



**HAL**  
open science

## Gas seeps and gas hydrates in the Amazon deep-sea fan

Joao Marcelo Ketzer, Adolpho Herbert Augustin, Luiz Frederico Rodrigues,  
Rafael S Oliveira, Daniel Praeg, Maria Alejandra Gomez Pivel, Antonio  
Tadeu dos Reis, Cleverson G Silva, Bruno Leonel

### ► To cite this version:

Joao Marcelo Ketzer, Adolpho Herbert Augustin, Luiz Frederico Rodrigues, Rafael S Oliveira, Daniel Praeg, et al.. Gas seeps and gas hydrates in the Amazon deep-sea fan. *Geo-Marine Letters*, 2018, 38 (5), pp.429-438. 10.1007/s00367-018-0546-6 . hal-02196115

**HAL Id: hal-02196115**

**<https://hal.science/hal-02196115>**

Submitted on 9 Oct 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



# Gas seeps and gas hydrates in the Amazon deep-sea fan

Joao Marcelo Ketzer<sup>1,2</sup>  · Adolpho Augustin<sup>1</sup> · Luiz Frederico Rodrigues<sup>1</sup> · Rafael Oliveira<sup>1</sup> · Daniel Praeg<sup>1,3</sup> · Maria Alejandra Gomez Pivel<sup>4</sup> · Antonio Tadeu dos Reis<sup>5</sup> · Cleverton Silva<sup>6</sup> · Bruno Leonel<sup>7</sup>

Received: 10 January 2018 / Accepted: 2 August 2018 / Published online: 17 August 2018  
© The Author(s) 2018

## Abstract

Deep-sea fans have been proposed to act as carbon sinks, rapid deposition driving shallow methanogenesis to favor net storage within the gas hydrate stability zone (GHSZ). Here, we present new evidence of widespread gas venting from the GHSZ on the upper Amazon deep-sea fan, together with analyses of the first samples of gas hydrates recovered offshore NE Brazil. Multibeam water column and seafloor imagery over an 18,000-km<sup>2</sup> area of the upper Amazon fan reveal 53 water column gas plumes, rising from venting features in water depths of 650–2600 m. Most gas vents (60%) are located along seafloor faults that record the ongoing gravitational collapse of the fan above deep *décollements*, while others (40%) are located in water depths of 650–715 m within the upper edge of the GHSZ. Gas compositions from hydrates recovered in vents at three locations on and north of the fan indicate biogenic sources (dominantly methane with 2–15% of CO<sub>2</sub>;  $\delta^{13}\text{C}$  from  $-81.1$  to  $-77.3\text{‰}$ ), whereas samples from vents adjacent to the fan proper include possible thermogenic contributions (methane 95%, CO<sub>2</sub> 4%, and ethane 1%;  $\delta^{13}\text{C} - 59.2\text{‰}$ ). These results concur with previous findings that the upper edge of the GHSZ may be sensitive to temporal changes in water temperatures, but further point to the importance of gas escape from within areas of gas hydrate stability. Our results suggest the role of fluid migration along pathways created by faulting within rapidly deposited passive margin depocenters, which are increasingly recognized to undergo gravitational collapse above *décollements*. Our findings add to evidence that gas can escape from sediments to the sea in areas where gas hydrates are stable on passive margins, and suggest the need of further studies of the dynamics of deep-sea depocenters in relation to carbon cycling.

## Introduction

Sediment burial in submarine depocenters drives biogeochemical processes that sequester organic carbon over geological timescales, but also convert part of it into mobile hydrocarbons, principally methane (Dickens et al. 2004). In the deep sea, methane that migrates toward the seabed may be stored in gas hydrates and/or authigenic carbonates (Arning et al. 2013), or released to the oceans by seafloor venting (Römer et al. 2014). Recent studies of continental slope

settings suggest seafloor gas venting to be a more widespread phenomenon than previously recognized (Skarke et al. 2014). While most vented gas may dissolve in the water column (McGinnis et al. 2006), a portion may reach the atmosphere (Solomon et al. 2009). The latter possibility is of interest in relation to carbon stable isotopic evidence that methane emissions are 60–110% greater than current global estimates (Schwietzke et al. 2016). An improved understanding of the occurrence and mechanisms of deep-sea gas venting is thus of importance for our understanding of global carbon cycling in

✉ Joao Marcelo Ketzer  
marcelo.ketzer@lnu.se

<sup>1</sup> Petroleum and Natural Resources Institute, Pontificia Universidade Católica do Rio Grande do Sul (PUCRS), Av. Ipiranga 6681, Porto Alegre 91619-900, Brazil

<sup>2</sup> Present address: Department of Biology and Environmental Sciences, Linnaeus University, 391 82 Kalmar, Sweden

<sup>3</sup> Géoazur, 250 rue Albert Einstein, 06560 Valbonne, France

<sup>4</sup> Instituto de Geociências, Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalves 9500, Porto Alegre 91509-900, Brazil

<sup>5</sup> School of Oceanography, Universidade do Estado do Rio de Janeiro (UERJ), R. Sao Francisco Xavier 524, Rio de Janeiro 20550-013, Brazil

<sup>6</sup> Department of Geology, Universidade Federal Fluminense (UFF), Av. Gen. Milton Tavares de Souza s.n., Niterói 24210-346, Brazil

<sup>7</sup> Seaseep Dados de Petróleo, R. Mexico 03, Rio de Janeiro 20031-144, Brazil

the context of ongoing climate-driven changes (Biastoch et al. 2011), of mass transfers between sediments and the ocean (Lamaitre et al. 2014), and of marine environmental and ecosystem dynamics (Hovland et al. 2012, and references therein).

Seafloor gas venting has been investigated in a variety of deep-sea settings worldwide, all associated with known or inferred occurrences of gas hydrates (Hovland et al. 2012). Gas plumes have been observed to align along the edge of the regional gas hydrate stability zone (GHSZ) in several areas, suggesting the climate-driven dissociation of gas hydrates (Westbrook et al. 2009; Skarke et al. 2014; Hautala et al. 2011; Johnson et al. 2015). However, gas venting also takes place at greater water depths within the GHSZ (Olu-Le Roy et al. 2007; Praeg et al. 2014; Johnson et al. 2015; Andreassen et al. 2017). Gas venting from the GHSZ has been explained in terms of mechanisms to elevate or modify the phase boundary (see Liu and Flemings 2007; Haacke et al. 2009), or alternatively by the creation of fluid migration pathways along faults or fractures (e.g., Hornbach et al. 2007; Riedel et al. 2010), or by seafloor erosion (Skarke et al. 2014). Deep structural pathways are recognized to be important for fluid migration through the GHSZ on convergent margins, and there is evidence that they also play a role on passive margins, notably where Cenozoic depocenters experience gravitational collapse above detachment surfaces (Rowan et al. 2004).

The Amazon River has one of the world's highest sediment discharges (Damuth and Kumar 1975) and is the largest supplier of terrestrial organic carbon to the oceans ( $31\text{--}55 \times 10^{12}$  g carbon per year; Richey et al. 1980). It culminates in one of the world's largest deep-sea fans, a Neogene depocenter within which loading drives ongoing gravitational collapse (Reis et al. 2010, 2016). The presence of gas hydrates in the Amazon deep-sea fan has been inferred from observations of a discontinuous bottom simulating reflector (BSR; Manley and Flood 1988; Tanaka et al. 2003; Berryman et al. 2015) and from pore water freshening in ODP 155 leg cores taken between 2400–4100 m depth below seafloor (Fig. 1; Piper et al. 1997). Here, we present the first evidence of gas release to the water column from the Amazon fan, using multibeam echosounder (MBES) imagery acquired across an area of 18,000 km<sup>2</sup>, in water depths of 250–3500 m (Fig. 1), which also allows us to map the distribution of gas flares in relation to seafloor vents and structures. We also present geochemical analyses of the first gas hydrate samples recovered from the NE continental margin of South America. Our findings provide new insights into the interaction of climate-driven changes and/or seasonal changes in water temperature in gas hydrate stability with gravitational tectonics on large deep-sea fans and their contribution to the global carbon cycle, and will help to guide future research investigations on global climate change, geohazards, and energy resources.

