Geophysical evidence of gas hydrates in shallow submarine mud volcanoes on the Moroccan margin

D. Depreiter, J. Poort, P. Van Rensbergen, and J. P. Henriet
Renard Centre of Marine Geology, Ghent University, Ghent, Belgium

Received 11 January 2005; revised 8 July 2005; accepted 15 July 2005; published 19 October 2005.

[1] Gas hydrates inside mud volcanoes have been observed in several locations but are generally found at water depths of 1000 m and deeper. We present the first observation of the base of a gas hydrate stability zone within a shallow mud volcano in the El Arraiche mud volcano field on the Moroccan Atlantic margin. The mud volcano base is located at about 475 m and is over 125 m high. On high-resolution seismics we observed an anomalous but coherent reflection under the slopes of the mud volcano. The event was interpreted as the base of a gas hydrate stability zone because of its inverse polarity and its morphology. Far from the crater, the event is nearly parallel to the seafloor. Closer toward the crater, the event shallows. Inside the mud volcano crater, no event is observed. A stability model using thermogenic gas compositions is applied to local P-T conditions, indicating that thermogenic gas hydrates can be stable at this depth. The high modeled heat flow in the crater of the mud volcano indicates a focused flow of warm fluids. Below the slopes of the mud volcano, the inferred heat flow is also elevated but less high. In areas of thermogenic gas production, gas hydrates can occur at shallow water depths, even in areas with high heat flow. This also suggests that dewatering of the accretionary wedge complex is mainly focused along fault surfaces and through seafloor structures, such as mud volcanoes.

Citation: Depreiter, D., J. Poort, P. Van Rensbergen, and J. P. Henriet (2005), Geophysical evidence of gas hydrates in shallow submarine mud volcanoes on the Moroccan margin, *J. Geophys. Res.*, *110*, B10103, doi:10.1029/2005JB003622.

1. Introduction

[2] Gas hydrate is an ice-like crystalline substance, consisting of a cage structure of water molecules with trapped methane or other light gases inside. Gas hydrates are stable under well-described *P-T* conditions [*Sloan*, 1998a, 1998b] and adequate gas concentrations [*Xu and Ruppel*, 1999]. The distribution of gas hydrates on continental margins is widespread [*Ginsburg and Soloviev*, 1998; *Kvenvolden*, 1998]. Stability of hydrates on margins is a very actively studied topic in regard to triggering sediment mass wasting through gas hydrate decomposition [*Bouriak et al.*, 2000; *Paull et al.*, 2003]. Gas hydrates are also regarded as an important potential economic target [*Collett*, 2002; *Gupta*, 2004] and their destabilization may have a large impact on global change [*Kvenvolden*, 1993; *Jacobsen*, 2001; *Kennett et al.*, 2000; *Kopf*, 2003].

[3] Gas hydrates in seafloor sediments occur within a restricted zone, the gas hydrate stability zone (GHSZ). The base of the GHSZ is often recognized as a bottom simulating reflection (BSR) on seismic data, since it mimics the seafloor in areas of a stable and constant local heat flow. The BSR is characterized by an inverse polarity of the seismic signal, originating from the presence of free gas trapped below the hydrate stability zone [e.g., *Bangs et al.*, 1993; *MacKay et al.*, 1994; *Holbrook et al.*, 1996]. Since the thermal gradient defines the lower boundary of the GHSZ, an elevated local heat flow will thin the GHSZ. In that case, the base of the GHSZ, expressed as a crosscutting reflection, can locally intercept with the seafloor reflection, for example, in gas hydrates associated to mud volcanoes or gas seeps [*De Batist et al.*, 2002; *Van Rensbergen et al.*, 2002].

[4] Submarine mud volcanoes (MVs) are seafloor structures with positive topography from which mud, fluid, and gas emanate [*Hedberg*, 1974]. Their distribution is mainly confined to areas with compressive tectonic activity, vertical compression due to sedimentary loading (burial) and generation and accumulation of hydrocarbons leading to overpressure [*Dimitrov*, 2002a; *Kopf*, 2003]. The general mechanism for their formation is related to a combination of the rise of overpressured liquefied clays toward the surface and the hydrofracturation of the overburden which opens a feeder pipe. The mobilized material pierces the overburden to expel a mixture of mud, fluids and gases along with brecciated rock derived from the overburden, the mud breccia.

[5] Gas hydrates inside mud volcanoes have been observed in several locations [*Dimitrov*, 2002a], but are generally found at water depths of 1000 m and deeper, e.g., on the Norwegian-Barents-Svalbard margin [*Ginsburg et al.*, 1999], the Gulf of Cadiz and on the Moroccan margin [*Gardner*, 2001; *Mazurenko et al.*, 2002], the eastern

0148-0227/05/2005JB003622$09.00

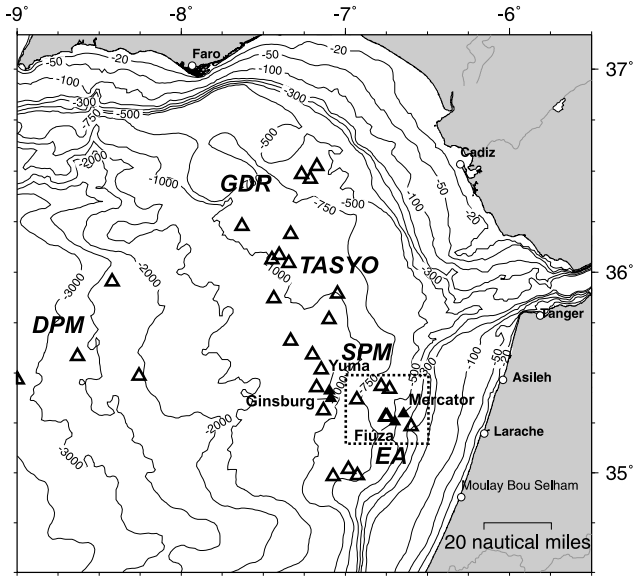

Figure 1. Gulf of Cadiz and NW Moroccan margin. Mud volcanoes and diapiric structures are indicated by triangles. Solid triangles are mud volcanoes mentioned in the text. DPM (Deep Portugese Margin) [*Pinheiro et al.*, 2003], TASYO and GDR (Guadalquivir Diapiric Ridge) [*Somoza et al.*, 2003], SPM (Spanish-Moroccan Field) [*Gardner*, 2001], EA (El Arraiche field) [*Van Rensbergen et al.*, 2005a]. The location of Figure 2 is indicated by the dotted box.

Mediterranean ridge [*Robertson et al.*, 1996], the Black Sea [*Soloviev and Ginsburg*, 1994; *Dimitrov*, 2002b; *Bohrmann et al.*, 2003], the Caspian Sea [*Huseynov and Guliyev*, 2004] and on the Barbados accretionary wedge [*Aloisi et al.*, 2002].

[6] In this paper, we present a reflection event within a mud volcano found in the El Arraiche mud volcano field on the Moroccan margin. The mud volcano is about 125 m high and its crater is situated at a depth of about 350 m below sea level (bsl). We will map the distribution of this event and calculate the local heat flow pattern, the results of which plead for the occurrence of hydrates of thermogenic hydrocarbon gases in this shallow location and the event to be the base of a GHSZ.

