Marine Geology 370 (2015) 87–98

Contents lists available at ScienceDirect

Marine Geology

journal homepage: www.elsevier.com/locate/margeo

U-Th isotope constraints on gas hydrate and pockmark dynamics at the Niger delta margin

Germain Bayon [a,*], Gideon M. Henderson [b], Joël Etoubleau [a], Jean-Claude Caprais [c], Livio Ruffine [a], Tania Marsset [a], Bernard Dennielou [a], Eric Cauquil [d], Michel Voisset [a], Nabil Sultan [a]

[a] IFREMER, Unité de Recherche Géosciences Marines, IFREMER, F-29280 Plouzané, France
[b] Department of Earth Sciences, Oxford University, Oxford, OX1 3PR, UK
[c] IFREMER, Unité de Recherche Etudes des Ecosystèmes Profonds, F-29280 Plouzané, France
[d] TOTAL, F-92069 Paris, France

ARTICLE INFO

Article history:
Received 8 June 2015
Received in revised form 2 October 2015
Accepted 17 October 2015
Available online 23 October 2015

Keywords:
Gas hydrates
Pockmarks
U-series
Authigenic carbonates
Niger delta

ABSTRACT

The application of uranium-thorium dating methods to authigenic carbonates provides unique constraints on the temporal evolution of methane seeps at ocean margins. In this study, we report U-Th isotope measurements for carbonate breccias collected from within a hydrate-bearing pockmark located at the Niger Delta margin. These concretions were extracted from a carbonate-rich layer in the upper two meters of a sediment core (N2-KS-44; ~1200 m water depth), well above the present-day sulphate-methane transition zone (about 3 m depth) and the presence of gas hydrates in the sediment. The stratigraphy of core N2-KS-44 was established by tuning its downcore Al/Ti profile to a well-dated nearby reference core, and carbonate ^{230}Th/U ages were calculated using isochron methods.

Our results indicate that a major event of aragonite precipitation occurred between about 13 and 2.5 ka at the studied location. Comparison of sediment accumulation rates at both core N2-KS-44 and the nearby reference site suggests that the initial stage of carbonate precipitation, between 13 and 10 ka, was associated with sediment winnowing, probably related to intense fluid seepage. In contrast, our data indicate that sedimentation rates rapidly increased within the pockmark after 7 ka. In agreement with the presence of carbonate breccias exhibiting U-Th ages older than their corresponding stratigraphic age, this observation would suggest that sediment reworking took place after that time, possibly caused by erosion of the surrounding sediment within the pockmark.

We hypothesize that the period of carbonate formation between 13 and 2.5 ka was related to an upward migration of gas-hydrate reservoirs to the near seafloor environment. After this pulse of enhanced fluid flow, the diminution of methane fluxes at the base of the local gas-hydrate occurrence zone would have led to hydrate dissolution in sub-surface sediments and pockmark formation, thereby explaining the progressive increase in sedimentation rates, the absence of recent carbonate concretions and the deepening of the sulphate-methane transition zone at site N2-KS-44 inferred from pore water data. Overall, these results provide further constraints about the relationship between gas hydrate dynamics and the evolution of pockmarks at ocean margins through time.

1. Introduction

Huge amounts of methane (CH_4) are stored as gas hydrates at ocean margins (Milkov, 2004; Wallmann et al., 2012), representing potentially an important component of the global carbon and methane cycles (Judd et al., 2002; Dickens, 2003). Gas hydrates are unstable phases in marine sediments, which may decompose in response to small changes in gas-saturation of the surrounding pore water, or to changes in the pressure and temperature conditions of the marine environment, such as those induced by sea-level changes, continental-slope failures, and the reorganisation of deep-ocean circulation or fluid pathway systems within the sediment column (Buffett, 2000). While isotopic records of atmospheric CH_4 in ice cores indicate negligible contribution from marine gas hydrate reservoirs during the Late Quaternary (Sowers, 2006), dissociation of gas hydrates stored at margins could have led episodically to substantial methane releases in the past, possibly affecting both the marine environment and the atmosphere (e.g. Nisbet, 1990; Haq, 1998; Kennett et al., 2000; Hesselbo et al., 2000; Bangs et al., 2010). At ocean margins, the occurrence of gas hydrates in near-seafloor sediments is often associated with the presence of pockmarks, which correspond to seabed depressions related to seepage of