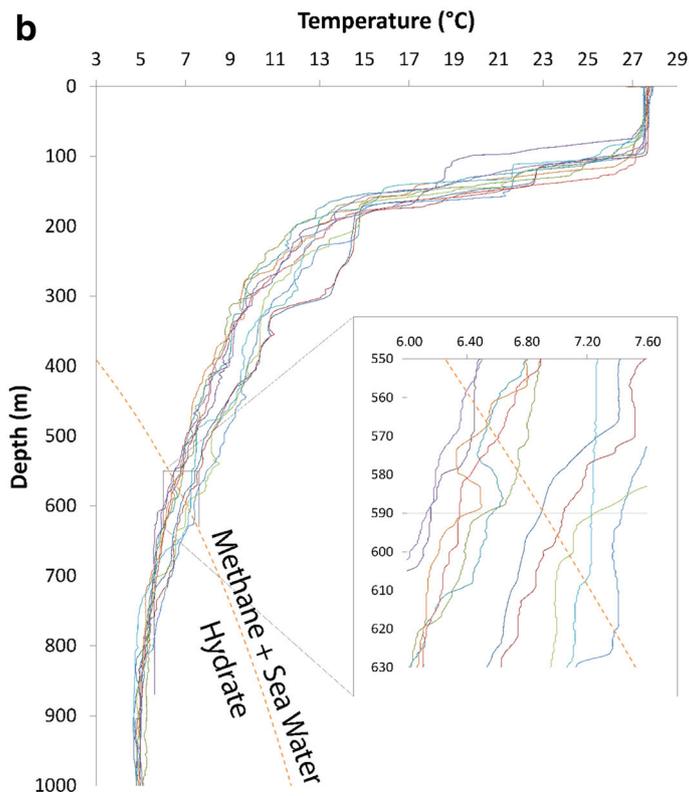
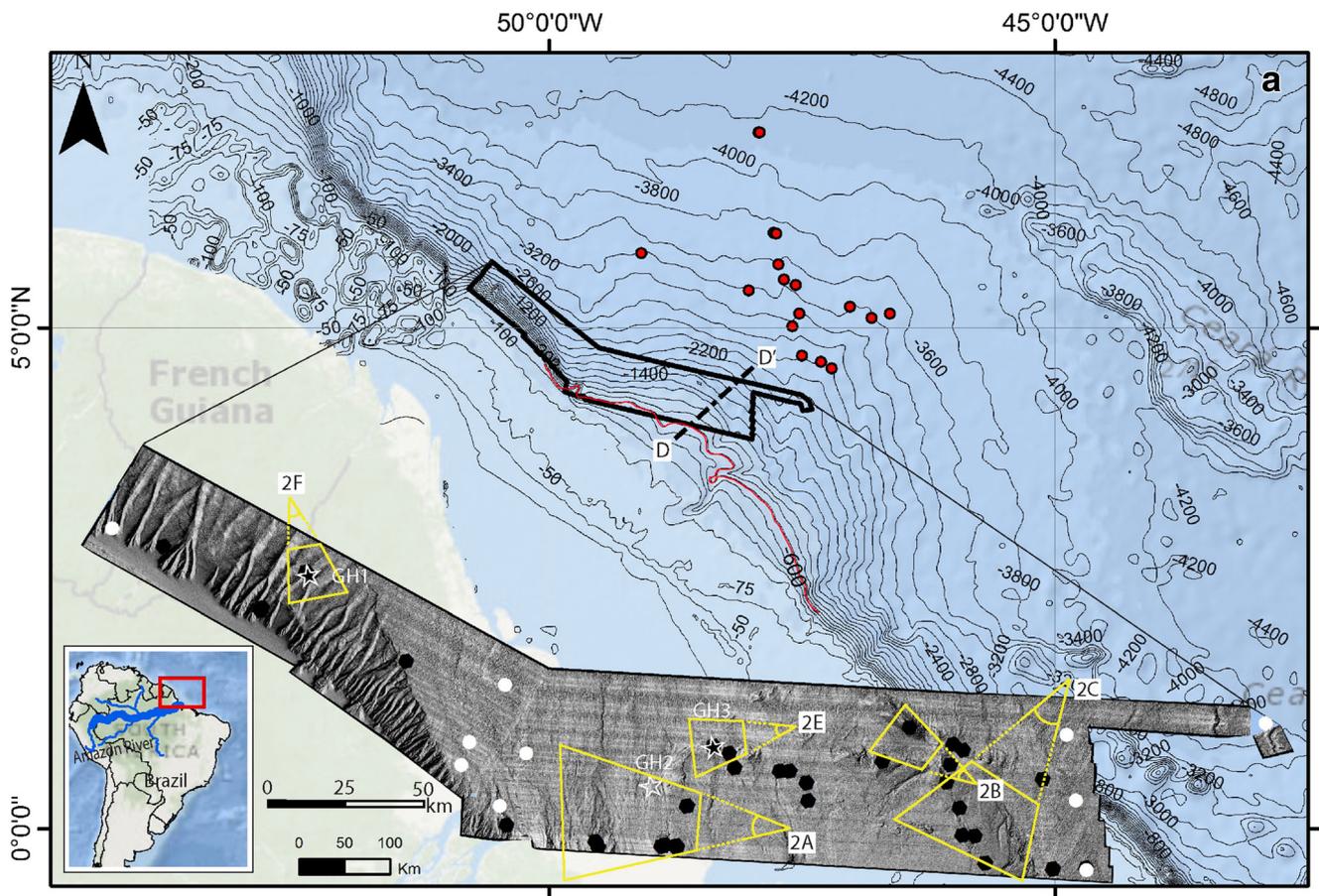
**Fig. 1** (a) Location map showing the upper Amazon fan study area (black polygon) and the multibeam echo sounder survey area in inset. Black hexagons show the location of (one or more) plumes; stars represent sites where gas hydrates were recovered in cores. White dots show the location of water column (XBT or CTD) measurements. Labels 2A, 2B, 2C, 2E, and 2F are viewpoints for Fig. 2(A, B, C, E, and F, respectively). Line D–D' indicates the position of the seismic line in Fig. 2D. Red dots indicate sites drilled during ODP Leg 155 (Piper et al. 1997). The isobath line of –600 m (in red) represents the approximate depth of the edge of the methane hydrate stability zone in the area. The two scale bars refer to the location map (lower bar) and multibeam echo sounder survey area in inset (upper bar). (b) Graphic representation of water column temperatures from XBT and CTD relative to the equilibrium field for pure methane hydrate in seawater (dashed line, from Dickens and Quinby-Hunt 1994)

## Geological setting

The Amazon fan extends 700 km seawards from the continental shelf to water depths of over 4000 m in the Demerara Abyssal Plain, occupying an area of 330,000 km<sup>2</sup> (Fig. 1). The fan is a depocenter up to 10 km thick that has built out rapidly since the Late Miocene in response to sedimentary supply linked to Andean uplift (Figueiredo et al. 2009). Loading is driving the gravitational collapse of the fan above deep *décollements*, expressed at seabed in paired extensional–compressional belts on the shelf and upper slope above water depths of 2000 m, including thrust-folds up to 500 m in seafloor relief (Silva et al. 2009; Reis et al. 2010, 2016). The upper slope is also the source area of giant mass-transport deposits (MTDs) that characterize the Neogene stratigraphic succession of the Amazon fan (Reis et al. 2010, 2016; Silva et al. 2016). The triggering of giant MTDs has been linked to climate-driven variations in sedimentation rate and/or gas hydrate stability during sea level changes, based on drilling results from four examples on the middle fan emplaced within the last 45 ka (Piper et al. 1997; Maslin et al. 1998, 2005). More recently, the emplacement of MTDs throughout the Neogene has been linked to tectonic activity within the upper slope compressional belt (Reis et al. 2016).

