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Millennial-scale shifts in the methane hydrate stability zone due to Quaternary climate change

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ABSTRACT

Establishing if past millennial-scale climate change affected the stability of marine methane hydrate is important for our understanding of climatic change and determining the fate of marine hydrates in a future warmer world. We show using three-dimensional seismic data offshore of Mauritania, that episodic, millennial-scale shifts of the base of the hydrate stability zone can be imaged below the ocean floor. Process modelling suggests the base of the hydrate stability zone should have shallowed and deepened in response to climate change over the last ~150,000 years. Specifically, there is seismic evidence for millennial-scale shifts during the Holocene (~11,700 years) at a temporal resolution that has previously been unrealised. This is the first evidence that millennial-scale climatic cycles caused hydrate

formation and dissociation and that hydrate instability should be expected in a warming world.

INTRODUCTION

If marine hydrates dissociate in a future warmer world, slope failures could occur (Li et al., 2016) and the released methane could exacerbate ocean de-oxygenation and acidification (Biastoch et al., 2011). Warming and cooling of bottom water should lead to shallowing and deepening of the hydrate stability zone (BHSZ) respectively. Where shallowing has been documented using seismic data and boreholes it has been attributed to climatic warming (Musgrave et al., 2006; Popescu et al., 2006). But the absence of methane from marine hydrate in ice cores that resolve rapid warming events during the late Quaternary has also led some to cast doubt as to whether marine methane hydrates became unstable due to warming episodes since the Last Glacial Maximum (LGM; ~18 k.y. (thousand years) ago) (Sowers, 2006). Furthermore, hydrate formation and dissociation driven by millennial-scale bottom water cooling and warming has not been documented before. We apply a new seismic methodology and process modelling to document the first evidence for multiple episodes of deepening and shallowing of the BHSZ. Some of these probably occurred during the Holocene, at approximately millennial timescales.

SETTING

The study area is characterised by deep water channels that make up the Cap Timiris Canyon (Krastel et al., 2006), slumps and erosional contourite moats that cut into the present day seabed (Fig. 1ABC). Thirteen gravity cores have been retrieved from the canyon

(Henrich et al., 2010). Of these, GeoB 8509-2, 8507-3 and 8502-2 are ~80 km down dip of the study area and penetrate the canyon floor, proximal levee and distal levees, respectively (Henrich et al., 2010). These cores and exploration boreholes, Ras Al Baida-A1 and Al Kinz-1 constrain the age of the succession. The gravity cores record sedimentation rates of 68.5, 18.2 and 10.0 cm/k.y., respectively (Zühlsdorff et al., 2007). The Ras Al Baida-A1 exploration well (location in Fig. 1B; Dahi et al., 2013) shows that the succession (Fig. 1C) is Quaternary in age, yielding a sedimentation rate of 19.2 cm/k.y., but we are unaware of any supporting biostratigraphic data to confirm this. The seismic record is punctuated by seven erosional sequence boundaries (SB1-7, DR1), which bound 6 depositional sequences, that are 50 – 200 m in thickness. SB7 is the present seabed and marked by considerable erosional relief (e.g. DR 1 part C). As the gravity cores are in a distal location relative to this slope setting we propose the highest sedimentation rate of 68.5 cm/k.y. is most appropriate, but we also consider the implications of lower sedimentation rates. Using 68.5 cm/k.y. we estimate the sequences have durations of 73 – 292 k.y.. The succession, measured at a mid-slope point is ~800 m thick (DR1) and given phases of erosion and non-deposition, the 6 depositional sequences span at least the last ~1.2 m.y..

