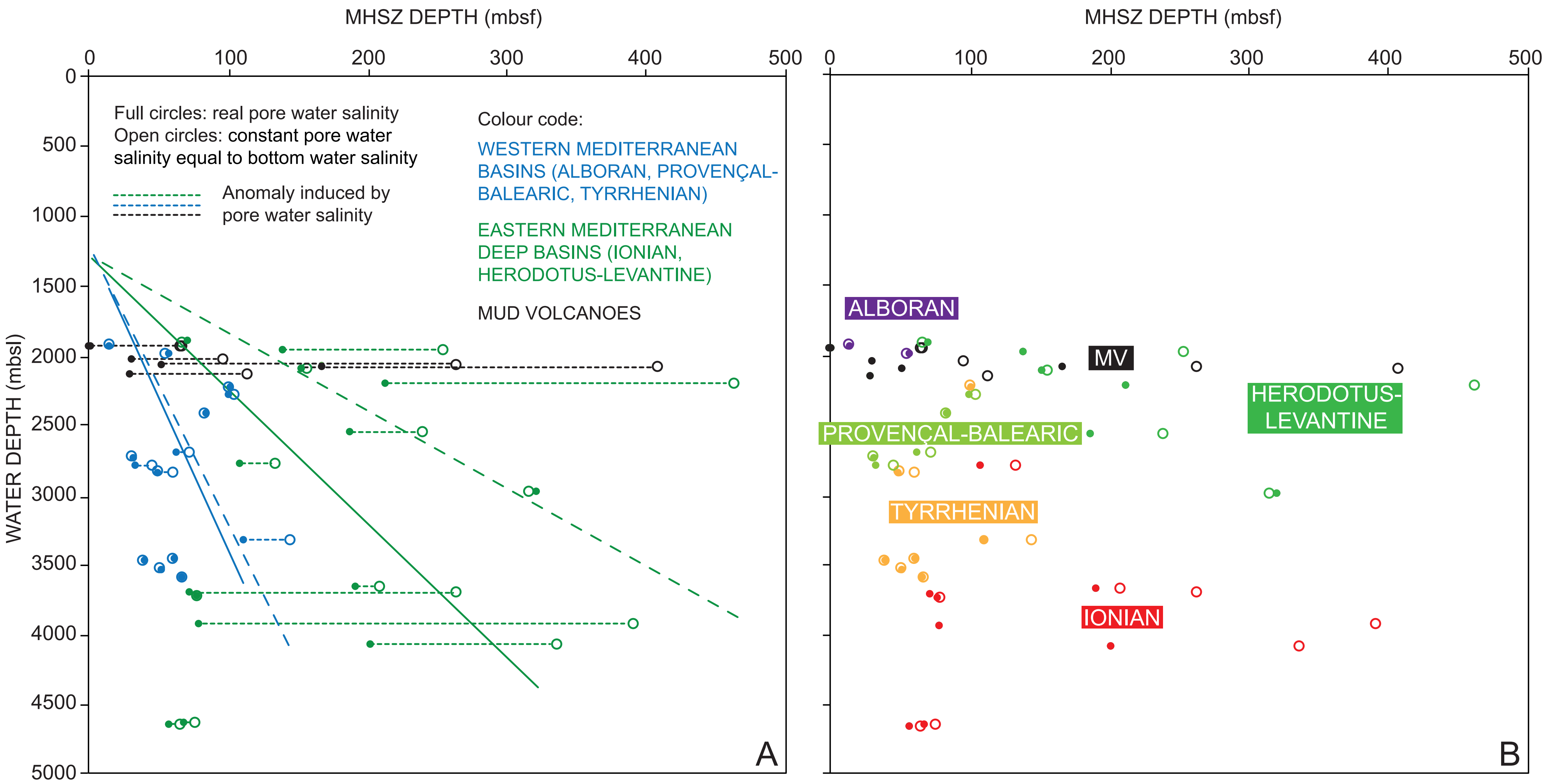
MHSZ DEPTH (mbsf)
0
100
200
300
400
500
WATER DEPTH (mbsl)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Full circles: real pore water salinity
Open circles: constant pore water salinity equal to bottom water salinity
Anomaly induced by pore water salinity
Colour code:
WESTERN MEDITERRANEAN BASINS (ALBORAN, PROVENÇAL-BALEARIC, TYRRHENIAN)
EASTERN MEDITERRANEAN DEEP BASINS (IONIAN, HERODOTUS-LEVANTINE)
MUD VOLCANOES
A
ALBORAN
MV
HERODOTUS-LEVANTINE
PROVENÇAL-BALEARIC
TYRRHENIAN
IONIAN
B

FIGURE S1

Table S2. Uncertainty values of the input primary variables for the Mediterranean water mass model provided by the MEDSEA_MULTIYEAR_PHY_006_004 CMEMS product.

Depth below sea level (m)	Temperature (± °C)	Salinity (±ppm)
0 – 10	0.7	0.47
10 – 100	0.85	0.21
100 – 500	0.28	0.08
500 – 1500	0.11	0.047
1500 – 2000	0.045	0.032
2000 – 2500	0.058	0.046

File Supplementary Information Plate P1 ODP boreholes.pdf

File Supplementary Information Plate P2 DSDP boreholes.pdf

Graphical results of the modelling of the analysed ODP and DSDP boreholes, displayed with lithostratigraphy.