## Data and methods

Seafloor features and water column gas flares were identified using Kongsberg EM122 12-kHz multibeam echosounder data acquired in 2012–2013 (horizontal grid size 30 × 30 m), visualized using QPS Fledermaus software, including the Midwater module. Subsurface structures were examined using two sets of multichannel seismic data, acquired for hydrocarbon exploration (made available by the Brazilian National Petroleum Agency - ANP) and interpreted using IHS Kingdom Suite software: (i) ca. 20,000 km of 2D seismic profiles acquired during the 1980s and 1990s by different companies using different air-gun acquisition arrays, with



record lengths of up to 10 s, frequency range between ~8–60 Hz (dominant frequency at ~40 kHz), and vertical resolution of ~10m; (ii) 3D blocks covering a total area of 3800 km<sup>2</sup>, record length of 8 s; frequency range between 12 and 100 Hz (dominant frequency at 80 kHz); vertical resolution of ~5 m).

Water column temperatures were obtained during the multibeam echo sounder survey for determination of the sound velocity using 10 XBT (expendable bathythermograph) measurements and one CTD (conductivity, temperature, depth) measurement (Fig. 1). The temperature vs. depth profiles generated by the XBT and CTD were also used to calculate the limits of the methane hydrate stability zone (MHSZ) in the area, applying the Dickens and Quinby-Hunt (1994) equilibrium equation for pure methane hydrates in seawater. Different gas compositions (e.g., a mixture of carbon dioxide and methane, or heavier hydrocarbons) will dislocate the calculated limit of GHSZ to shallower depths (upslope). The XBT and CTD data showed a significant variation in temperatures for the same depth (ca. 1.7 °C) and, therefore, we estimated the edge of the GHSZ for a depth interval. Our time-limited temperature measurements may not cover the full range of natural variability of water temperatures in the area and, therefore, the estimated depth range is approximated.

Piston cores up to 6 m long were obtained from selected sites in 2015 using the *R/V Teknik Perdana*. Transparent core liners were used to allow visual identification of gas hydrates on deck. Gas hydrates observed in three cores were immediately sampled using a spatula and placed in IsoJar containers at room temperature. Headspace gas composition within Isojars were determined using a GC-2014 Shimadzu gas chromatograph equipped with a VP-Plot Alumina/KCl capillary column. Stable isotopes of carbon were analyzed using a Thermo Fisher Scientific gas chromatograph coupled to a DELTA-V Plus mass spectrometer via an IsoLink and ConFlo IV interface. Isotopic data is reported using the delta notation ( $\delta^{13}\text{C}$ ) in parts per thousand (‰) with ratios relative to the international standard Vienna Pee Dee Belemnite (V-PDB).

## Results

### Seafloor seeps and water column gas plumes

Analyses of MBES data reveal 53 hydroacoustic anomalies within the study area, interpreted as gas plumes that rise sub-vertically from the seafloor to 85–1720 m in the water column (Figs. 1 and 2). Observations from seepage sites worldwide show that such anomalies may be formed of several individual bubble streams, located meters to tens of meters apart (Römer et al. 2012, 2016). In the Amazon study area, the gas plumes are associated with different seafloor signatures that allow us

to distinguish four types of seeps (Fig. 2). Type I seeps are observed in water depths of 650–715 m (Fig. 2(A)), where a high density of plumes (23 in total) is observed in three main clusters, each associated with a seafloor mound 10–20 m high, similar to plumes of types II and III described below.

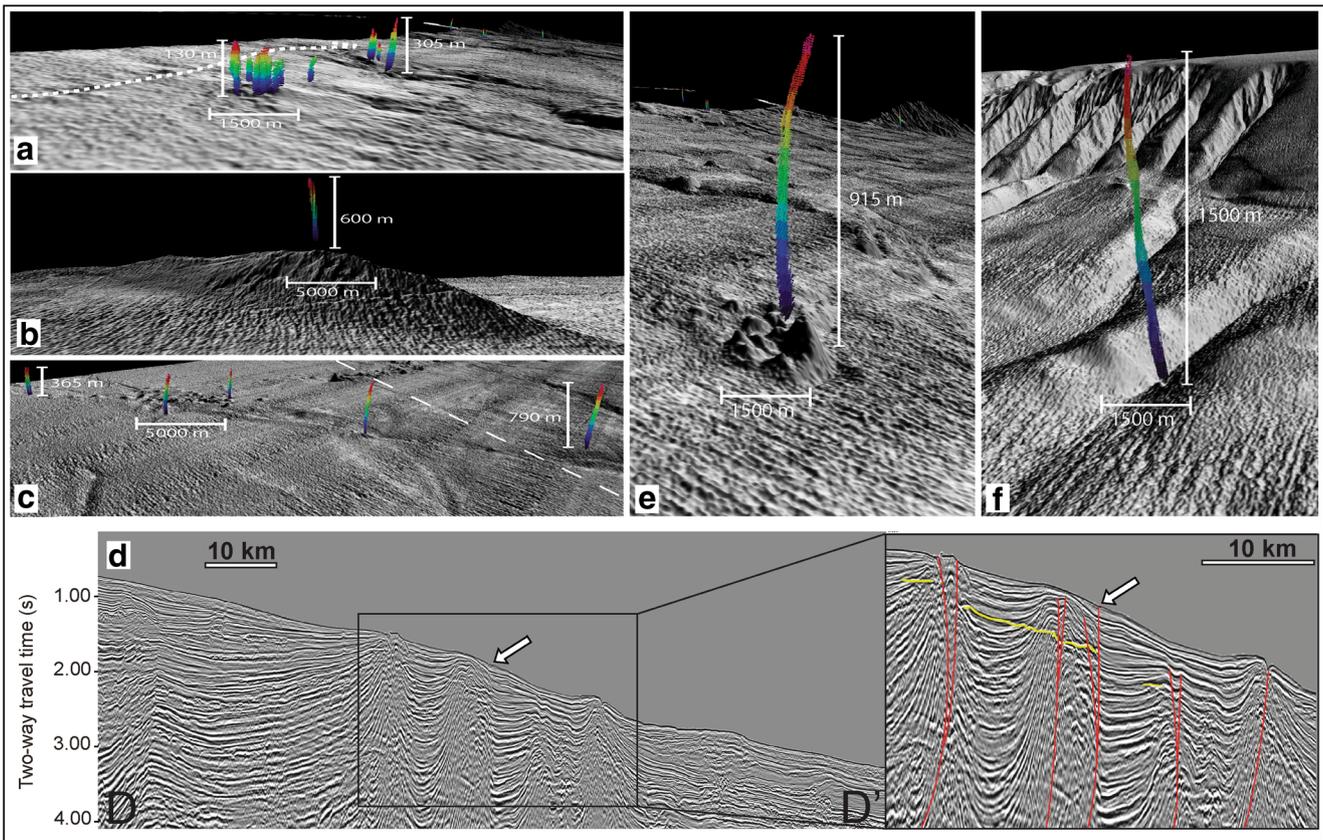
Type II seeps show a clear spatial relationship with seafloor lineaments observed on MBES imagery (Fig. 2(B and C)), which seismic profiles show correspond to structures related to the compressional thrust-fold belt of the upper Amazon fan (Fig. 2(D)). A total of 17 seeps are observed in water depths of 1000–1800 m and are associated with seafloor mounds 10–20 m high located on or a few hundred meters from the lineaments (Fig. 2(C)). Type III seeps occurring at seven sites in the same area as Type II are also associated with seafloor mounds 10–20 m high (Fig. 2(E)) but are not clearly associated with seafloor lineaments. Type IV seeps correspond to six sites observed north of the Amazon fan proper, within slope-confined canyons in water depths between 1000 and 2600 m (Fig. 2(F)).

