THE MEDITERRANEAN SEA: A NATURAL LABORATORY TO STUDY GAS HYDRATE DYNAMICS?

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ABSTRACT

Gas hydrates have been proven by coring at one site in the (eastern) Mediterranean Sea, but their wider extent remains uncertain. Here we present results from investigations of the potential Mediterranean gas hydrate system, suggesting that clathrates occur more widely and have been strongly impacted by glacial-interglacial climate forcing. Modeling of the methane hydrate stability zone (MHSZ) shows it to be present in most of the Mediterranean Sea, albeit in deep waters (>1000 m) due to warm bottom waters (12.5-14°C) and in greater thicknesses (200-500 m) in the geothermally cooler eastern basin. Comparison of the MHSZ with known or possible zones of gas flux to seabed suggests prospective areas for hydrate occurrence, mainly in the eastern basin. One is the Nile fan, where evidence of the first BSR in the Mediterranean Sea (presented sseparately, Praeg et al. this volume) confirms the potential for additional hydrate discoveries. During glacial stages, gas hydrate stability in the Mediterranean increased due to bottom waters up to 4°C cooler; even allowing for sea levels 125 m lower, the modeled glacial-stage MHSZ was up to 25% thicker and 300 m shallower on basin margins. Glacial-to-interglacial transitions thus corresponded to a marked reduction in hydrate stability, with downslope migration of the upper limit of the MHSZ across depths of c. 700-1000 m. A compilation of submarine landslides in the Mediterranean Sea indicates a peak in the age of slide deposits during the last deglaciation and includes abundant headwalls in mid- to upper slope depths (<1200 m), including on the Nile fan. Together these results suggest that the Mediterranean Sea, in particular its gas-rich eastern basin, offers natural laboratory conditions to test the hypothetical linkages between climate-driven changes in gas hydrate stability and slope instabilities over glacial-interglacial timescales.

Keywords: gas hydrate stability, prospectivity, glacial-interglacial climate change

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INTRODUCTION

Changes in gas hydrate stability during glacial-interglacial climate cycles have been hypothesised by various authors to be causally linked to sediment failures on continental margins [1-3]. In the Mediterranean Sea, gas hydrate destabilization during lowered sea levels has been proposed as a possible trigger for the emplacement of late-glacial megaturbidites on the floors of the western and eastern basins [4,5]. To date, however, gas hydrates have been proven to occur at only one location in the eastern basin, in short cores from mud volcanoes [6]. Despite evidence that methane hydrates are stable over larger areas, bottom simulating reflections (BSRs) that might indicate their occurrence have not been reported from the Mediterranean Sea [7]. This has led to doubts as to whether BSRs have not been recognized, or gas hydrates simply do not occur widely [7].

Here we summarise results from investigations by OGS and partners into the gas hydrate system in the Mediterranean Sea, undertaken in the context of recent EC projects (HYDRAMED, HERMES) and an ongoing collaboration (HYDRANIL) that has led to a discovery of a BSR on the Nile fan, presented separately [8]. The work is based on modeling of methane hydrate stability, for present-day and glacial-stage conditions, as a guide to geological observations relevant to prospective occurrences and their dynamics. The results point to a wider occurrence of hydrates, particularly in the eastern Mediterranean Sea, and to natural laboratory conditions for testing their relationship to climate forcing and sediment failure.

DATA AND METHODS

The stability zone for methane hydrate in equilibrium with seawater (35‰ NaCl) was calculated using a phase boundary curve obtained from HWHYD [9], which lies between curves from CSMHYD [10] and that used by [7], see Fig. 1. The thickness of the stability zone was calculated, following [7, 11], from the intersection of the curve with 3 parameters (input as 2 minute grids): bathymetry (OGS in-house, C. Zanolla pers. comm.), bottom water temperatures [12], and geothermal gradients (compiled for the HYDRAMED project).