METHODS

We use three-dimensional (3-D) seismic data acquired in 2012 (Fig. 1C). The bin spacing is 12.5 × 25 m and the vertical resolution is ~ 8 m. These data are zero-phase, displayed in depth and a positive polarity represents an increase in the acoustic impedance and a black-red-black reflection. The location of the BHSZ can be identified on seismic data on the basis of a bottom simulating reflection (BSR) which has a high acoustic impedance contrast caused by the hydrate to free gas transition. These are often approximately parallel to the seabed and can cross-cut other seismic reflections (Shipley et al., 1979). Relict BSRs are identified on the same basis and probably represent earlier positions of the BHSZ during different pressure and temperature conditions (Fig. 2A; Davies et al., 2012). In the absence of a BSR or relict BSR, Davies et al., (2012) used another 3-D seismic dataset offshore of Mauritania (Fig. 1A) to show that the position of present and past BHSZs can also be located using a map of the root mean square (RMS) of the seismic amplitude of a cross-cutting reflection. The maps reveal approximately parallel, abrupt, curvilinear changes in the amplitude of the reflection which were termed the lines of intersection (LoIs) of the past and present BHSZ with that reflection. LoIs could occur in the hydrate stability zone (HSZ) and free gas zone (FGZ), either side of the present LoI, where the present BSR intersects the reflection (Fig. 2). Davies et al., (2012) proposed the changes in acoustic impendence are caused by either the precipitation of iron sulfide, due to the pre-existence of hydrate or variations in the saturation of residual gas that remained after hydrate dissociation (Zander et al., 2017). In the HSZ, the latter could be preserved as variations in the concentration of hydrate that cause impedance contrasts (Carcione and Tinivella, 2000). Earlier LoIs would be overprinted by later ones.

Changes in the depth of the BHSZ are mainly controlled by variations in sea level and ocean bottom temperature. We modelled shifts in the BHSZ with time by using an empirical expression for the hydrate stability curve (HSC) (Lu and Sultan, 2008) for a mixture of brine (with seawater salinity of 3.5%) and pure methane and assumed a constant geothermal gradient of 40^{o}C km^{-1}. Bottom water temperature was estimated by adding the past bottom water temperature anomalies to the present vertical temperature profile using a 400,000-year long time series of zonally averaged ocean temperatures through the entire water column at 20^{o}N, extracted from an integration of the CLIMBER-2 intermediate complexity climate model (Ganopolski and Calov, 2011; ‘GC’ anomalies). Changes in sea level were extracted from the time series by Bintanja and van de Wal (2008). The present BHSZ was calculated using a vertical profile of observed modern ocean temperatures characteristic of the wider oceanic area around the Cap Timiris Canyon. The profile was extracted from the World Ocean Atlas (WOA) (Locarnini et al., 2013) and consisted of annual mean temperatures averaged within the region 18-22^o N, 21-17^o W. Changes in the temperature profile of the sediment due to variations in bottom water temperature were calculated vertically using a one-dimensional (1-D), uniform and constant heat diffusivity of 10^{-6} m^2s^{-1} (e.g., Muraoka et al., 2014), a geothermal gradient of 40^{o}C km^{-1} with a boundary condition 10 km below the seafloor. Given typical hydrate volumetric concentrations of 1%-10% (Archer et al., 2009), heat fluxes associated with the formation or dissociation of hydrates would be 10 to a 100 times smaller than typical marine geothermal heat flows of 0.1 W m^{-2} (e.g., Hofmann and Morales Maqueda, 2009) and have therefore been ignored. We applied a subsidence rate of 68.5 cm/k.y but also included an erosional event which was assumed to start at 10 k.y. until the present which is clearly evidenced at the present seabed on the seismic data (Figs 1B and 3C; DR1).

SEISMIC OBSERVATIONS AND INTERPRETATION

A representative seismic cross section shows that the present BSR is comprised of a continuous reflection or a series of high amplitude reflections that shallow landward, terminating immediately below the seabed (Fig. 1C). There are at least 5, deeper relict BSRs that have a similar curved form to the present BSR and have consistent vertical separations of between 40 – 100 m (marked 1-5, Fig. 1C). Measured in a mid-slope position the distance between the deepest and shallowest is ~ 400 m (Fig. 1C).

The RMS amplitude map (Fig. 3AB) of a selected cross-cutting reflection (Fig. 3C) reveals several LoIs, both landward and seaward of the present LoI. They have separations of 0.1 – 1 km. LoIs within the present day HSZ are often too subtle to be identified on seismic cross sections although there are some exceptions (gray dots - Fig. 3CD). There are at least 12 LoIs seaward of the present LoI within the HSZ which are marked i-xii on the RMS amplitude map (Fig. 3A). There is evidence for erosion at the present seabed to the west, which is part of a deep moat that truncates the reflection (Figs. 1C and 3C). The moats are north-south orientated, ~1 km wide, up to 200 m deep and where they amalgamate form erosional troughs that are up to 8 km wide (DR1 part B). LoIs are distinct from seismic artefacts seen in some of the amplitude maps (Fig. 3B). Seismic ‘chimneys’ are located between relict BSRs (Fig. 1C).