Considering all observed seeps, there is a clear correlation between water depth and the height of gas plumes (Fig. 3). Interestingly, we observe that the top of the gas plumes does not necessarily coincide with the top of the MHSZ (Fig. 3). Type I plumes (< 715 m water depth) are less than 350 m high and rise a few tens to hundreds of meters above the top of the MHSZ at 550–620 m water depth (Fig. 1). Type II–IV plumes (water depths > 1000 m) are not observed to rise above the MHSZ (Fig. 3).

### Gas hydrates

The composition of venting gases was examined using samples of hydrates recovered from three sites. Two samples (GH2 and GH3) are from the Amazon fan proper; the third (GH1) is from a site on the canyonised continental slope some 50 km to the west (Fig. 1). The two samples from the Amazon fan proper both consist of small hydrate nodules (1–10 mm diameter) dispersed in a muddy matrix (Fig. 4(A)), and can be described as “nodular type” (Malone 1985). The gas hydrate nodules occur in association with authigenic carbonate nodules (millimeter to centimeter size), as well as fragments of a possible chemosynthesis-based community (shells, tube worms; Fig. 4(B)). The gas contained in the hydrates is predominantly methane (85–98%), with variable amounts of CO<sub>2</sub> (2–15%), and trace amounts of ethane (Table 1). Methane  $\delta^{13}\text{C}$  values range from –81.1 to –77.3‰ (Table 1).

In contrast, the gas hydrates recovered west of the Amazon fan from a site on the canyonised continental slope consist of pieces up to 10 cm in length that can be described as “massive type” (Malone 1985). Gas analyses show methane to dominate (95%), followed by CO<sub>2</sub> (4%) and ethane (1%; Table 1). The methane has a  $\delta^{13}\text{C}$  value of –59.2‰ (Table 1).



**Fig. 2** Multibeam echo sounder imagery of sea floor seeps associated with water column gas plumes: **(a)** cluster near the upper limit of the methane hydrate stability zone (the dashed line corresponds approximately to the calculated limit of the stability zone at 620 m water depth—type I seeps); **(b)** plume associated to the fold and thrust belt outcropping on the seafloor (type II seep); **(c)** aligned along a geological structure on the sea floor (dashed line corresponds to the

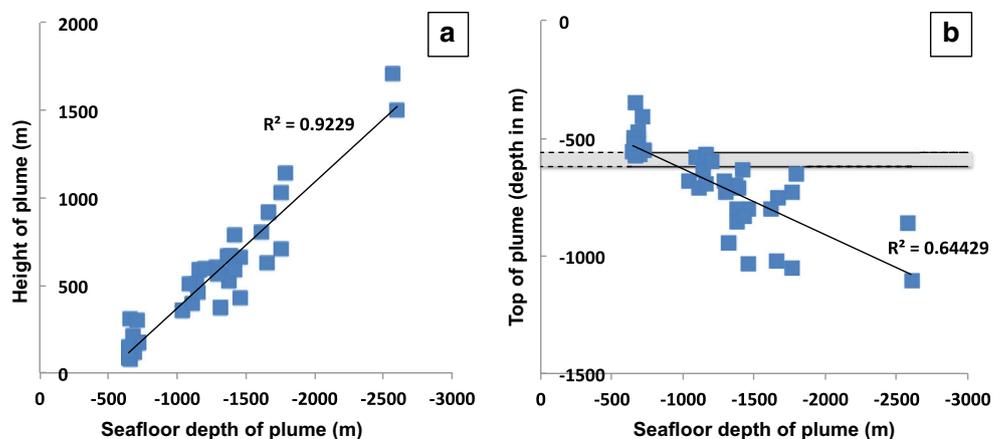
trace of the seismic line in 2D—type II seeps); **(d)** seismic profile crossing the fault (arrows) shown in 3C (dashed line), and a detail of the profile showing the bottom simulating reflector (yellow line) and the structure as a deep fault (red line); **(e)** type III seeps associated with sea floor mounds; **(f)** type IV seeps within canyons north of the Amazon fan. See Fig. 1 for locations of the images

**Discussions**

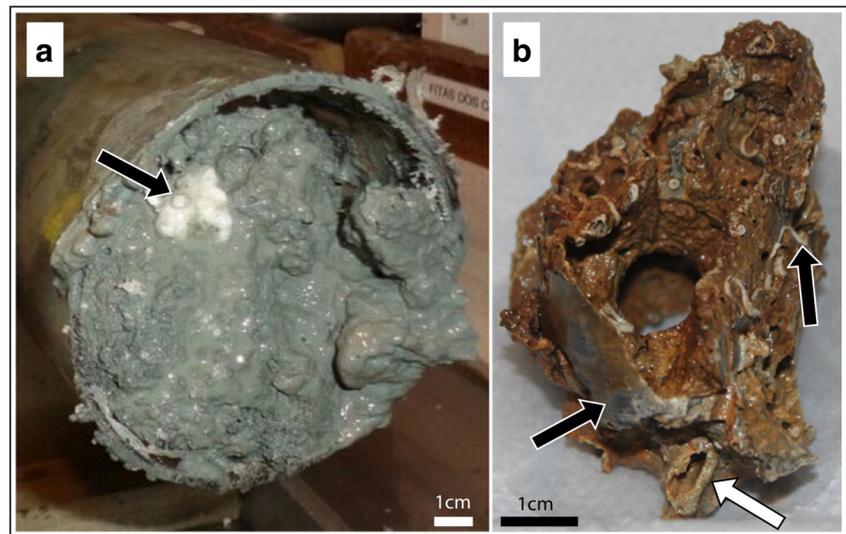
The results presented above allow us to identify two mechanisms that promote ongoing gas seepage from the Amazon fan over Plio-Quaternary timescales. One is the dissociation of gas hydrates along the edge of their stability zone (Fig. 5), inferred

to be the cause of 40% of the seeps mapped in our study. Such a process has been recognized on other continental margins and may be driven by warming of ocean bottom waters over post-glacial or anthropogenic timescales (Skarke et al. 2014; Hautala et al. 2014; Johnson et al. 2015) and/or by seasonal variations in bottom water temperatures (Berndt et al. 2014).