METHANE HYDRATE STABILITY

Present-Day

The thickness below seabed of the methane hydrate stability zone (MHSZ) is shown in Fig. 2.

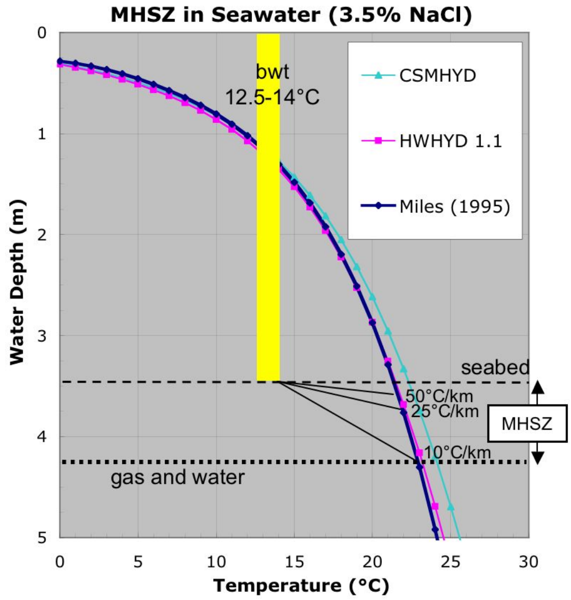

Figure 1. Phase boundary curve for methane hydrate in equilibrium with seawater from HWHYD [9] compared to two others [7,10]; superimposed are typical parameters for the Mediterranean Sea.

The deep Mediterranean Sea is characterized by warm bottom waters (12.5-14°C), meaning that methane hydrates are stable below water depths of 1000-1200 m (Fig. 1), at least twice typical stability limits of 300-500 m in the world ocean [8]. Methane hydrates are nonetheless stable throughout the western and eastern Mediterranean basins, each of which reach depths over 3000 m (locally >5000 m in the east). The MHSZ is relatively thin in the western basin (mainly <150 m), due to higher geothermal gradients (typically 50-100°C/km), whereas the geothermally cooler eastern basin (<50°C/km) includes large areas 200-500 m thick; local maxima >500 m (Fig. 2) reflect the sensitivity of the stability zone calculation to individual sites of low (≤10°C/km) geothermal gradient (see Fig. 1).

Glacial Stages

Oxygen isotope ($\partial^{18}O$) variations in cores from the Mediterranean Sea reveal glacial-interglacial cycles of large amplitude, reflecting coevel changes in ice volume (sea level), water temperature and salinity [13, 14]. Changes in $\partial^{18}O$ values in planktonic and benthic foraminifera since the last glacial maximum (LGM) are interpreted to indicate bottom waters that were saltier and up to 4°C cooler in the eastern basin [14]. This is consistent with estimates based on planktonic assemblages of LGM reductions in