2. Regional Setting

[7] The Gulf of Cadiz is situated between 9°W to 6°45′W and 34°N to 37°15′N (Figure 1), bounded by the Iberian peninsula and Morocco, west of the Gibraltar area. The geological setting of the Gulf of Cadiz is extremely complex and still under debate [*Sartori et al.*, 1994; *Maldonado et al.*, 1999; *Gutscher et al.*, 2002]. The area is characterized by the presence of an accretionary wedge formed by westward motion of the front of the Gibraltar Arc (the Betic-Rif mountain chain) during middle Miocene. Formation of the allochthonous nappes took place during the Tortonian, as a consequence of increased subsidence [*Maldonado et al.*, 1999]. The African-Eurasian convergence since the Cenozoic yields a compressional-transpressional tectonic regime, reactivating many normal faults and causing widespread diapirism in the north of the Gulf of Cadiz [*Berastegui et al.*, 1998; *Somoza et al.*, 2003]. Mud volcanoes in the Gulf of Cadiz are associated with these diapiric structures [*Somoza et al.*, 2003; *Pinheiro et al.*, 2003]. The main part of the olistostrome unit occupies the central part of the Gulf of Cadiz as a lobe-shaped structure that extends over 300 km into the Atlantic Ocean, its extent seems not well defined yet [*Maldonado et al.*, 1999; *Somoza et al.*, 2003; *Medialdea et al.*, 2004; *Maestro et al.*, 2003].

[8] The El Arraiche mud volcano field is located on top of the accretionary wedge of the Gulf of Cadiz, at depths between 200 and 800 m at the NW Moroccan continental slope [*Van Rensbergen et al.*, 2005a] (Figures 1 and 2). The local structure of the study area is characterized by extensional tectonics, in contrast to the main part of the Gulf of Cadiz. This is expressed as large rotated blocks bound by lystric faults that created Plio-Pleistocene depocenters [*Flinch*, 1993, 1996]. The extension might be a response to the advancement of the allochthonous sheets as was reported for the northern Gulf of Cadiz by *Medialdea et al.* [2004].

[9] The mud volcanoes of the El Arraiche mud volcano field are positioned above large normal faults that bound the rotated blocks and serve as fluid migration pathways, fuelling the mud volcanoes [*Van Rensbergen et al.*, 2005a]. The normal faults are probably superposed on relict thrust anticlines [*Maldonado et al.*, 1999] or Triassic salt diapiric structures [*Berastegui et al.*, 1998; *Somoza et al.*, 2003]. The source of the overpressured fluids is believed to be located at the base of the accretionary wedge body since rock clasts in the mud breccia are reported to be of an age up to early Eocene [*Ovsyannikov et al.*, 2003].

[10] Gas hydrates on the Moroccan margin and in the Gulf of Cadiz have only been reported from a small number of deep-water mud volcanoes: Ginsburg mud volcano (1100 m bsl) [*Gardner*, 2001; *Mazurenko et al.*, 2002, 2003], Bonjardim mud volcano (2200 m bsl) [*Kenyon et al.*, 2001; *Pinheiro et al.*, 2003] and Capt. Arutyunov mud volcano (1800 m bsl) [*Kenyon et al.*, 2003]. *Casas et al.* [2003] observed possible BSR features at a subbottom depth of 150 ms two-way travel time (TWTT), associated with mud volcanoes and diapirs at a water depth of 388 m on the Gulf of Cadiz slope. They attributed the hydrate stability to elevated pore pressure conditions caused by the diapiric intrusions. Reports of a widespread regional BSR are not yet made.

[11] The Mercator and Fiúza mud volcanoes are situated in the El Arraiche mud volcano field (Figure 2). The Mercator mud volcano's top is at a water depth of 350 m, the deepest part of the surrounding moat is about 475 m deep. Its diameter is nearly 2.5 km. There is a crater present, with a dome form extrusion in the center. The flanks of the mud volcano are characterized by a stepped or terrace-like morphology. The Fiúza MV is located deeper, with its top at 400 m and its base around 525 m. All morphological details are reported by *Van Rensbergen et al.* [2005b].

3. Methods and Results

3.1. Seismic Reflection Profiling

[12] The El Arraiche mud volcano field was covered with detailed multibeam bathymetry (Kongsberg EM1002) and

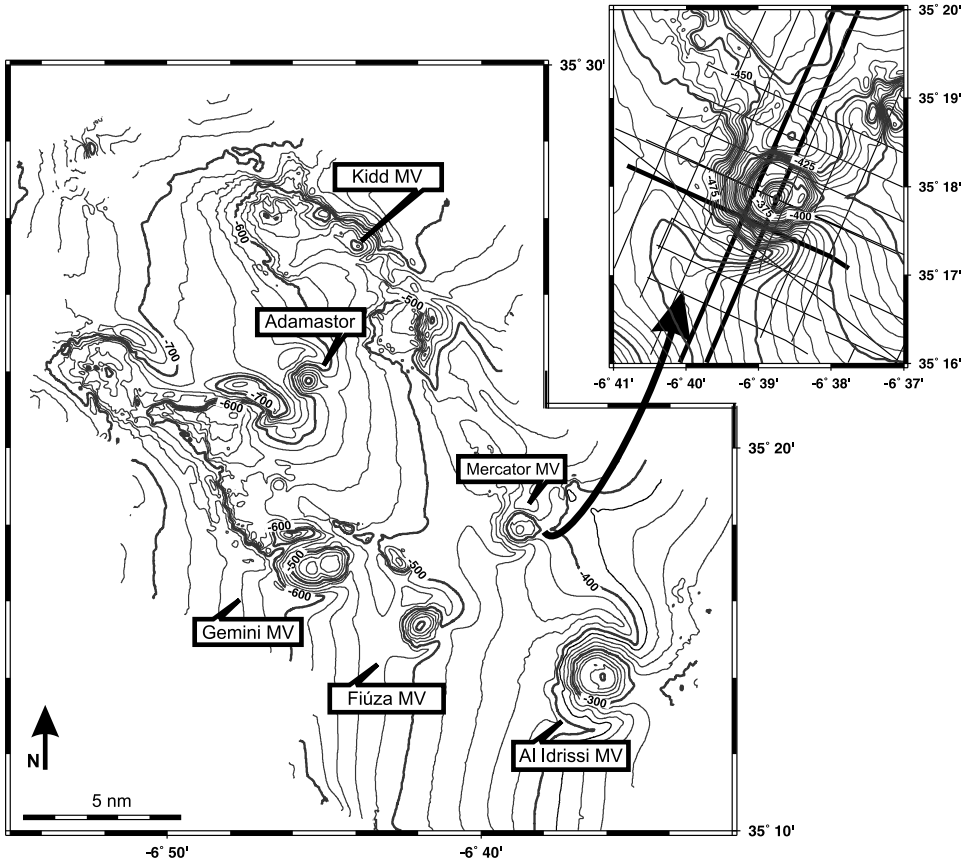

Figure 2. Bathymetric map of the El Arraiche mud volcano field with indication of major mud volcanoes. Inset shows a detail of the Mercator mud volcano with 2-D seismic track lines; bold lines are profiles displayed in Figure 3.

high-resolution seismics (80 electrode 500J sparker, 35 cubic inch Sodera GI gun and the Ifremer Deeptow Chirp Sonar system). The seismic data were acquired in three narrowly spaced orthogonal grids over three large mud volcanoes: Al Idrissi, Mercator, and Gemini MVs. Interpretation was executed in the Kingdom Suite seismic interpretation software package (Seismic Micro-Technology, Inc.) and further handling with the GMT mapping tools [*Wessel and Smith*, 1991].

3.2. Event Observation

[13] The Mercator and Fiúza mud volcanoes both show an anomalous but coherent subbottom reflection, which we name the H event (Figure 3). The depth of the H event varies from 0 m near the mud volcano crater to over 50 ms further away. The presence of any coherent signal is unexpected since mud volcanoes are mainly built up by an extruded mud-supported breccia, hence lacking any internal structure and only a chaotic seismic facies is expected. The depth of this event was mapped over the Mercator mud volcano, a seismic grid over the Fiúza MV is not present.