**Fig. 3** Plots showing a linear correlation between: **(a)** water depth and the height of gas plumes, and **(b)** depth of the top of plumes versus seafloor depth (the gray area represents the depth range of the methane hydrate stability zone for pure methane hydrate in equilibrium with seawater in the study area, cf. Dickens et al. 1994; see Fig. 1 inset)



**Fig. 4** Photographs of sediments recovered in piston cores from the Amazon deep-sea fan, showing (a) nodule of gas hydrate (arrow) in sediments (sample GH3; see Fig. 1 for location), and (b) carbonate concretion with shells (black arrows) and tubeworm (white arrow) fragments found together with GH3 gas hydrate sample



A second mechanism is methane migration through the MHSZ to the seafloor along structural pathways, inferred to account for 60% of the seeps that we map on the upper Amazon fan (Fig. 5). We infer this process to have operated throughout gravitational collapse of the fan, which has been underway at least since the Pliocene (Reis et al. 2016).

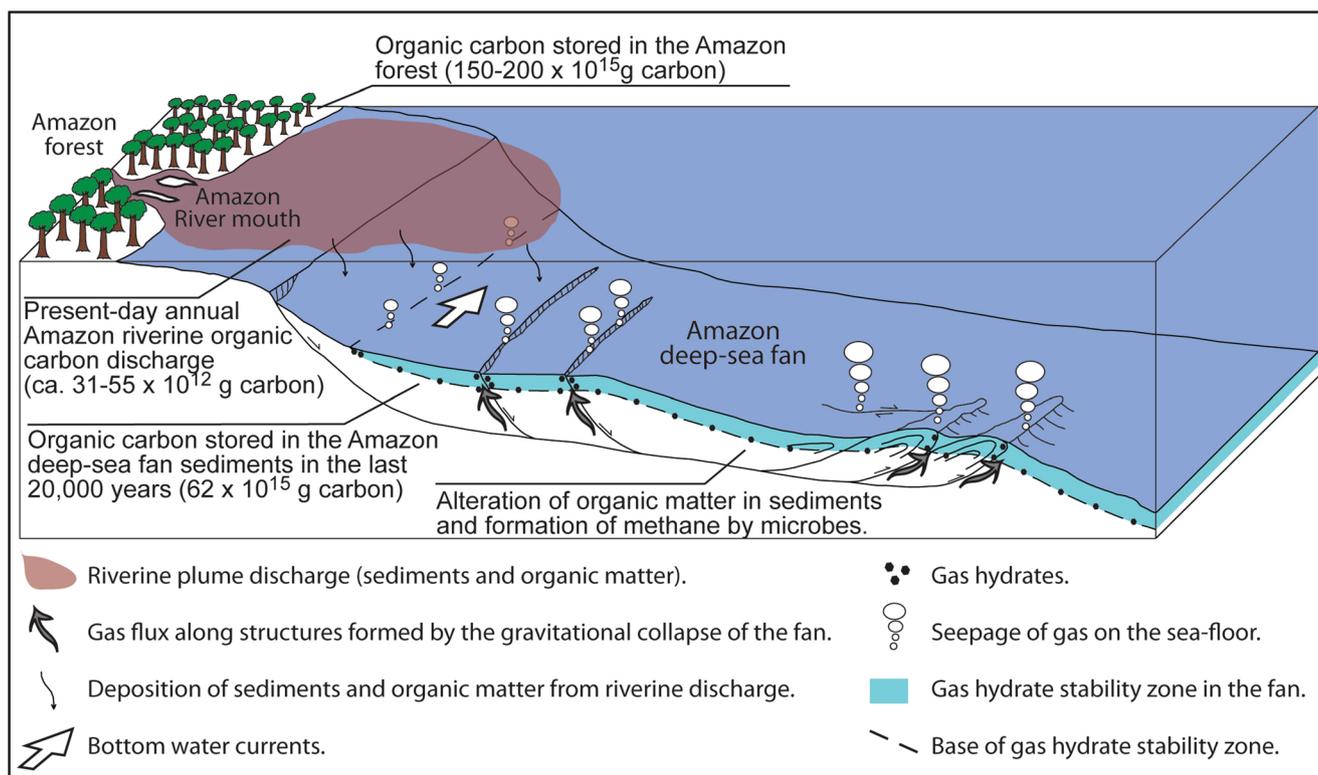
The type I seeps lie in water depths of 650–715 m, near the upper limit or “feather edge” of the methane hydrate stability zone (MHSZ), which our measurements of water column temperatures suggest to lie in water depths of 560–620 m, assuming pure methane hydrate in equilibrium with seawater (Fig. 1). A wider depth range (e.g., 520–680 m) results if water temperature measurements from the World Ocean Data Base (WODB; Boyer et al. 2013) are used to calculate the limits of the methane hydrate stability zone. This suggests that the distribution of type I seeps may be related to the dissociation of gas hydrates near the edge of their stability field (Hautala et al. 2014). Gas hydrates in such a setting are sensitive to changes in pressure and bottom water temperatures, even if the latter are small ( $< 1\text{ }^{\circ}\text{C}$ ) and of short duration ( $< 1$  year; Berndt et al. 2014). Warming of bottom waters since the last glacial maximum, including in response to present-day climate change, has been proposed as the main cause of gas hydrate dissociation at the upper edge of the stability zone in several basins

around the world (Westbrook et al. 2009; Skarke et al. 2014; Hautala et al. 2014). During last glacial maximum (LGM), colder bottom water temperatures in these depths imply the stability zone to have been shallower/thicker, so that the type I seeps lie in an area in which thinning may have liberated free gas accumulated within gas hydrates. Venting implies that free gas is migrating along pathways through the thin GHSZ, which might have been formed by the overpressures created during dissociation of gas hydrates (Stranne et al. 2017). The liberation of free gas in sediments owing to slow dissociation of gas hydrates since the LGM has been modeled for other areas (Foucher et al. 2009; Stranne et al. 2016). Alternatively, the dissociation of gas hydrates at the edge of the gas hydrate stability zone could be caused by seasonal variations in bottom water temperatures (not necessarily related to climate change), promoting the periodic formation and dissociation (with methane venting) of near seafloor gas hydrates (Berndt et al. 2014).

The depth range of type II and III seeps and associated bottom water temperatures ( $3.5\text{--}5\text{ }^{\circ}\text{C}$ ) lies well within the stability zone of methane hydrates, indicating that neither are related to phase boundary changes driven by ocean warming. The spatial relationship between type II seeps and gravity-driven structures at the seafloor, which in depth correspond to transfer and thrust faults (Fig. 2(D)), indicates that the gravitational collapse of the Amazon fan creates active pathways for deep gas migration through the GHSZ until the seafloor. A more detailed study is underway to investigate whether type III seeps may be connected with gas migration through buried structures. The origin of gas in the area of lower sedimentation rate adjacent to the Amazon fan (type IV seeps) is unclear, but could either be deep-sourced and brought to the surface via faults, or shallow-sourced and leaking in response to erosional processes such as canyon/gully incisions, and/or mass wasting, which can

**Table 1** Chemical and isotopic composition of gases trapped in 3 gas hydrate samples recovered in piston cores of three sites (GH1, GH2, and GH3) in the Amazon fan. See Fig. 1 for site location

Sample	CH <sub>4</sub> (ppm)	C <sub>2</sub> H <sub>6</sub> (ppm)	CO <sub>2</sub> (ppm)	CO (ppm)	$\delta^{13}\text{C}$ (CH <sub>4</sub> )
GH1	299,319.6	3629.43	12,492.2	361.49	−59.2‰
GH2-A	83,521.8	2.8	13,938.6	398.08	−81.1‰
GH2-B	11,361.99	N.D.	8803.98	367.76	−80.9‰
GH3	231,072.28	100.56	5405.29	390.17	−77.3‰



**Fig. 5** Schematic diagram showing the Amazon discharge of sediment and organic matter from the continent to the deep sea. Part of the organic matter deposited in the deep-sea fan will be altered to methane by microbes, which will, in turn, migrate upward to be trapped as free gas, gas hydrates and authigenic carbonates. However, another part will seep from the seafloor, either along the edge of the gas hydrate stability zone in response to, for instance, bottom water warming, or along structural

pathways including extensive and compressive fault systems formed by gravitational collapse of deep-sea fans. For reference, the total mass of carbon stored in sediments of the Amazon fan from Late Miocene to Recent is equivalent to several times the quantity stored at present-day in the Amazon Forest (carbon budgets presented in this figure are from Richey et al. 1980; Schlünz et al. 1999; Brienen et al. 2015)

physically cut gas hydrate deposits or accumulations of free gas in subjacent sediments (Skarke et al. 2014).