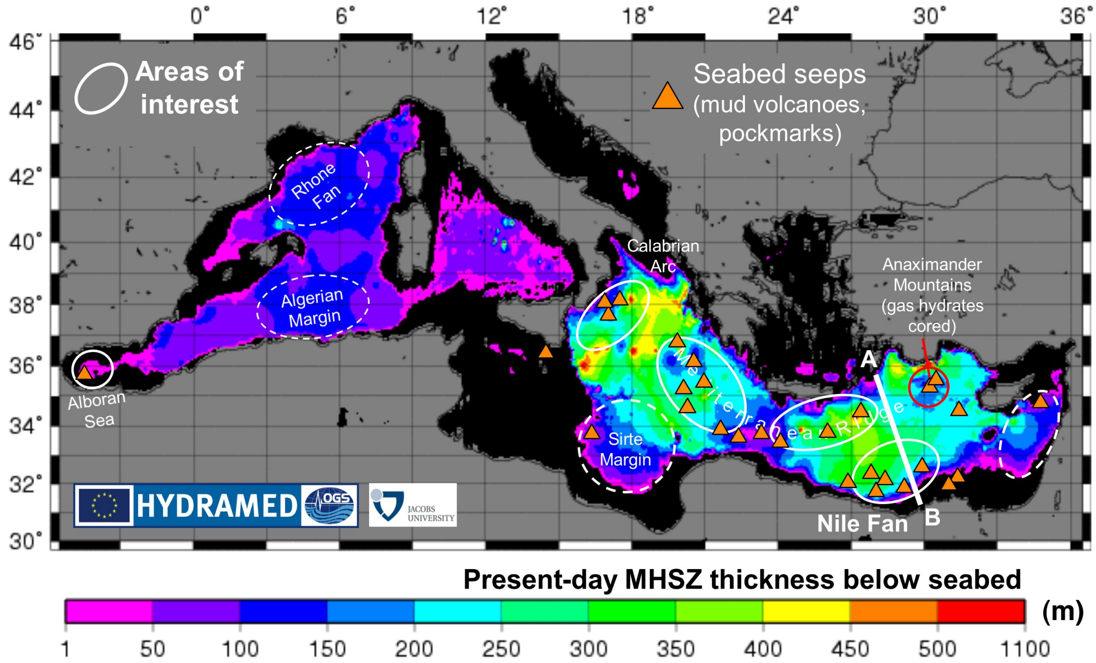

Figure 2. Modelled methane hydrate stability zone for present-day conditions, with areas of interest for hydrate occurrence; orange triangles indicate the general locations of known seabed seeps (various sources).

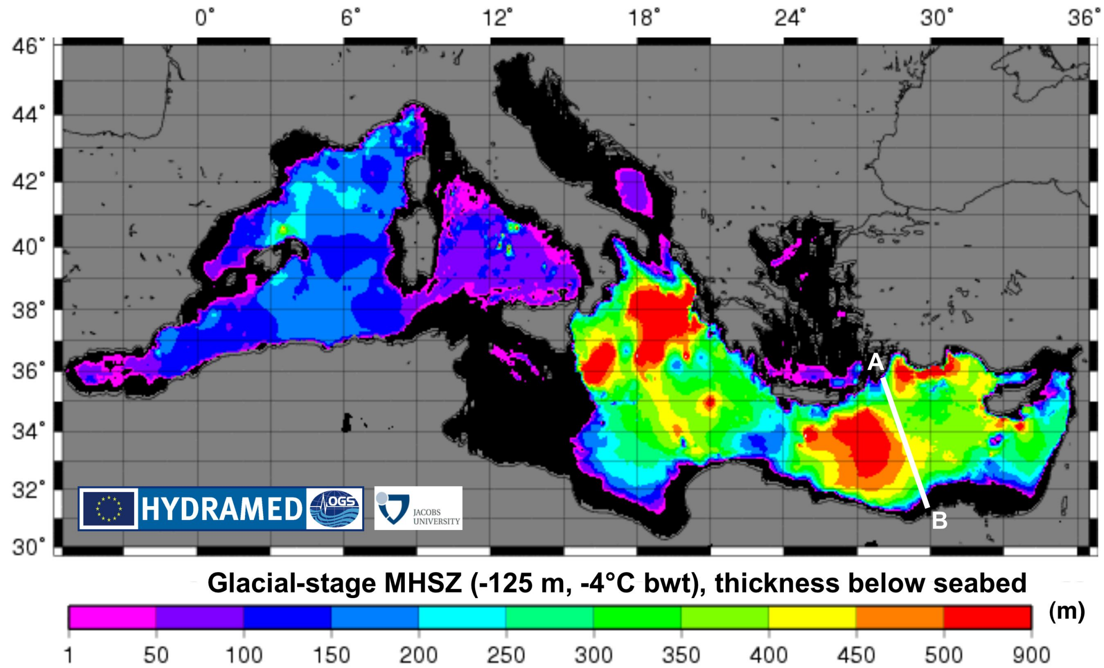

Figure 3. Modelled methane hydrate stability zone for glacial stage conditions.