* Corresponding author.
E-mail address: gbayon@ifremer.fr (G. Bayon).

http://dx.doi.org/10.1016/j.margeo.2015.10.012

methane-rich fluids (Hovland and Judd, 1988; Suess, 2014). Over the past decades, there has been increasing evidence for widespread distribution of both active and inactive pockmarks at margins, which questions their relationship to past fluid seepage and potential episodes of gas hydrate dissociation (e.g. Hovland et al., 2002; Loncke et al., 2004; Davy et al., 2010; Sultan et al., 2010; Pau et al., 2014). While pockmarks are being increasingly studied, however, there are still significant uncertainties on the factors controlling their activity and their evolution through time. In particular, knowledge on both the timing and duration of pockmark activity is important for constraining the possible links between climate change and methane seeps in the past.

Evidence for past methane releases and gas hydrate destabilisation in marine sediments has come primarily from carbon isotope signals in geological records (e.g. Dickens et al., 1995; Kennett et al., 2000; Hesselbo et al., 2000; Hill et al., 2004; Panieri et al., 2014). Because methane stored in sedimentary gas hydrates exhibits highly negative carbon isotope signatures, large negative $\delta^{13}C$ excursions recorded by foraminifera in marine sediments have been interpreted as indicators for past circulation of methane-rich fluids potentially related to the dissociation of methane hydrates (e.g. Kennett et al., 2000; Smith et al., 2001; Panieri et al., 2014). Authigenic carbonates represent another potential archive of past fluid flow and gas-hydrate dissociation on continental margins (Bohrmann et al., 1998; Naehr et al., 2000; Greinert et al., 2001). The occurrence of authigenic carbonate deposits (e.g. chemoherm carbonates, carbonate crusts and nodules) has been reported at many seeps worldwide (Suess, 2014). Cold seep carbonates result primarily from the microbial anaerobic oxidation of methane (AOM) in sediments (Boetius et al., 2000), which typically leads to enhanced alkalinity levels in surrounding pore waters and, as a consequence, to carbonate precipitation. In gas-hydrate-bearing sediments, authigenic carbonates often occur as millimeter- to centimeter-size nodules of carbonate-cemented mudclast breccias or nodules (Bohrmann et al., 1998; Naehr et al., 2000; Greinert et al., 2001; Bayon et al., 2007). It has been suggested that such carbonates represent suitable paleo-indicators for the presence of gas hydrates in marine sediments (Naehr et al., 2000; Pierre et al., 2000; Bayon et al., 2007).

Absolute dating of authigenic carbonate breccias or nodules recovered at various depths within hydrate-bearing sediments can thus provide unique constraints on past methane fluxes, and the evolution of gas-hydrate reservoirs in marine sediments through time. Conventional ^{14}C dating is usually not applicable to authigenic carbonates because their carbon partly derives from old fossil sources (i.e. methane), but several studies have now demonstrated that uranium-thorium dating techniques could be successfully applied to seep carbonates (Lalou et al., 1992; Teichert et al., 2003; Kutterolf et al., 2008; Watanabe et al., 2008; Bayon et al., 2009a, 2009b; Liebetrau et al., 2010; Feng et al., 2010; Wirsig et al., 2012; Bayon et al., 2013; Crémière et al., 2013; Tong et al., 2013; Liebetrau et al., 2014; Han et al., 2014; Berndt et al., 2014). Most of these studies have focused on seafloor carbonate crusts, chimneys or chemoherms (Lalou et al., 1992; Teichert et al., 2003; Bayon et al., 2009a, 2009b; Liebetrau et al., 2010; Feng et al., 2010; Wirsig et al., 2012; Bayon et al., 2013; Crémière et al., 2013; Tong et al., 2013; Han et al., 2014), and drilled carbonate mounds (Kutterolf et al., 2008; Liebetrau et al., 2014). To date, only a few investigations have been dedicated to the analysis of buried carbonate nodules at methane seeps (Watanabe et al., 2008; Crémière et al., 2013). Although such approach may offer the opportunity to investigate gas-hydrate dynamics in marine sediments during the Late Quaternary, it can be complicated by diagenetic issues such as dissolution (Luff et al., 2005) and the presence of significant initial ^{230}Th derived from terrigenous material (Watanabe et al., 2008; Bayon et al., 2009a, 2009b; Wirsig et al., 2012), which hence require the use of isochron dating methods.