[14] The seismic signal shows that the H event has an inverse polarity in regard to the seafloor reflection (Figure 4). The H event only occurs within the mud volcano body and does not extend into the layered hemipelagic sedimentary environment around the mud volcanoes. Hence it is not a crosscutting reflection. Away from the crater, the reflection is parallel to the seafloor, where it forms a bottom simulating reflector (BSR) at a depth of about 50 milliseconds below the seafloor. The H event shallows toward the center of the mud volcano and intercepts with the seafloor reflection at the edge of the crater (Figures 3 and 5).

[15] We introduce the hypothesis that the H event is the base of a gas hydrate stability zone. We test this hypothesis by modeling the gas hydrate occurrence and deriving the H event inferred heat flow in the mud volcano.

3.3. Modeling Gas Hydrate Occurrence

[16] Modeling the hydrate stability zone requires information on the composition of the hydrate gas, on the bottom water temperature and geothermal gradient as well as the pore space salinity. Gas hydrates recovered from the nearby Ginsburg mud volcano, which is located at a water depth of 1100 m, had a composition of 81% of CH_4 and 19% of C_{2+} hydrocarbons [*Mazurenko et al.*, 2002]. From CTD data we know that the seafloor temperature in the area is 10°C which is unfavorable for gas hydrate stability. Pore water salinity estimates are derived from mud volcanoes from the Moroccan margin. [*Blinova and Bileva*, 2003] reported an average chlorinity of 500 mmol L^{-1}. According to equation (1), this can be converted to 3.2% salinity, which is comparable to ocean water salinity.

$$S = 1.80655[\mathrm{Cl}^-] \quad (1)$$

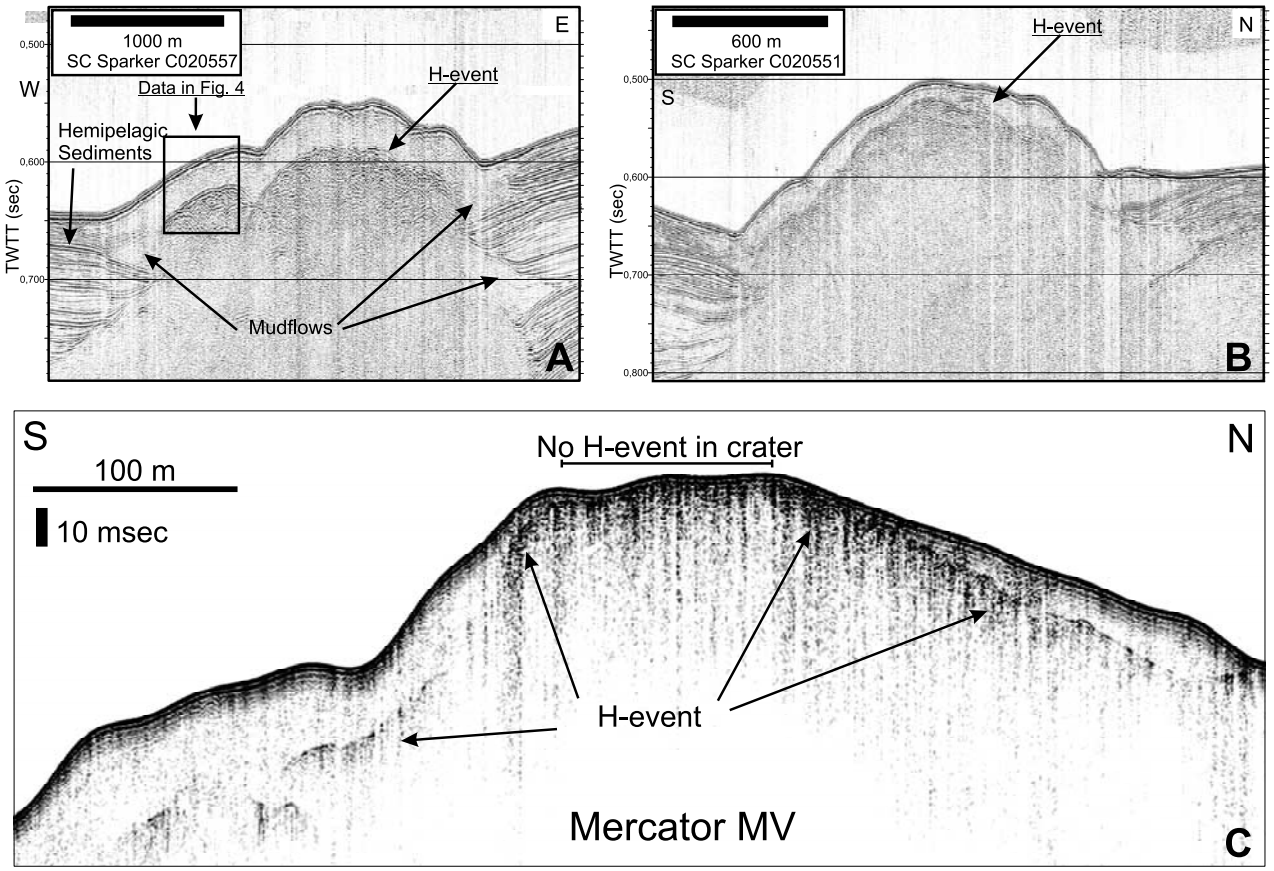

Figure 3. (a and b) High-resolution sparker and (c) very high resolution chirp sonar (courtesy Ifremer) seismic lines over Mercator MV. The stratified seismic facies at the sides of Mercator MV (Figures 3a and 3b) represents hemipelagic sediments. The mud volcano itself has no internal structure; therefore a chaotic to transparent facies is observed. The unexpected H event reflector is visible on all profiles, Figure 3a is a profile far away from the crater and therefore the event occurs deepest. Figure 3b is a profile that passes next to the crater; therefore the H event is shallower near the crater than elsewhere. Figure 3c line crosses the crater and shows the H event intercepting the seafloor reflection.

Equation (1) expresses a conversion from salinity to chlorinity, with S the salinity and $[Cl^-]$ the chlorinity, both in parts per million (ppm) [*Wooster et al.*, 1969].

[17] The gas hydrate equilibrium conditions were determined using the program CSMHYD [*Sloan*, 1998a] for the given composition of the gas hydrates and salinity of the pore waters. This resulted in the polynomial regression equation

$$\log P = a + bT + cT^2 \tag{2}$$

with parameters $a = -0.1929$, $b = 0.0395$ and $c = 0.0009$, P in MPa and T in degrees Celsius, and the regression coefficient $R^2 = 0.998$. In Figure 6a, the resulting hydrate stability curve is plotted with a seafloor depth of 380 m. The hydrate stability curve for pure methane is plotted for comparison. This result shows that at this water depth and for the given gas composition and seafloor temperature, gas hydrates can be stable. For a thermal gradient of 60 mK m^{-1}, which is a normal background value for the North Atlantic Ocean [*Sclater et al.*, 1980], the depth of the base of the GHSZ is almost 100 m deeper than the present observed H event (Figure 6a, with H event in Figure 6b).

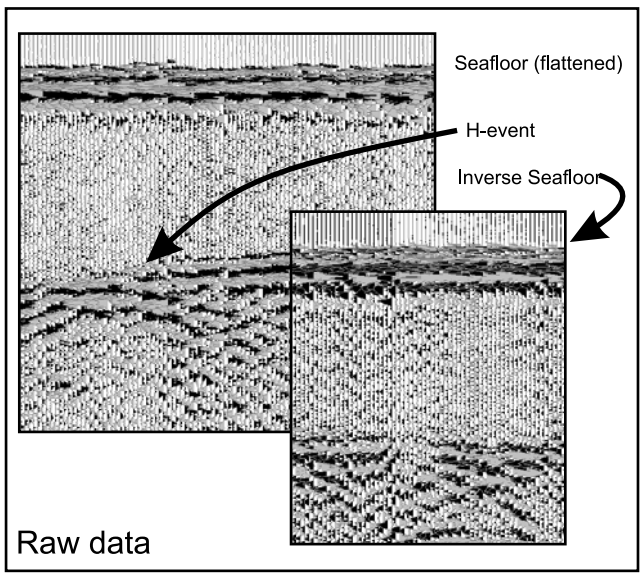

Figure 4. Inverse seismic polarity of the H event with regard to the seafloor reflector.