winter sea surface temperatures of 4-6°C in the northern Mediterranean, where bottom waters are formed [15]. A 4°C reduction in bottom water temperatures (bwts) has been confirmed by Ca/Mg palaeothermometry of benthic foraminifera in a core from the western basin [16]. However, the lowest bwts occurred c. 40 kyr BP, versus LGM bwts up to 3°C lower, as part of fluctuations of several degrees throughout the 50 kya record [16].

The MHSZ for glacial stage conditions was modelled by assuming uniformly lower sea level (-125 m) and cooler bottom waters (-4°C). The results (Fig. 3) show that the effects of lowered sea level in increasing hydrate stability were greatly outweighed by the reduction in bottom water temperatures, such that during glacial stages the stability zone was up to 25% thicker and up to 300 m shallower on basin margins (Fig. 4). Thus glacial-to-interglacial transitions throughout the Mediterranean would have corresponded to a marked reduction in hydrate stability, with downslope migration of the upper limit of the MHSZ across depths of c. 700-1000 m (Fig. 4).

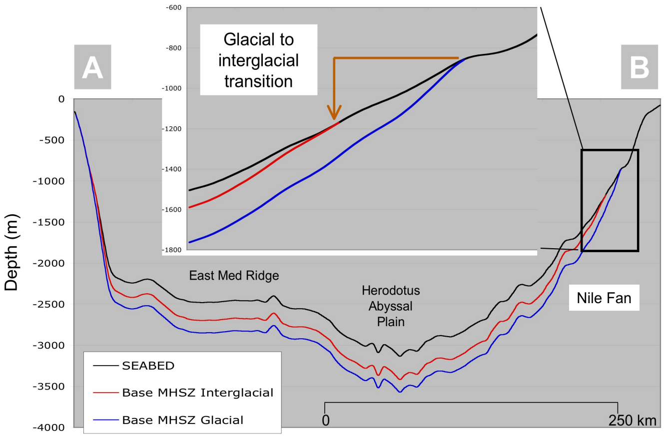

Figure 4. Transect of modelled methane hydrate stability zones in the eastern Mediterranean.

HYDRATE PROSPECTIVITY

The dominance of methane in gas hydrate occurrences worldwide means that the MHSZ has been found to provide a useful first approximation to their thicknesses, despite local variations in hydrate stability due to variations in gas composition or pore water salinity [17]. Areas of interest for gas hydrate occurrence in the Mediterranean Sea were identified by comparing the MHSZ with known or possible sites of gas flux to seabed. This suggests a wide prospective occurrence, particularly in the eastern Mediterranean (Fig. 2).

In the western Mediterranean, gas hydrate prospectivity is lower due to the paucity of evidence for deep-water gas flux into a relatively thin (<150 m) MHSZ. Mud volcanoes have been proven only in the Alboran Sea, where evidence of episodic activity since the Pliocene [18] implies a long history of gas flux to seabed. Two other areas of possible gas seepage are postulated. One is the Algerian margin, a convergent tectonic setting affording pathways for upward fluid migration and an area of current interest for deep-water hydrocarbon exploration [19]. Another is the Rhone fan, a Plio-Quaternary depocentre up to 2 km thick [20] that could consitute a source of biogenic gas. In all three areas (Fig. 2), the base of the MHSZ is within 150 m of seabed, complicating the identification of any BSRs.