The deposition sequences have durations of 73 – 292 k.y. which is within the eccentricity period of Milankovitch cycles. During glacial lowstands, extensive sand seas and large dune fields progressed onto the continental shelf (Henrich et al., 2010) in response to strengthened northeasterly trade winds. Sedimentation rates were high. During interglacials, sedimentation rates dropped and deep water erosion processes probably dominated. Erosion, evidenced by the moats cutting into the present seabed (Figs 1C, 3C and DR1) is consistent with the Holocene interglacial.

The vertical separations of the relict BSRs are too large for them to be active boundaries for higher order gas compositions (see Popescu et al., 2006). The even vertical distribution of the relict BSRs suggests that they were created at regular time intervals. We assume a balance between subsidence and sedimentation, so the average subsidence rate is similar to the sedimentation rate of 68.5 cm/k.y. Therefore, 400 m of subsidence which is the vertical distance between the modern BSR and the deepest relict BSR, would have occured over a period of 584 k.y.. Since there are 5 relict BSRs, their separation in time is about 117 k.y., which is comparable to the eccentricity period of Milankovitch cycles. We rule out much lower sedimentation rates such as 10.0 cm/k.y. as this would not be consistent with exploration borehole dating of the succession (Ras Al Baida-A1 well; Dahi, et al., 2013). We speculate they may mark Quaternary glacial cycles (e.g. Zander et al., 2017).

The physical explanation for LoIs remains uncertain. Episodes of shallowing of the BHSZ would have resulted in a new BHSZ, with *in situ* gas liberation due to hydrate dissociation below it, resulting in changes in gas saturation and therefore seismic impedance (Zander et al., 2017). Or gas could have migrated and ponded below a BHSZ that was undergoing successive episodes of deepening (Davies et al., 2012). Variations in gas saturation would cause variations in hydrate saturation which accounts for LoIs in the present HSZ. Their preservation could be accounted for by low rates of gas migration due to low free gas saturation and a low permeability of the host sediment (Zander et al., 2017). The parallelism of some LoIs with the present LoI makes other explanations for the acoustic impedance contrasts, such as sedimentary variabilities or seismic artefacts very unlikely. Lastly, the occurrence of vertical gas pipes connecting relict BSRs (Fig. 1C) indicates methane periodically migrated vertically through the succession probably after an episode of hydrate dissociation.

DISCUSSION AND CONCLUSIONS

There remain uncertainties around the formation of relict BSRs (e.g. Zander et al., 2017) and LoIs generally (Davies et al., 2012). Furthermore applying a different sedimentation rate and therefore sea level and bottom water temperature (e.g. Bintanja and van de Wal, 2008) would result in a different model of the shifts in the LoIs. Given the uncertainties we do not propose that there is a direct match between the seismic data and the modelled shifts, but the model serves to demonstrate that multiple landward and seaward shifts in the BHSZ of the scale we observe should have occurred due to Quaternary climate change. Our interpretation that relict BSRs represent Quaternary glaciations is also tentative (*cf.* Zander et al., 2017). Despite this the occurrence of multiple relict BSRs and 6 depositional sequences bounded by erosion surfaces is important context for the observation of multiple LoIs seaward of the present LoI. There are two basic, very important, seismic observations that show they formed recently during the Holocene and therefore at a frequency approaching a millennial-scale. Firstly, deep erosional moats are evident at the present seabed (Fig. 3C; DR1) and therefore erosion occurs at the present day and in the recent past. Erosion is consistent with the Holocene interglacial (the last 11.7 k.y.), when sedimentation rates dropped and deep water erosion processes dominated (Henrich et al., 2006). Secondly the present LoI and the LoIs seaward of it have similar orientations and curvilinear planforms (Fig. 3AB) to these erosional features which demonstrates contemporaneity. So they formed during the Holocene and at a temporal resolution that has previously been unrealised. The resolution is considerably higher than Davies et al., (2012) who identified LoIs caused by 100 k.y. glacial-interglacial cycles. The erosion would have led to a cooling of the succession and localised deepening of the BHSZ (Fig. 4B). This is consistent with a climatically driven reduction in sedimentation rates from over 100 cm/k.y. to less than 40 cm/k.y. since the beginning of the Holocene (Holz, 2004) and sediment removal by bottom currents dominating over deposition. Abrupt, post-LGM oscillations, such as the Heinrich stadial 1, Bølling-Allerød warm period or the Younger Dryas could also account for some of the LoIs located seaward of the present one, as long as the magnitude of the bottom water temperature increase exceeded present day bottom water temperatures. We rule out seasonal variations of the seabed temperature because with a typical thermal diffusivity of 10^{-6} m^2s^{-1}, a temperature perturbation at the seafloor would take about 300 years to reach a depth of 100 m below the seabed, which is rapid enough for millennial-shifts and too slow for seasonal ones to occur (Berndt et al., 2014). Sedimentation by itself can also be ruled out as a driver for seaward shifts as the magnitudes of the shifts over the last 18 k.y. are too substantial. The Holocene, erosion-driven deepening caused methane capture rather than release, which is counter to many reports of warming induced dissociation across significant tracts of oceans (Skarke et al., 2014). Therefore the relationship between glacial-interglacial cycles and local hydrate dynamics could be more complex than previously proposed.