In this study, we report U-Th analyses for cm-size nodules of carbonate breccias recovered at various depths from a hydrate-bearing sediment core at the Niger Delta margin. We show below that, when combined with a well-constrained core stratigraphy, this approach can provide unique information on the evolution of gas-hydrate reservoirs and pockmark dynamics through time.

2. Material and methods

2.1. Regional setting and sampling sites

The Niger Delta is a large sedimentary edifice on the West African margin, which extends southward into the Gulf of Guinea deep basin. In its deep province, gravity tectonism has deformed sediments significantly, leading to folding, diapirism and faulting, all of which have resulted in the migration of gas-rich fluids within continental slope sediments. Numerous occurrences of fluid escape sedimentary structures and gas hydrate deposits have been reported previously on the Niger Delta deep province (Brooks et al., 1994; Bayon et al., 2007; Sultan et al., 2007; Sultan et al., 2010; Bayon et al., 2011; Ruffine et al., 2013; Sultan et al., 2014).

The pore water, carbonate and sediment samples used for this study were collected by sediment coring during two expeditions on the continental slope off Nigeria in 2003 and 2004 (NERIS 1 & 2; chief scientist: M. Voisset). All samples were recovered from a pockmark-rich area of ~20 km^2, at about 1200 m water depth (Fig. 1). The geological setting, occurrence of gas hydrates and geochemical processes related to carbonate precipitation in the study area have been described previously (Bayon et al., 2007; Sultan et al., 2007; Sultan et al., 2010; Rongemaille et al., 2011). This area corresponds to the collapsed summit of an anticline, which is delimited by two deep-rooted normal faults oriented N130. Between those two major faults, the central domain is characterised by the presence of numerous pockmarks of variable shape and diameter (from ~10 m to 400 m; see Fig. 1). As discussed in Bayon et al. (2007), apart from the recovery of a few seafloor chemoherm deposits along the major faults, the carbonate samples collected in this central domain correspond almost exclusively to carbonate breccias similar to other gas hydrate-associated carbonates described elsewhere (e.g. Greinert et al., 2001). Geophysical data, sediment coring and geotechnical measurements acquired during the NERIS project revealed that both free gas and gas hydrates occur abundantly in this central domain, in the near-seafloor environment (Sultan et al., 2007). The studied area is located well within the stability field of gas hydrates in the marine environment (Fig. S1). Piston core N2-KS-44 (length 6.6 m; 1174 m water depth) was retrieved from one 15-m deep hydrate-bearing pockmark in this area (Fig. 1). Core lithology is presented in Fig. 2. No evidence for the presence of turbidites or any other mass-transport deposits was encountered in core N2-KS-44. Abundant carbonate concretions were observed between 30 and 180 cm sediment depth, while gas-hydrate nodules occurred deeper in the sediment, below ~400 cm (Fig. 2). Hydrate-bearing sediments from a few other cores in the central domain (N1-KSF-23 and N1-KSF-20) and a nearby reference core not affected by any fluid seepage (N1-KSF-39; lat. 3°12.208'N; long. 6°41.003'E; length 10.60 m; 1243 m water depth) were also analysed during this study (Fig. 1).

2.2. Core stratigraphy

In this study, conventional oxygen isotope stratigraphy and AMS radiocarbon dating were not applicable to core N2-KS-44, due to the presence of methane-derived carbonate phases dispersed along the entire core (Bayon et al., 2007). Sedimentary sequences accumulated on the Niger Delta deep province display however large fluctuations in major element composition, which can be used for the purpose of stratigraphic correlation. In particular, the aluminium/titanium (Al/Ti) ratio represents a proxy for past chemical weathering, related to the alternance of wet and dry periods in the Niger River basin during the Late Quaternary (Zabel et al., 2001). Both Al and Ti are mainly hosted by silicate detrital phases; hence Al/Ti ratios are unlikely to be affected