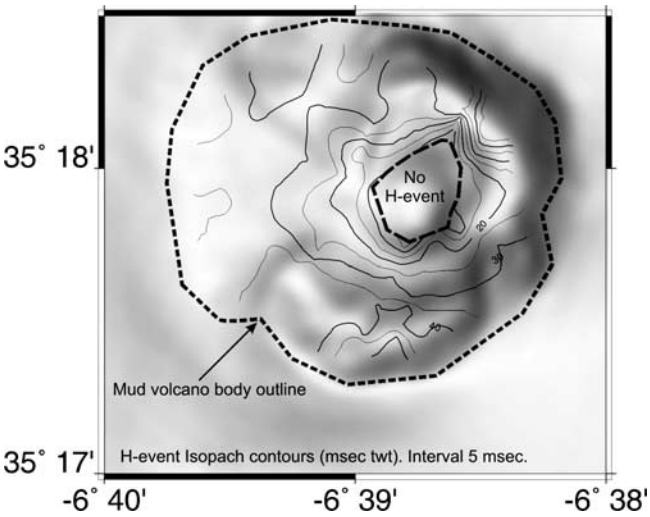

Figure 5. Subbottom depth of the H event in the Mercator mud volcano in two-way travel time. The concentric shallowing of the H event toward the crater is shown by the contours. Background figure is a shaded relief map of the Mercator mud volcano (illuminated from west).

[18] Since thermogenic gas hydrates can theoretically occur at this location, this supports our hypothesis that the H event is the base of a GHSZ. We will map this horizon and infer the thermal gradient and heat flow from it.

3.4. Inferred Heat Flow

[19] Bottom simulating reflections have often been used to estimate thermal gradients or heat flow [*Yamano et al.*, 1982]. The calculation assumes that the BSR coincides with the three-phase gas hydrate-water-gas vapor boundary, and consists of the following steps [*Vanneste et al.*, 2003]: (1) conversion from TWTT to subbottom depth based on a velocity model, (2) calculation of in situ hydrostatic and lithostatic pressure, (3) derivation of the equivalent three-phase gas hydrate equilibrium temperature for these pressure values at the inferred BSR depth, and (4) determination of the geothermal gradient and heat flow.

[20] A relation between pressure, depth, and time is needed for the conversion from two-way travel times to depth and pressure values, which are needed for thermal gradient and heat flow calculations. Data from Ocean Drilling Program Leg 160 (eastern Mediterranean) Site 970 (Milano Dome) and 971 (Napoli Dome) [*Robertson et al.*, 1996] shows that pebbly mud (holes 970A, 970B, 970D and 971A, 971B, 971D, 971E) has *p* wave velocities from 1500 to 2000 m s^{-1}. When averaging over depth for these holes, values around 1800 m s^{-1} are retrieved. For nanofossil ooze with sapropels (hole 970B), the velocity average is about 1600 m s^{-1}. All values refer to the first tens of meters; therefore we assume an average velocity for the deposits of the top of the Mercator mud volcano of 1800 m s^{-1}. Then, on the basis of a *p* wave velocity 1.5 km s^{-1} in water and 1.8 km s^{-1} in the sediment and with a density of water ρ_w = 1030 kg m^{-3} and sediment ρ_c = 2300 kg m^{-3} (based on a ρ_s = 2650 kg m^{-3} for the sediment and ρ_h = 900 kg m^{-3} for the hydrates [*Gei and Carcione*, 2003], in a 80% sediment to 20% hydrate mixture), the two-way travel time of the seismic sections was converted to depth (Figure 7a) and pressure (Figure 7b). The calculated pressure field at the H event reflector displays a nearly concentric pattern around the crater of the mud volcano and pressure increases from the crater (3500 kPa) to the deepest point (6000 kPa).

[21] On the basis of the thickness of the layer between the seafloor and the H event, we reconstructed the thermal

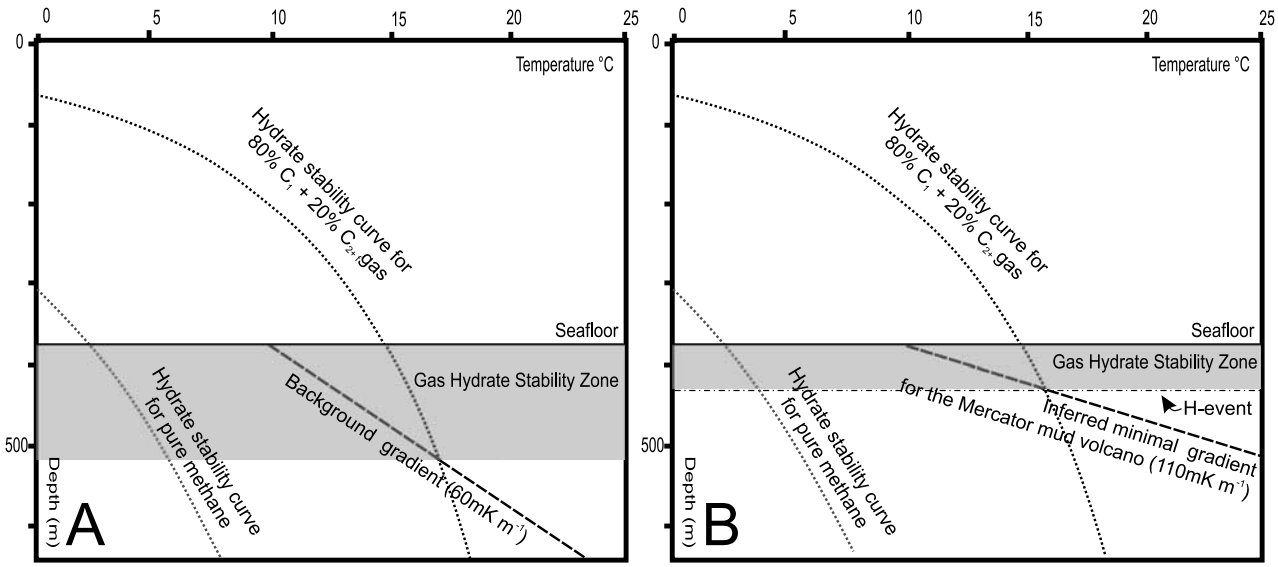

Figure 6. Theoretical gas hydrate stability graphs for gas composition measured at Ginsburg mud volcano [*Mazurenko et al.*, 2002] and pure methane for comparison. Pure methane hydrates are unstable in either case. (a) Situation with a background gradient curve of 60 mK m^{-1} and a bottom water temperature of 10°C. Gas hydrates are stable to 140 m below seafloor if gas contains higher-order hydrocarbons. (b) Situation for lowest inferred thermal gradient (110 mK m^{-1}) in Mercator mud volcano, where hydrates with higher-order hydrocarbons are stable up to 60 m bsf.