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FIGURES

Figure 1 A: Map of the northwestern African margin including two dip magnitude maps of the seabed. Northern one – this study area. Southern one – the study area for Davies et al., (2012). Gray dashed lines – bathymetry (m). B: Zoom-in of the dip magnitude map of the seabed for the study area. CM - contourite moat in this and subsequent figures. Black dashed line – the eastern boundary to the deep water erosion evidenced in figure 3. Red dot – location of gravity cores. Yellow – Cap Timiris Canyon. C: Representative seismic line showing present BSR (yellow dashed line), 5 relict BSRs and seismic chimney (black vertical arrow).

Figure 2 A: 1-D illustrative temperature and hydrate stability curve for a deep water marine setting. Yellow dot – present position of the BHSZ. B: 3-D schematic of a dipping seismic reflection intersected by a BHSZ that has shallowed and deepened over geologic time due to changes in pressure and temperature conditions. Present and past positions of the BHSZs are marked by a present BSR, a relict BSR and LoIs (see Davies et al., 2012). LoIs represent intersections of the BHSZ which may or may not be marked by a BSR or relict BSR. FGZ – free gas zone; HSZ – hydrate stability zone.

Figure 3 A: An RMS amplitude map of a selected cross-cutting reflection. White line – present LoI; black lines – LoIs; black lines marked by i-xii – past LoIs seaward of the present one; Z – deflections in LoIs due to an overlying canyon (see Davies et al., 2012). B: Zoom-in of the RMS amplitude map of the reflection showing the typical curvilinear amplitude changes. C: Representative seismic line showing the BSR and the selected reflection. Yellow dashed line – BSR; white dashed line – the selected cross-cutting reflection. Gray dots – changes in seismic amplitude on other cross-cutting reflections indicative of a LoI. D: Zoom-in of the BSR showing a potential relict BHSZ marked by changes in reflection amplitude.

Figure 4. Model of the shifts in space and time of the intersection between the BHSZ and the selected stratal reflection. A: Time series of GC temperature anomalies near the seafloor relative to present deep global ocean temperature (blue curve; Ganopolski and Calov, 2011) and sea level (red curve; Bintanja, and van de Wal, 2008). B: Trace of the LoI for a stratal reflection that was at the seafloor 150 k.y. ago estimated using the GC anomalies (black line). The present seafloor has a slope of 32 m/km (~2^o) landward of x=-6 km and of 53 m/km (~4^o) in the seaward direction. This change in slope is the result of current erosion resulting in a contourite moat, which we prescribe to have started at the beginning of the Holocene (~10 k.y.). The red, yellow and green lines show the position of the stratal reflection (SR) at 125 k.y., 18 k.y. and present respectively and the red, yellow and green dots mark where the LoIs are for 125 k.y., 18 k.y. and the present day. Warming caused seaward shifts, cooling caused landward shifts.

[1] DR1 A: Dip magnitude of the seabed (the same as in part B of Fig. 1). Representative seismic lines that are oblique (B), following the strike (C) and along the dip (D) of the slope. Vertical black lines – intersections between the seismic lines.

[1] GSA Data Repository item 201Xxxx, Dip magnitude map of the seabed and representative seismic lines showing 6 depositional sequences is available online at www.geosociety.org/pubs/ft20XX.htm, or on request

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