Gas hydrate prospectivity is higher in the eastern Mediterranean basin (Fig. 2), where the MHSZ is thicker and evidence of gas flux to seabed is widespread. The eastern Mediterranean contains one of the world's highest abundances of mud volcanoes [21], most of which lie along the accretionary system formed by subduction of the African beneath the European plate [21, 22]. Gas hydrates have been cored in mud volcanoes in the eastern part of the accretionary system in the Anaximander Mountains [6], an area where the stability zone thins to <200 m (Fig. 2). Gas hydrates have not been proven in other mud volcanoes of the accretionary system, despite a false report from the Milano mud volcano based on pore water profiles acquired during ODP leg 160 [23, 24]. However, these and other investigations of mud volcanoes within the accretionary system, from the Calabrian Arc to Cyprus, have found geological and biological evidence of ongoing seepage of gas-rich fluids and free gas, mainly biogenic methane [25, 26]. These findings have been noted to suggest that gas hydrate occurrences may be widespread along the accretionary system [25].

Areas of interest are also present to the south along the passive margins of northern Africa (Fig. 2), from Libya to the Levant, which are currently a focus for oil and gas exploration [27]. Of particular interest is the Nile deep-sea fan, a Plio-Quaternary depocentre up to 4 km thick that is rich in seabed features of fluid seepage (e.g. mud volcanoes, pockmarks, carbonate crusts) [28,29]. Several of these features have been shown to emit gas and gas-rich fluids, including thermogenic methane and higher hydrocarbons [30,31]. In the central Nile fan, an area of pockmarks and carbonate crusts, investigations by OGS and partners have yielded evidence of a BSR, in water depths of c. 2000-2500 m, consistent with a gas hydrate occurrence zone up to 250 m thick [8]. This discovery serves to confirm the potential for additional discoveries of gas hydrates in the Mediterranean Sea, particularly its eastern basin.

GLACIAL-INTERGLACIAL DRIVERS

Glacial-interglacial changes in sea level (pressure) have an instantaneous and pervasive effect on gas hydrate stability, but can be countered by even small (<1°C) temperature changes, moreso at greater depths as the phase boundary curve steepens (Fig. 1). Changes in bottom water temperatures must diffuse to the base of the stability zone, over timescales typically up to 10^3 years [17], but that decrease as the stability zone thins towards its upper limit, the so-called critical wedge [1]. The world ocean has experienced an increase in bwts of between 2-5°C since the last glaciation [32] and a number of studies have shown they were capable of destabilising gas hydrates despite rising sea levels [33-35]. The impact is less at greater depths, where bottom waters tend to be with a few degrees of freezing, but increases to a maximum impact at upper slope depths, i.e. within the critical wedge [35]. A different impact is recognized in enclosed basins such as the Black Sea, where the entire deep-water (>700 m) gas hydrate stability zone is argued to be undergoing contraction following marine flooding 7.1 kyr BP that increased bottom water temperatures by between 2-5.5°C [36].

In the Mediterranean Sea, the deglacial increase in bottom water temperatures took place >15 kyr ago and so should have largely diffused through the gas hydrate stability zone [see 34-36]. Thus the entire zone of hydrate stability will have been modified by the large increase in bwts, inferred above to have driven basin-wide reductions in thickness of up to 25% and downslope migration of the critical wedge across depths of c. 700-1000 m (Fig. 4). These findings provide a new perspective on the possible causes of slope instabilities in the Mediterranean Sea, which have previously been considered only in relation to reductions in gas hydrate stability due to falling (or lowered) sea levels [4,5,37].

A recent compilation of submarine landslides in the Mediterranean Sea [38] shows a peak in the age of failures between c. 10-20 ka BP (Fig. 5), following the last glacial maximum and coincident with the deglacial rise in sea levels. Most slide headwalls lie in depths less than 1200 m on the mid- to upper continental slope (Fig. 5). The longest record of sediment failure comes from the Nile fan, where 7 mass transport deposits (MTDs) date back over 100 ka to the last interglacial [37]. Only one of these MTDs, dated to isotopic stage 5d, coincided with falling sea levels that could have driven gas hydrate destabilization [37]. Another is of deglacial age, forming part of the peak in Fig. 5. Interestingly, subsequent work has dated one of the Nile fan MTDs to c. 35-40 kyr BP [39], just after the 40 kyr bwt minimum recorded by Ca-Mg palaeothermometry in the western Med, argued to be a regional climate signal that also affected the eastern Mediterranean [16]. Unfortunately no independent records of bottom water temperatures are available for the eastern Mediterranean basin, which may have experienced palaeoceanographic conditions resulting in differing thermohaline circulation histories.