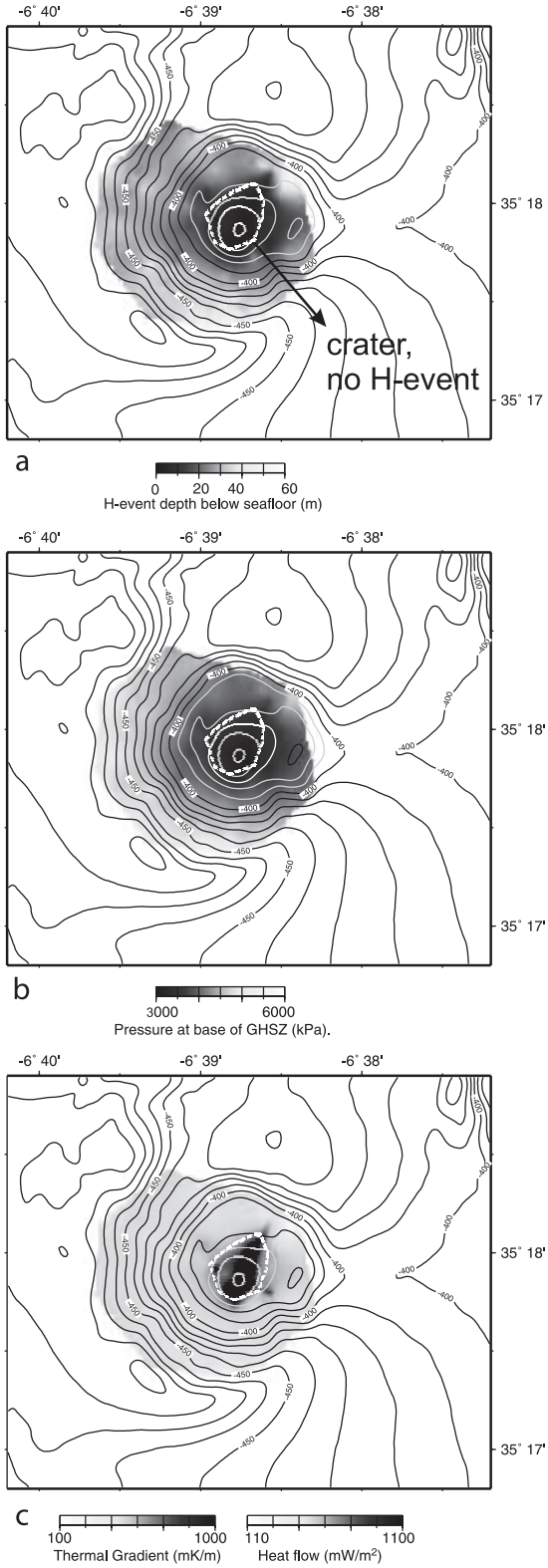

Figure 7. (a) Depth of the H event in meters in the Mercator mud volcano. (b) Calculated pressure at the depth of the H event. (c) Calculated thermal gradient and heat flow inferred from the occurrence of the H event. The thermal gradient and heat flow display a quasi-radial pattern around the mud volcano crater, increasing toward it. In the crater area, no H event was observed. See color version of this figure at back of this issue.

gradient field and the heat flow pattern in the mud volcano. Inside the crater, no H event is observed, so the thickness is set to 0. The calculation of the thermal gradient field, based on the distribution of a BSR, is derived from equation (2) as

$$G_t = \frac{T - T_{sf}}{d_{\mathrm{bsr}}} \tag{3}$$

with

$$T = \frac{-b + \sqrt{b^2 + 4c(\log P - a)}}{2c} \tag{4}$$

where G_t is the temperature gradient, T is the temperature (°C) defined by equation (4), T_{sf} is the temperature at the seafloor (C), d_{bsr} is the depth of the BSR in meters below seafloor, and P is the in situ pressure at the BSR in MPa. For the conversion from the thermal gradient field to the heat flow Φ_Q according equation (5), we supposed a thermal conductivity k_t of 1.1 W K^{-1} m^{-1}, with

$$\Phi_Q = k_t G_t \tag{5}$$

and Φ_Q in mW m^{-2} and G_t in mK m^{-1}. This value for k_t is used since it is a typical value for this kind of sediments [e.g., *Grevemeyer et al.*, 2004] report k_t = 1.17 W K^{-1} m^{-1} for sediments at the Mound Culebra mud dome offshore Nicoya Peninsula, Costa Rica). The thermal gradient and heat flow values calculated on the mud volcano are cut off at 1 K m^{-1} or 1.1W m^{-2} near the edge of the crater because at that location, values move asymptotically to infinite since d_{bsr} approaches zero in equation (3).

[22] The inferred heat flow and thermal gradient fields show a more or less concentric pattern around the crater of the Mercator mud volcano (Figure 7c). The local minimal value of the heat flow in the Mercator mud volcano is 110 mW m^{-2} (Figure 6b) and increases to about 250 mW m^{-2} craterward. Near the edge of the crater, the heat flow quickly rises to 600 mW m^{-2} and then increases quickly to 1100 mW m^{-2} at the crater edge. Within the crater, the heat flow cannot be extrapolated because of the asymptotical rise of the calculated values toward infinity. All we can infer here is that heat flow inside the crater is higher than 1100 mW m^{-2}.

3.5. Accuracy Estimate

[23] Each of the steps to calculate the heat flow from a BSR occurrence is a source of errors. The error on the pressure field at the depth of the H event depends on changes in p wave velocity and density of the mud breccia. If we vary the p wave velocity between 1500 and 2000 m s^{-1} and the density between 1800 and 2300 kg m^{-3}, relative errors for the pressure vary between about −6.5 and 2%. It is unlikely that density will be higher than the value we used for the calculations, since porosity, which we assumed to be zero and all pores filled by hydrate, will have a bulk density decreasing effect. However, because of the logarithmic function in the temperature calculation, this error is strongly reduced. The most important factor for the thermal gradient is the p wave velocity since it appears in the denominator of equation (3). All together, the varying p wave velocity and bulk density induces an overall error on the thermal gradient

of +16.3% for a p wave velocity of 1500 m s^{-1} and −8.2% for a p wave of 2000 m s^{-1}. The influence of a variable density is less, and the error values above are the overall extremes. An error for k_t will further affect the heat flow values. If k_t is 0.9 W m^{-1} K^{-1}, a value typical for normal hemipelagic sediments, this induces an error of about 18%. Long-term bottom water changes will affect the heat flow pattern according to equation (3). More importantly, they can influence the hydrate stability field with bottom water warming causing gas hydrate dissociation. Nevertheless, we rely on the CTD data and assume that temporal fluctuations are small. The overall error on the H event inferred thermal gradient is assumed to be no larger than 15% and the error on the heat flow no larger than 25%. Another source of uncertainty is the gas hydrate composition since the values we used were not obtained from in situ sampling. However, we assume that source fluids and gases are comparable throughout the region and fluctuations are low.

4. Interpretation and Discussion

[24] The H event is recognized as a coherent reflector with negative polarity under the seafloor below the Mercator mud volcano's slope. The H event shallows toward the mud volcano's center and disappears in the crater. We interpret the H event as the base of a gas hydrate stability zone, which is affected in the center of the mud volcano by focused fluid flow. We modeled the gas hydrate stability zone in this very shallow area by using a gas hydrate composition reported for the region. The seismic interpretation is supported by the model. Alternative interpretations of this seismic event are possible but can be rejected based on several issues.

[25] First, the H event may have been covered by a layer of rocks and clasts, extruded by the mud volcano. This is deemed unlikely since so far, no observations indicate that a complete mud volcano surface would be covered with extruded clasts or rocks. This suggestion can be rejected since it cannot explain the morphology of the seismic event (i.e., the shallowing toward the crater) since different mud extrusion types as described by *Van Rensbergen et al.* [2005b] cannot produce such a morphology. Second, the event might represent a transition to sedimentary deposits created during a period of inactivity of the mud volcano. This is unlikely as a sedimentary layer would drape the whole mud volcano, therefore also the crater area. Third, a diagenetic boundary may produce a seismic event in a mud volcano. Again, the morphology of such a boundary is hard to explain. For all of these propositions, the inverse polarity of the seismic signal is also not explained. Thus we conclude that the interpretation of the H event as the base of a gas hydrate stability zone is the most reliable.