Our observation that there is a linear, positive correlation between water depth and the height of gas plumes, and that bubbles become totally dissolved and/or unresolvable by echosounding techniques before reaching the top of the MHSZ (seep types II, III, and IV), is indicative that coating of bubbles by a protective hydrate skin exerts influence (Rehder et al. 2002), but it is not the single dominant control of the permanence of gas flares in the water. The variability of plume heights in the same water depth, both within and above the MHSZ, may suggest that other controls like pressure (depth), temperature, original bubble size, and/or gas composition may exert important controls too (McGinnis et al. 2006; Waite et al. 2017).

The molecular and stable carbon isotope compositions of methane trapped in hydrates in the two sites in the Amazon fan (sites GH2 and GH3; Fig. 1 and Table 1) indicate a dominant biogenic origin. This is consistent with results from disseminated and nodular gas hydrates sampled in other basins worldwide, particularly in areas of high sedimentation rates and large organic matter accumulations, such as other deep-

sea fan structures (Miller et al. 2015). Gas hydrates in the adjacent continental slope (site GH1; Fig. 1 and Table 1), however, show different molecular and stable carbon isotopic compositions. Although a biogenic origin is still indicated, the presence of heavier hydrocarbon (ethane) and depletion in the <sup>12</sup>C isotope in the methane gas suggests a possible thermogenic contribution, distinct from the biogenic character of the two samples from the Amazon fan proper. This result supports the idea that deep-sea fans such as the Amazon are loci for the accumulation of large quantities of organic matter (Schlünz et al. 1999) that, in turn, provide the source for biogenic methane production (Arning et al. 2013), which may mask thermogenic signatures in gas seeps at the seafloor.

The Amazon and other large deep-sea fans have been suggested to act as net carbon sinks, in which rapid deposition and shallow methanogenesis favor carbon storage within methane hydrates, and as authigenic carbonates (Arning et al. 2013). Our results show that part of the organic carbon stored within the Amazon fan is being released by methane venting through the seafloor to the ocean (Fig. 5). Modeling of biogenic methane formation in Amazon fan sediments at ODP sites at water depths between 3000–4000 m (see Fig. 1 for location)

indicates that methanogenesis occurs at burial depths greater than 10 m down to hundreds of meters below the sea floor (Arning et al. 2013), possibly mobilizing carbon stored thousands to hundreds of thousands of years ago. This ongoing process of methanogenesis could be the source for the venting sites described here or, alternatively, venting gas could be sourced by deeper (and older) methane reservoirs.

More generally, our work demonstrates that large deep-sea fans like the Amazon are complex systems that play an important role in the accumulation of organic carbon. On one hand, they sequester significant amounts of organic carbon, which is, in the case of the Amazon fan (e.g.,  $62 \times 10^{16}$  g carbon deposited only during the last 20 k.y.; Schlünz et al. 1999), equivalent to several times the quantity stored at present day in the Amazon Forest ( $150\text{--}200 \times 10^{15}$  g carbon; Brienen et al. 2015). On the other hand, they are characterized by long-term geological dynamics (e.g., gravitational collapse) and shorter-term sensitivity to climate changes and/or seasonal variations in bottom water temperatures (e.g., gas hydrate instability) that favor the release of part of this carbon to the oceans. Gravitational collapse of depocenters above shale or salt detachment surfaces is increasingly recognized in passive margin settings as a long-term (millions of years) component of their evolution (Rowan et al. 2004; Boyd et al. 2011; Tassy et al. 2015). It has been argued that most methane emitted from seafloor seeps will not normally reach the atmosphere, owing to dissolution and oxidation in the water column (McGinnis et al. 2006; Mau et al. 2007), but it has been proposed that catastrophic slope failure may allow massive methane release from gas hydrates (Maslin et al. 2004; Maslin et al. 2005). The dynamics of carbon cycling in deep-sea fans are still poorly understood, so the nature and impact of methane emissions from these systems remain speculative and may be significantly underestimated (Römer et al. 2012; Skarke et al. 2014).

## Conclusions

Our study documented for the first time the occurrence of widespread gas seeps, both as seafloor structures and acoustic anomalies in the water column, in the Amazon deep-sea fan and adjacent continental slope area. The observed gas flares lie in two main settings: (1) near the limit of the gas hydrate stability zone (40% of the observed features), possibly related to the dissociation of gas hydrates owing to warming of ocean bottom waters, over post-glacial or anthropogenic timescales, and/or seasonal variations in bottom water temperatures; and (2) along the trace of seafloor faults (60% of the observed features) marking deeper structures related to the gravitational collapse of the fan. The latter shows that gas can migrate through the gas hydrate stability zone to reach the deep oceans, and suggests that this process is facilitated by the gravitational collapse of

passive margin depocenters. Gas in the continental slope area adjacent to the Amazon fan possibly reaches the seafloor via faults, or is shallow-sourced and leaking in response to erosional processes such as canyon/gully incisions, and/or mass wasting, which can physically cut gas hydrate deposits or accumulations of free gas in subjacent sediments.

Our results also include analyses of the first gas hydrate samples recovered from the NE continental margin of South America. The molecular and isotopic compositions of gas trapped in hydrates in sediments of the Amazon fan proper are consistent with a biogenic origin (dominantly methane with 2–15% of CO<sub>2</sub>;  $\delta^{13}\text{C}$  from  $-81.1$  to  $-77.3\text{‰}$ ), whereas those on the adjacent continental slope to a possible thermogenic contribution to the gas mix (methane 95%, CO<sub>2</sub> 4%, and ethane 1%;  $\delta^{13}\text{C} = -59.2\text{‰}$ ). These results are consistent with the generation of large amounts of mobile biogenic methane within the Amazon fan, which may be diluting contributions from deeper thermogenic sources as observed on the adjacent slope.

This paper demonstrated the potential of deep-sea fans for studies of gas hydrate systems as an interaction between externally driven climate changes and the internal dynamics of passive margin depocenters. We suggest a systematic study of large deep-sea fans on the world's continental margins to refine the global methane emission and gas hydrate inventories, and improve our understanding of the natural versus anthropogenic drivers of climate change.

**Acknowledgements** We are grateful to SeaSeep for providing multibeam echosounder data acquired during campaigns of the R/V Teknik Perdana in 2012–2013, and cores acquired during campaigns of the R/V Inspector II in 2015. Seismic profiles were obtained from the Brazilian National Petroleum Agency (ANP). We thank IHS Global Inc. Educational/Academic Grant Program for the use of the Kingdom Software.