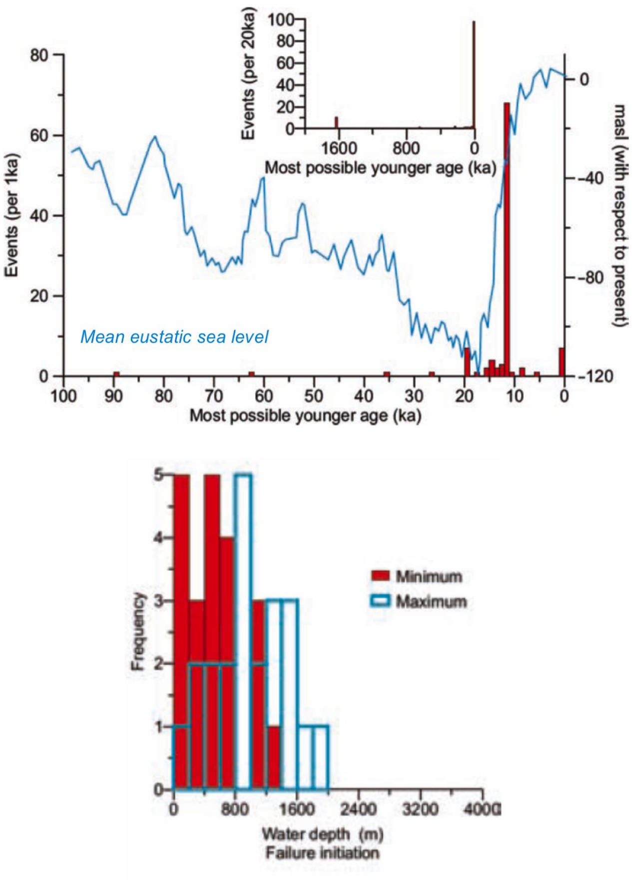

Figure 5. Ages and headwall depths of submarine landslides in the Mediterranean Sea (from Camerlenghi et al. 2010).

Several other factors may trigger submarine landslides, e.g sediment supply, fluid flow, seismicity [37]. Nonetheless, evidence that the Mediterranean Sea has experienced large glacial-interglacial changes in bottom water temperatures suggest that, where they occur, destabilization of gas hydrates represents a viable triggering mechanism for sediment failure. This mechanism could account for the observed deglacial peak in submarine landslides (Fig. 5), including on the Nile fan where gas hydrates are inferred to be present [8]. Inversely, additional investigations of the Mediterranean Sea, in particular its eastern basin, offer the opportunity to test the relationship of climate-driven changes in hydrate stability of high amplitude against long stratigraphic records of sediment failure. To take advantage of this opportunity requires an independent record of bottom water temperatures through time in the eastern basin, as well as additional information both on the ages and sources of failures.

CONCLUSIONS

The preceding shows that methane hydrates are stable throughout the Mediterranean deep water (>1000 m) basins and potentially occur more widely in the gas-rich eastern basin; this potential is confirmed by the identification of a BSR on the Nile fan [8]. In addition, hydrate stability is shown to have significantly decreased since the last glaciation due to an increase in bottom water temperatures by up to 4°C, which could account for a deglacial peak in the ages of submarine landslides. These results invite further investigations for which the Mediterranean, in particular its eastern basin, appears to offer natural laboratory conditions to test the linkages between high-amplitude climate-drivers, changes in gas hydrate stability and slope instabilities over glacial-interglacial timescales.

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