4.1. Focused Fluid Flow in Mud Volcanoes

[26] The Mercator mud volcano exactly shows what *Ginsburg* [1998] proposed in a model concerning hydrate stability in mud volcanoes. Therefore, although the Mercator MV is not visibly active in a sense that it extrudes mudflows, it is inferred to be active as a fluid vent. The concentric pattern of the heat flow distribution is a consequence of lateral heat diffusion away from the feeder pipe [*Poort and Klerkx*, 2004]. Diffusion of gas away from the feeder pipe is the source of hydrocarbon gases hydrate. Hydrates generally occur at continental margins where conversion of high inputs of organic carbon or focusing of methane bearing fluids supply the hydrocarbon gases required for hydrate formation [*Davie et al.*, 2004]. The absence of any regional BSR or H event in the surrounding hemipelagic sediments could be explained by an insufficient methane flux which would be needed for gas hydrate formation. A methane flux lower than the theoretical methane solubility would also imply the absence of free gas. The lack of an acoustic impedance inversion at the interface between gas-free and gas-bearing sediments, may explain the absence of a widespread regional BSR. This would mean that the degassing and dewatering of the accretionary wedge in the Gulf of Cadiz mainly happens through focused flow along faults associated fluid expulsion seafloor structures, and only partly by widespread diffusive processes.

[27] The inferred heat flow in the mud volcano, and especially in and near the crater, is very high. However, literature reports indicate that the calculated result is not abnormal for mud volcanoes. Heat flow in active mud volcanoes is known to easily rise above 1 W m^{-2}. The best know case-study is the Håkon Mosby MV on the Norwegian Margin. The crater of the mud volcano has also thermal gradient values of over 1000 mK m^{-1} [*Eldholm et al.*, 1999] and even values of over 10,000 mK m^{-1} have been estimated by *Vogt et al.* [1999] in the mud volcano crater. In Lake Baikal, both in situ measured and BSR-derived heat flow evidenced elevated heat flow values compared to background at the Malenki mud crater [*Vanneste et al.*, 2003]. *Henry et al.* [1996] report a steady state surface heat flow of 5000 mW m^{-2} on average in the center of the Atalante mud volcano in the Barbados Trough.

4.2. Very Shallow Gas Hydrate Occurrence and Significance

[28] Theoretically, gas hydrate occurrence up to 250 m is possible when thermogenic gases are involved. In the Gulf of Mexico, gas hydrate occurrence has been reported up to about 440 m [*Sassen et al.*, 1999]. Here we now observe gas hydrates at a water depth up to nearly 350 m (Figure 5). Many shallow hydrate accumulations have been found at water depths below 500 m because the hydrates mainly consist of methane. The uppermost limit for methane hydrate occurrence is about 500 m [*Sloan*, 1998a]. The result in this paper gives an indication that the volume of gas trapped as gas hydrate may be much larger than formerly thought, since many estimates of gas hydrates only account for methane hydrates.

[29] An estimate of the quantity of gas hydrate in the Mercator mud volcano was calculated based on the seismic data and a gas hydrate volume percentage of 5%. Volume percentage estimates for Ginsburg mud volcano were 4–19% [*Mazurenko et al.*, 2003] and at the Hydrate Ridge [*Trehu et al.*, 2004] conclude gas hydrates contents up to 26 vol % at the summit of the ridge and an average of about 3–6 vol % in the upper tens of meters of sediments in the GHSZ. We also used a gas hydrate density of 900 kg^{-3} and the same velocity estimates as above. This model leads to a hydrate quantity between 2.5 Mt hydrate stored in this single mud volcano, or with the estimate that 1 m^3 contains

160 m^3 of methane, a quantity of 40×10^8 m^3 methane is obtained.

5. Conclusion

[30] An anomalous reflection (H event) has been observed in shallow mud volcanoes on the Moroccan margin. The H event was mapped in the Mercator mud volcano and was interpreted as the base of a gas hydrate stability zone, based on its inverse polarity and the fact that it mimics the seafloor away from the mud volcano's crater. Inside the crater, the H event is absent. This was supported by the fact that gas hydrate stability modeling with reported thermogenic gas compositions, indicated that gas hydrates can be stable at this shallow location. BSR inferred heat flow showed a concentric heat flow pattern around the crater, with a very sharp rise in heat flow near the crater, consistent with our interpretation that the gas hydrate layer is affected by a focused flow of warm fluid in the crater. Modeled heat flow values near the crater edge run-up to 1100 mW m^{-2} and must be still higher inside the crater. Although this is very high compared to background heat flow values, it is not abnormal for mud volcanoes. The absence of a bottom simulating reflection in the surrounding sediments may be explained by a low regional methane flux through the sediments. Consequently, dewatering of the accretionary wedge complex is mainly focused along fault surfaces and through seafloor structures, such as mud volcanoes.

[31] **Acknowledgments.** Thanks go to the shipboard party of the R/V *Belgica*, during the CADIPOR [2002] cruise on the Moroccan margin. The deep-tow Chirp sonar data were acquired in cooperation with Ifremer (B. Marsset). This work frames in the ESF Euromargins (Moundforce, MVSeis) and FWO GeNesis projects. D.D. is working on a specialization Ph.D. grant of the Institute for the Promotion of Innovation by Science and Technology in Flanders (IWT). J.P. and P.V.R. are funded by FWO-Flanders.

References

Aloisi, G., C. Pierre, J. M. Rouchy, and J. C. Faugeres (2002), Isotopic evidence of methane-related diagenesis in the mud volcanic sediments of the Barbados accretionary prism, *Cont. Shelf Res.*, *22*(16), 2355–2372.

Bangs, N., D. Sawyer, and X. Golovchenko (1993), Free gas at the base of the gas hydrate zone in the vicinity of the Chile triple junction, *Geology*, *21*, 905–908.

Berastegui, X., C. J. Banks, C. Puig, C. Taberner, D. Waltham, and M. Fernandez (1998), Lateral diapiric emplacement of Triassic evaporites at the southern margin of the Guadalquivir Basin, Spain, in *Cenozoic Foreland Basins of Western Europe*, edited by A. Mascle et al., *Geol. Soc. Spec. Publ.*, *143*, 49–68.

Blinova, V., and E. Bileva (2003), Some geochemical characteristics of relatively active and passive mud volcanoes (Gulf of Cadiz and Alboran Sea), in *Geological and Biological Processes at Deep-Sea European Margins and Oceanic Basins*, *IOC Workshop Rep.*, vol. 187, edited by M. Marani, G. Akhmanov, and A. Suzyumov, p. 17, UNESCO, Paris.

Bohrmann, G., et al. (2003), Mud volcanoes and gas hydrates in the Black Sea: New data from Dvurechenskii and Odessa mud volcanoes, *Geo Mar. Lett.*, *23*(3–4), 239–249.

Bouriak, S., M. Vanneste, and A. Saoutkine (2000), Inferred gas hydrates and clay diapirs near the Storegga slide on the southern edge of the Voring Plateau, offshore Norway, *Mar. Geol.*, *163*, 124–148.

Casas, D., G. Ercilla, and J. Baraza (2003), Acoustic evidences of gas in the continental slope sediments of the Gulf of Cadiz (E Atlantic), *Geo Mar. Lett.*, *23*(3–4), 300–310.

Collett, T. (2002), Energy resource potential of natural gas hydrates, *AAPG Bull.*, *86*(11), 1971–1992.

Davie, M. K., O. Y. Zatsepina, and B. A. Buffett (2004), Methane solubility in marine hydrate environments, *Mar. Geol.*, *203*(1–2), 177–184.

De Batist, M., J. Klerkx, P. Van Rensbergen, M. Vanneste, J. Poort, A. Y. Golmshtok, A. A. Kremlev, O. M. Khlystov, and P. Krinitsky (2002), Active hydrate destabilization in Lake Baikal, Siberia?, *Terra Nova*, *14*(6), 436–442.