**Funding information** J.M.K., A.T.R., and C.S. received research grant Nos. 309915/2015-5, No. 313086/2017-6, No. 308164/2015-6, respectively, from the Brazilian National Research Council (CNPq). J.M.K., D.P., A.T.R., and C.S. are supported by the Brazilian Coordination for the Improvement of Higher Education Personnel (CAPES) research grant No. 0558/2015. D.P. is supported under the SEAGAS project, which has received funding from the European Union's Horizon 2020 research and innovation program under Marie Skłodowska-Curie grant agreement No. 656821.

**Open Access** This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

## References

- Andreassen K, Hubbard A, Winsborrow M, Patton H, Vadakkepulyambatta S, Plaza-Faverola A, Gudlaugsson E, Serov P, Deryabin A, Mattingsdal R, Mienert J, Bünz S (2017) Massive blow-out craters formed by hydrate-controlled methane expulsion from the Arctic seafloor. *Science* 356:948–953 <https://doi.org/10.1126/science.aal4500>

- Aming ET, van Berk W, Santos Neto EV, Naumann R, Schulz HM (2013) The quantification of methane formation in Amazon fan sediments (ODP leg 155, site 938) by hydrogeochemical modeling solid–aqueous solution–gas interactions. *Journal of South American Earth Sciences* 42:205–215
- Berndt C, Feseker T, Treude T, Kraster S, Liebetrau V, Niemann H, Bertics VJ, Dumke I, Dünnbier K, Ferré B, Graves C, Gross F, Hissmann K, Hühnerbach V, Krause S, Lieser K, Schauer J, Steinle L (2014) Temporal constraints on hydrate-controlled methane seepage off Svalbard. *Science* 343:284–287
- Berryman J, Kearns H, Rodriguez K (2015) Foz do Amazonas Basin—a case for oil generation from geothermal gradient modelling. *First Break* 33:91–95
- Biastoch A, Treude T, Rüpke LH, Riebesell U, Roth C, Burwicz EB, Park W, Latif M, Bönning CW, Madec G, Wallmann K (2011) Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification. *Geophysical Research Letters* 38:L08602
- Boyd D, Anka Z, Di Primio R, Kuhlmann G, De Wit MJ (2011) Passive margin evolution and controls on natural gas leakage in the Orange Basin, South Africa. *S Afr J Geol* 114:415–432
- Boyer TP, Antonov JI, Baranova OK, Coleman C, Garcia HE, Grodsky A, Johnson DR, Locarnini RA, Mishonov AV, O'Brien TD, Paver CR, Reagan JR, Seidov D, Smolyar IV, Zweng MM (2013) World ocean database 2013. NOAA atlas NESDIS 72, S. Levitus, Ed., A. Mishonov, technical ed.; Silver Spring, MD, 209 pp., doi: <https://doi.org/10.7289/V5NZ85MT>
- Brienen RJW, Phillips OL, Feldpausch TR, Gloor E, Baker TR, Lloyd J, Lopez-Gonzalez G, Monteagudo-Mendoza A, Malhi Y, Lewis SL, Vásquez-Martinez R, Alexiades M, Álvarez-Dávila E, Alvarez-Loayza P, Andrade A, Aragão LEOC, Araujo-Murakami A, Arets EJMM, Arroyo L, Aymard GA, Bánki OS, Baraloto C, Barroso J, Bonal D, Boot RGA et al (2015) Longterm decline of the Amazon carbon sink. *Nature* 519:344–348. <https://doi.org/10.1038/nature14283>
- Damuth JE, Kumar N (1975) Amazon cone, morphology, sediments, age, and growth pattern. *Geol Soc Am Bull* 86:863–878
- Dickens GR, Quinby-Hunt MS (1994) Methane hydrate stability in seawater. *Geophys Res Lett* 21:2115–2118
- Dickens AF, Geélinas Y, Masiello CA, Wakeham S, Hedges JI (2004) Reburial of fossil organic carbon in marine sediments. *Nature* 427:336–339
- Figueiredo J, Hoom C, van der Ven P, Soares E (2009) Late Miocene onset of the Amazon River and the Amazon deep-sea fan: evidence from the Foz do Amazonas Basin. *Geology* 37:619–622. <https://doi.org/10.1130/G25567A.1>
- Foucher J-P, Westbrook GK, Boetius A, Ceramicola S, Dupré S, Mascle J, Mienert J, Pfannkuche O, Pierre C, Praeg D (2009) Structure and drivers of cold seep ecosystems. *Oceanography* 22:92–109. <https://doi.org/10.5670/oceanog.2009.11>
- Haacke RR, Hyndman RD, Park KP, Yoo DG, Stoian I, Schmidt U (2009) Migration and venting of deep gases into the ocean through hydrate choked chimneys offshore Korea. *Geology* 37:531–534
- Hautala S, Solomon E, Johnson HP, Harris RN, Miller UK (2014) Dissociation of Cascadia margin gas hydrates in response to contemporary ocean warming. *Geophysical Research Letters* 41:8486–8494 <https://doi.org/10.1002/2014GL061606>
- Hornbach MJ, Ruppel C, Van Dover CL (2007) Three-dimensional structure of fluid conduits sustaining an active deep marine cold seep. *Geophysical Research Letters* 34:L05601 <https://doi.org/10.1029/2006GL028859>
- Hovland M, Jensen S, Fichler C (2012) Methane and minor oil macroseep systems—their complexity and environmental significance. *Marine Geology* 332–334:163–173 <https://doi.org/10.1016/j.margeo.2012.02.014>
- Johnson HP, Miller UK, Salmi MS, Solomon EA (2015) Analysis of bubble plume distributions to evaluate methane hydrate decomposition on the continental slope. *Geochem Geophys Geosys* 16:3825–3839 <https://doi.org/10.1002/2015GC005955>
- Lamaitre N, Bayon G, Ondréas H, Caprais JC, Freslon N, Bollinger C, Rouget ML, Prunelé A, Ruffine L, Olu-Le Roy K, Sarthou G (2014) Trace element behaviour at cold seeps and the potential export of dissolved iron to the ocean. *Earth and Planetary Science Letters* 404:376–388 <https://doi.org/10.1016/j.epsl.2014.08.014>
- Liu X, Flemings PB (2007) Dynamic multiphase flow model of hydrate formation in marine sediments. *Journal of Geophysical Research - Solid Earth* 112:B03101 <https://doi.org/10.1029/2005JB004227>
- Malone RD (1985) Gas hydrates topical report. DOE/METC/SP, U.S. Department of Energy
- Manley PL, Flood RD (1988) Cyclic sediment deposition within Amazon deep-sea fan. *Am Assoc Petrol Geol Bull* 72:912–925
- Maslin M, Mikkelsen N, Vilela C, Haq B (1998) Sea-level- and gas-hydrate-controlled catastrophic sediment failures of the Amazon fan. *Geology* 26:1107–1110
- Maslin M, Owen M, Day S, Long D (2004) Linking continental-slope failures and climate change: testing the clathrate gun hypothesis. *Geology* 32:53–56 <https://doi.org/10.1130/G20114.1>
- Maslin M, Vilela C, Mikkelsen N, Grootes P (2005) Causes of catastrophic sediment failures of the Amazon fan. *Quater Sci Rev* 24:2180–2193
- Mau S, Valentine DL, Clark JF, Reed J, Camilli R, Washburn L (2007) Dissolved methane distributions and air-sea flux in the plume of a massive seep field, Coal Oil Point, California. *Geophys Res Lett* 34:L22603 <https://doi.org/10.1029/2007GL031334>
- McGinnis DF, Greinert J, Artemov Y, Beaubien SE, Wuest A (2006) Fate of rising methane bubbles in stratified waters: how much methane reaches the atmosphere? *Journal of Geophysical Research* 111:C09007 <https://doi.org/10.1029/2005JC003183>
- Miller DJ, Ketzner JM, Viana AR, Kowsmann RO, Freire AF, Oreiro SG, Augustin AH, Lourega RV, Rodrigues LF, Heemann R, Preissler AG, Machado CX, Sbrissa GF (2015) Natural gas hydrates in the Rio Grande Cone (Brazil): a new province in the western South Atlantic. *Mar Petrol Geol* 67:187–196
- Olu-Le Roy K, Caprais JC, Fifis A, Fabri MC, Galéron J, Budzinsky H, Le Ménach K, Khripounoff A, Ondréas H, Sibuet M (2007) Cold-seep assemblages on a giant pockmark off West Africa: spatial patterns and environmental control. *Marine Ecology* 28:1–16
- Piper DJW, Pirmez C, Manley PL, Long D, Flood RD, Normark WR, Showers W (1997) Mass-transport deposits of the Amazon fan. *Proc Ocean Drill Program, Sci Results* 155:109–146
- Praeg D, Ketzner JM, Augustin AH, Migeon S, Ceramicola S, Dano A, Ducassou E, Dupré S, Mascle J, Rodrigues LF (2014) Fluid seepage in relation to seabed deformation on the Central Nile Deep-Sea fan, part 2: evidence from multibeam and sidescan imagery. In: Krastel et al. (eds) *Submarine mass movements and their consequences: advances in natural and technological hazards research* 37:141–150
- Rehder G, Brewer PW, Peltzer ET, Friederich G (2002), Enhanced lifetime of methane bubble streams within the deep ocean. *Geophys Res Lett* 29:1731. [10.1029/2001GL013966](https://doi.org/10.1029/2001GL013966)
- Reis AT, Perovano R, Silva CG, Vendeville BC, Araújo E, Gorini C, Oliveira V (2010) Two-scale gravitational collapse in the Amazon Fan: a coupled system of gravity tectonics and mass-transport processes. *J Geol Soc* 167:593–604. <https://doi.org/10.1144/0016-76492009-035>
- Reis AT, Araújo E, Silva CG, Cruz AM, Gorini C, Droz L, Migeon S, Perovano R, King I, Bache F (2016) Effects of a regional décollement level for gravity tectonics on late Neogene to recent large-scale slope instabilities in the Foz do Amazonas Basin, Brazil. *Mar Petrol Geol* 75:29–52. <https://doi.org/10.1016/j.marpetgeo.2016.04.011>
- Richey JE, Brook JT, Naiman RJ, Wissmar RC, Stallard RF (1980) Organic carbon: oxidation and transport in the Amazon River. *Science* 207:1348–1351