Dimitrov, L. I. (2002a), Mud volcanoes: The most important pathway for degassing deeply buried sediments, *Earth Sci. Rev.*, *59*(1–4), 49–76.

Dimitrov, L. (2002b), Contribution to atmospheric methane by natural seepages on the Bulgarian continental shelf, *Cont. Shelf Res.*, *22*(16), 2429–2442.

Eldholm, O., E. Sundvor, P. R. Vogt, B. O. Hjelstuen, K. Crane, A. K. Nilsen, and T. P. Gladczenko (1999), SW Barents Sea continental margin heat flow and Håkon Mosby mud volcano, *Geo Mar. Lett.*, *19*(1–2), 29–37.

Flinch, J. (1993), Tectonic evolution of the Gibraltar Arc, Ph.D. thesis, 381 pp., Rice Univ., Houston, Tex., Aug.

Flinch, J. F. (1996), Accretion and extensional collapse of the external Western Rif (northern Morocco), in *Peri-Tethys Memoir 2: Structure and Prospects of Alpine Basins and Forelands., Mem.*, vol. 170, edited by P. A. Ziegler and F. Horvath, pp. 61–86, Mus. Natl. d'Hist. Nat., Paris.

Gardner, J. M. (2001), Mud volcanoes revealed and sampled on the Western Moroccan continental margin, *Geophys. Res. Lett.*, *28*(2), 339–342.

Gei, D., and J. M. Carcione (2003), Acoustic properties of sediments saturated with gas hydrate, free gas and water, *Geophys. Prospect.*, *51*(2), 141–157.

Ginsburg, G. D. (1998), Gas hydrate accumulation in deep-water marine sediments, in *Gas Hydrates: Relevance to World Margin Stability and Climatic Change*, edited by J. Henriet and J. Mienert, *Geol. Soc. Spec. Publ.*, *137*, 51–62.

Ginsburg, G., and V. Soloviev (1998), *Submarine Gas Hydrates*, 216 pp., VNIIOkeangeologia, Saint Petersburg, Russia.

Ginsburg, G. D., A. V. Milkov, V. A. Soloviev, A. V. Egorov, G. A. Cherkashev, P. R. Vogt, K. Crane, T. D. Lorenson, and M. D. Khutorskoy (1999), Gas hydrate accumulation at the Håkon Mosby mud volcano, *Geo Mar. Lett.*, *19*(1–2), 57–67.

Grevemeyer, I., et al. (2004), Fluid flow through active mud dome Mound Culebra offshore Nicoya peninsula, Costa Rica: Evidence from heat flow surveying, *Mar. Geol.*, *207*(1–4), 145–157.

Gupta, A. (2004), Marine gas hydrates: Their economic and environmental importance, *Curr. Sci.*, *86*(9), 1198–1199.

Gutscher, M. A., J. Malod, J. P. Rehault, I. Contrucci, F. Klingelhoefer, L. Mendes-Victor, and W. Spakman (2002), Evidence for active subduction beneath Gibraltar, *Geology*, *30*, 1071–1074.

Hedberg, H. D. (1974), Relation of methane generation to undercompacted shales, shale diapirs, and mud volcanos, *AAPG Bull.*, *58*(4), 661–673.

Henry, P., et al. (1996), Fluid flow in and around a mud volcano field seaward of the Barbados accretionary wedge: Results from Manon cruise, *J. Geophys. Res.*, *101*(B9), 20,297–20,323.

Holbrook, W., H. Hoskins, W. Wood, R. Stephen, and D. Lizarralde (1996), Methane hydrate and free gas on the Blake Ridge from vertical seismic profiling, *Science*, *273*, 1840–1843.

Huseynov, D. A., and I. S. Guliyev (2004), Mud volcanic natural phenomena in the South Caspian basin: Geology, fluid dynamics and environmental impact, *Environ. Geol.*, *46*(8), 1012–1023.

Jacobsen, S. (2001), Gas hydrates and deglaciations, *Nature*, *412*, 691–693.

Kennett, J., K. Cannariato, I. Hendy, and R. Behl (2000), Carbon isotopic evidence for methane hydrate instability during quaternary interstadials, *Science*, *288*, 128–133.

Kenyon, N., M. Ivanov, A. Akhmetzhanov, and G. Akhmanov (2001), Interdisciplinary geoscience research on the north east Atlantic margin and Mid-Atlantic Ridge, *IOC UNESCO Tech. Ser. 60*, 76 pp., UNESCO, Paris.

Kenyon, N., M. Ivanov, A. Akhmetzhanov, and G. Akhmanov (2003), Interdisciplinary geoscience research on the north east Atlantic margin, Mediterranean Sea and Mid-Atlantic Ridge, *IOC UNESCO Tech. Ser.*, *67*, 32 pp., UNESCO, Paris.

Kopf, A. J. (2003), Global methane emission through mud volcanoes and its past and present impact on the Earth's climate, *Int. J. Earth Sci.*, *92*(5), 806–816.

Kvenvolden, K. (1993), Gas hydrates: Geological perspective and global change, *Rev. Geophys.*, *31*(2), 173–187.

Kvenvolden, K. (1998), A primer on the geological occurrence of gas hydrate, in *Gas Hydrates: Relevance to World Margin Stability and Climatic Change*, edited by J. Henriet and J. Mienert, *Geol. Soc. Spec. Publ.*, *137*, 9–30.

MacKay, M., R. Jarrard, G. Westbrook, and R. Hyndman (1994), Origin of bottom simulating reflectors: geophysical evidence from the Cascadia accretionary prism, *Geology*, *22*, 459–462.

Maestro, A., L. Somoza, T. Medialdea, C. J. Talbot, A. Lowrie, J. T. Vazquez, and V. Diaz-Del-Rio (2003), Large-scale slope failure involving triassic and middle miocene salt and shale in the Gulf of Cadiz (Atlantic Iberian margin), *Terra Nova*, *15*(6), 380–391.

Maldonado, A., L. Somoza, and L. Pallares (1999), The Betic orogen and the Iberian-African boundary in the Gulf of Cadiz: Geological evolution (central North Atlantic), *Mar. Geol.*, *155*(1–2), 9–43.

Mazurenko, L. L., V. A. Soloviev, I. Belenkaya, M. K. Ivanov, and L. M. Pinheiro (2002), Mud volcano gas hydrates in the Gulf of Cadiz, *Terra Nova*, *14*(5), 321–329.

Mazurenko, L. L., V. A. Soloviev, J. M. Gardner, and M. K. Ivanov (2003), Gas hydrates in the Ginsburg and Yuma mud volcano sediments (Moroccan margin): Results of chemical and isotopic studies of pore water, *Mar. Geol.*, *195*(1–4), 201–210.

Medialdea, T., R. Vegas, L. Somoza, J. T. Vazquez, A. Maldonado, V. Diaz-Del-Rio, A. Maestro, D. Cordoba, and M. C. Fernandez-Puga (2004), Structure and evolution of the 'olistostrome' complex of the Gibraltar Arc in the Gulf of Cadiz (eastern central Atlantic): Evidence from two long seismic cross-sections, *Mar. Geol.*, *209*(1–4), 173–198.

Ovsyannikov, D. O., A. Y. Sadekov, and E. V. Kozlova (2003), Rock fragments from mud volcanic deposits of the Gulf of Cadiz: An insight into the Eocene-Pliocene sedimentary succession of the basin, *Mar. Geol.*, *195*(1–4), 211–221.

Paull, C. K., P. G. Brewer, W. Ussler, E. T. Peltzer, G. Rehder, and D. Clague (2003), An experiment demonstrating that marine slumping is a mechanism to transfer methane from seafloor gas-hydrate deposits into the upper ocean and atmosphere, *Geo Mar. Lett.*, *22*(4), 198–203.

Pinheiro, L. M., et al. (2003), Mud volcanism in the Gulf of Cadiz: Results from the TTR-10 cruise, *Mar. Geol.*, *195*(1–4), 131–151.

Poort, J., and J. Klerkx (2004), Absence of a regional surface thermal high in the Baikal rift: New insights from detailed contouring of heat flow anomalies, *Tectonophysics*, *383*, 217–241.

Robertson, A., et al. (1996), Mud volcanism on the Mediterranean Ridge: Initial results of Ocean Drilling Program Leg 160, *Geology*, *24*, 239–242.

Sartori, R., L. Torelli, N. Zitellini, D. Peis, and E. Lodolo (1994), Eastern segment of the Azores-Gibraltar line (central-eastern Atlantic): An oceanic plate boundary with diffuse compressional deformation, *Geology*, *22*, 555–558.

Sassen, R., S. Joye, S. T. Sweet, D. A. Defreitas, A. V. Milkov, and I. R. Macdonald (1999), Thermogenic gas hydrates and hydrocarbon gases in complex chemosynthetic communities, Gulf of Mexico continental slope, *Org. Geochem.*, *30*(7), 485–497.

Sclater, J. G., C. Jaupart, and D. Galson (1980), The heat flow through oceanic and continental crust and the heat loss of the Earth, *Rev. Geophys.*, *18*(1), 269–311.

Sloan, E. (1998a), *Clathrate hydrates of natural gases*, 705 pp., CRC Press, Boca Raton, Fla.

Sloan, E. (1998b), Physical/chemical properties of gas hydrates and application to world margin stability and climatic change, in *Gas Hydrates: Relevance to World Margin Stability and Climatic Change*, edited by J. Henriet and J. Mienert, *Geol. Soc. Spec. Publ.*, *137*, 31–50.

Soloviev, V., and G. Ginsburg (1994), Formation of submarine gas hydrates, *Bull. Geol. Soc. Denmark*, *41*, 86–94.

Somoza, L., et al. (2003), Seabed morphology and hydrocarbon seepage in the Gulf of Cadiz mud volcano area: Acoustic imagery, multibeam and ultra-high resolution seismic data, *Mar. Geol.*, *195*(1–4), 153–176.

Trehu, A. M., et al. (2004), Three-dimensional distribution of gas hydrate beneath southern Hydrate Ridge: Constraints from ODP Leg 204, *Earth Planet. Sci. Lett.*, *227*(3–4), 557–558.

Vanneste, M., J. Poort, M. De Batist, and J. Klerkx (2003), Atypical heat-flow near gas hydrate irregularities and cold seeps in the Baikal Rift zone, *Mar. Pet. Geol.*, *19*(10), 1257–1274.

Van Rensbergen, P., M. De Batist, J. Klerkx, R. Hus, J. Poort, M. Vanneste, N. Granin, O. Khlystov, and P. Krinitsky (2002), Sublacustrine mud volcanoes and methane seeps caused by dissociation of gas hydrates in Lake Baikal, *Geology*, *30*, 631–634.

Van Rensbergen, P., et al. (2005a), The El Arraiche mud volcano field at the Moroccan Atlantic slope, Gulf of Cadiz, *Mar. Geol.*, *219*(1), 1–17.

Van Rensbergen, P., D. Depreiter, B. Pannemans, and J. Henriet (2005b), Seafloor expression of sediment extrusion and intrusion at the El Arraiche mud volcano field, Gulf of Cadiz, *J. Geophys. Res.*, *110*, F02010, doi:10.1029/2004JF000165.

Vogt, P. R., J. Gardner, and K. Crane (1999), The Norwegian-Barents-Svalbard (NBS) continental margin: Introducing a natural laboratory of mass wasting, hydrates, and ascent of sediment, pore water, and methane, *Geo Mar. Lett.*, *19*(1–2), 2–21.

Wessel, P., and W. Smith (1991), Free software helps map and display data, *Eos Trans. AGU*, *72*, 441, 445–446.

Wooster, W., A. Lee, and G. Dietrich (1969), Redefinition of salinity, *Deep Sea Res. Oceanogr. Abstr.*, *16*(3), 321–322.

Xu, W., and C. Ruppel (1999), Predicting the occurrence, distribution, and evolution of methane gas hydrates in porous marine sediments, *J. Geophys. Res.*, *104*(B3), 5081–5095.

Yamano, M., S. Uyeda, Y. Aoki, and T. H. Shipley (1982), Estimates of heat-flow derived from gas hydrates, *Geology*, *10*(7), 339–342.

D. Depreiter, J. P. Henriet, J. Poort, and P. Van Rensbergen, Renard Centre of Marine Geology, Ghent University, Krijgslaan 281 S8, B-9000 Ghent, Belgium. (davy.depreiter@ugent.be)

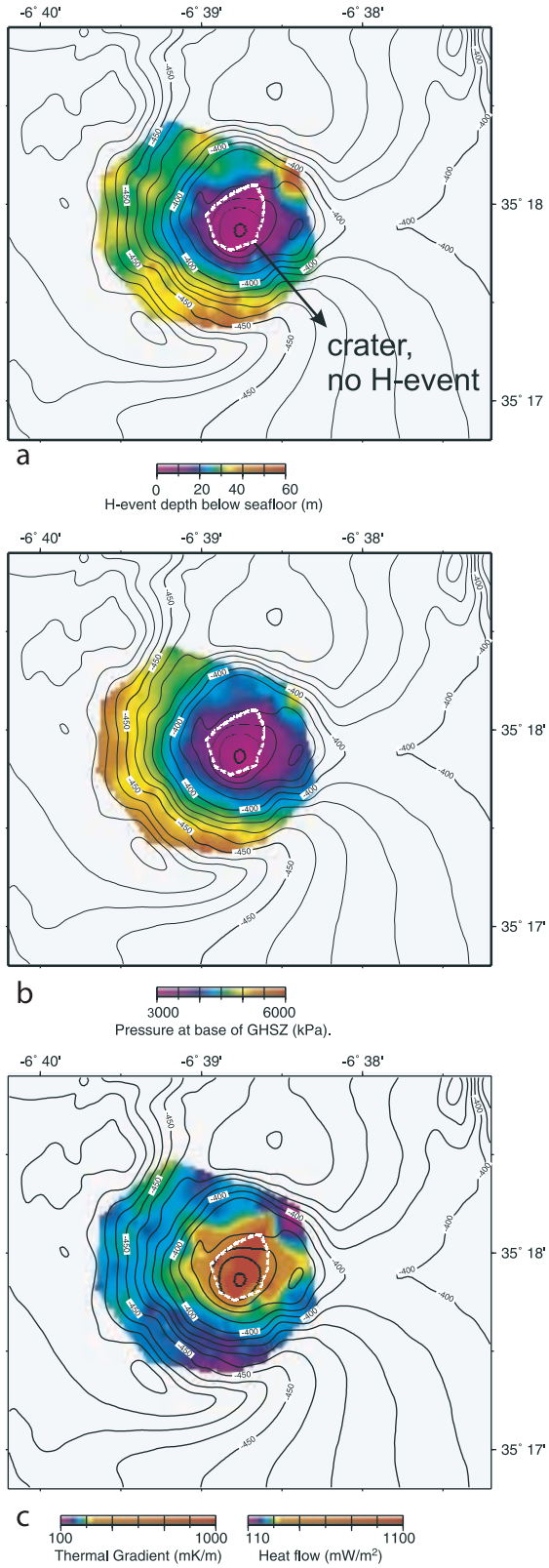

Figure 7. (a) Depth of the H event in meters in the Mercator mud volcano. (b) Calculated pressure at the depth of the H event. (c) Calculated thermal gradient and heat flow inferred from the occurrence of the H event. The thermal gradient and heat flow display a quasi-radial pattern around the mud volcano crater, increasing toward it. In the crater area, no H event was observed.