- Riedel M, Tréhu AM, Spence GD (2010) Characterizing the thermal regime of cold vents at the northern Cascadia margin from bottom-simulating reflector distributions, heat-probe measurements and borehole temperature data. *Mar Geophys Res* 31:1–16
- Römer M, Sahling H, Pape T, Bahr A, Feseker T, Wintersteller P, Bohrmann G (2012) Geological control and magnitude of methane ebullition from a high-flux seep area in the Black Sea—the Kerch seep area. *Marine Geology* 319–322:57–74
- Römer M, Sahling H, Pape T, dos Santos FC, Wenzhöfer F, Boetius A, Bohrmann G (2014) Methane fluxes and carbonate deposits at a cold seep area of the Central Nile Deep Sea Fan, Eastern Mediterranean Sea. *Mar Geol* 347:27–42
- Rowan MG, Peel FJ, Vendeville BC (2004) Gravity-driven fold-belts on passive margins, in McKay, K.R., ed., Thrust tectonics and hydrocarbon systems. *Am Assoc Petrol Geol Memoir* 82:157–182
- Schlünz B, Schneider RR, Müller PJ, Showers WJ, Wefer G (1999) Terrestrial organic carbon accumulation on the Amazon deep sea fan during the last glacial sea level low stand. *Chem Geol* 159:263–281
- Schwietzke S, Sherwood OA, Bruhwiler LMP, Miller JB, Etiope G, Dlugokencky EJ, Michel SE, Arling VA, Vaughn BH, White JWC, Tans PT (2016) Upward revision of global fossil fuel methane emissions based on isotope database. *Nature* 538:88–91. <https://doi.org/10.1038/nature19797>
- Silva R, Reis AT, Silva CG, Vendeville B, Gorini C, Araújo EFS (2009) O processo de colapso gravitacional e a estruturação da seção marinha da bacia da Foz do Amazonas - Margem equatorial brasileira. *Rev Bras Geofis* 27:459–484. <https://doi.org/10.1590/S0102-261X2009000300012>
- Silva CC, Reis AT, Perovano RJ, Gorini MA, Santos MVM, Jeck IK, Tavares AAA, Gorini C (2016) Multiple megaslide complexes and their significance for the Miocene stratigraphic evolution of the offshore Amazon Basin. In: Lamarche G. et al. (eds) Submarine mass movements and their consequences. *Advances in Natural and Technological Hazards Research* 41:49–60. Springer, [https://doi.org/10.1007/978-3-319-20979-1\\_5](https://doi.org/10.1007/978-3-319-20979-1_5)
- Skarke A, Ruppel C, Kodis M, Brothers D, Lobecker E (2014) Widespread methane leakage from the sea floor on the northern US Atlantic margin. *Nat Geosci* 7:657–661. <https://doi.org/10.1038/ngeo2232>
- Solomon EA, Kastner M, MacDonald IR, Leifer I (2009) Considerable methane fluxes to the atmosphere from hydrocarbon seeps in the Gulf of Mexico. *Nat Geosci* 2:561–565
- Stranne C, O'Regan M, Dickens GR, Crill P, Miller C, Preto P, Jakobsson M (2016) Dynamic simulations of potential methane release from East Siberian continental slope sediments. *Geochem, Geophys, Geosyst* 17:872–886. <https://doi.org/10.1002/2015GC006119>
- Stranne C, O'Regan M, Jakobsson M (2017) Modeling fracture propagation and seafloor gas release during seafloor warming-induced hydrate dissociation. *Geophys Res Lett* 44:8510–8519. <https://doi.org/10.1002/2017GL074349>
- Tanaka MD, Silva CG, Clennell MB (2003) Gas hydrates on the Amazon Submarine Fan, Foz do Amazonas Basil, Brazil. AAPG Search and Discovery Article #90013, AAPG Annual Meeting, May 11–14, 2003, Salt Lake City, Utah
- Tassy A, Crouzy E, Gorini C, Rubino JL, Bouroulec JL, Sapin F (2015) Egyptian Tethyan margin in the Mesozoic: evolution of a mixed carbonate-siliciclastic shelf edge (from Western Desert to Sinai). *Mar Petrol Geol* 68:565–581. <https://doi.org/10.1016/j.marpetgeo.2015.10.011>
- Waite WF, Weber T, Fu X, Juanes R, Ruppel C (2017) Laboratory observations of the evolution and rise rate of bubbles with and without hydrate shells. *Proceedings of the 9th International Congress on Gas Hydrates*, Denver
- Westbrook GK, Thatcher KE, Rohling EJ, Piotrowski AM, Pälke H, Osborne AH, Nisbet EG, Minshull TA, Lanoiselle M, James RH, Huhnerbach V, Green D, Fisher RE, Crocker AJ, Chabert A, Bolton C, Beszczynska-Möller A, Berndt C, Aquilina A (2009) Escape of methane gas from the seabed along the West Spitsbergen continental margin. *Geophys Res Lett* 36:1–5. <https://doi.org/10.1029/2009GL039191>