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

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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 230Th/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.
Highlights

► Breccias from hydrate-bearing sediments can be successfully dated with U-series. ► Seep carbonates precipitated between 13.0 and 2.5 kyr at the studied pockmark. ► Evidence for hydrate dissolution and SMTZ fluctuations during the Holocene. ► Co-evolution of gas hydrate and pockmark dynamics through time.

Keywords: Gas hydrates, Pockmarks, U-series, Authigenic carbonates, Niger delta
1. Introduction

Huge amounts of methane ($\text{CH}_4$) 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 $\text{CH}_4$ 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. Nisbett, 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 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,b; 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 chemohersms (Lalou et al., 1992; Teichert et al., 2003; Bayon et al., 2009a,b; 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., 2009; 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 chemohem 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 by methane seepage at cold seeps. The age model for core N2-KS-44 was therefore established by tuning its downcore Al/Ti profile to the nearby reference core N1-KSF-39 (Fig. 3). Bulk major element composition of N2-KS-44 and N1-KSF-39 sediments was determined by wavelength-dispersive X-ray fluorescence (WD-XRF) analysis of fusion beads. The chronology for core N1-KSF-39 relies on nine $^{14}$C-AMS radiocarbon analyses of mixed planktonic foraminifera fractions (Table 1), and tuning of its Al/Ti profile to the Al/Ti curve of core GeoB4901-8 (Fig. 3); a well-dated sediment record also recovered in the Niger Delta deep province (Zabel et al., 2001). These radiocarbon dates were converted into calendar ages using the Calib 7.1 program (Stuiver et al., 2013), and applying a marine reservoir age of 400 yr. While this approach suffers from inherent uncertainty associated with tuning methods, and especially here with the fact that the Al/Ti profile for core N2-KS-44 is not particularly smooth, the relatively good correlation observed between Al/Ti signals of all three sedimentary records suggest that it can provide, to a first approximation, a reliably good estimate for core N2-KS-44 stratigraphy (Fig. 3). Based on these chronologies, down-core variations in sedimentation rates were calculated for both core N1-KSF-39 (Table 1) and N2-KS-44 (Fig. 3).

2.3. Pore-water analyses

On board, pore waters were extracted from core N2-KS-44 sediments by centrifugation, immediately after sampling, filtered using acetate cellulose filters (0.45 μm diameter) and stored in a refrigerator. Dissolved sulphate ($SO_4^{2-}$) and chloride (Cl$^-$) concentrations were measured onshore in 1:10 diluted solutions by ion chromatography. Calcium contents were also determined with an Element2 HR-ICP-MS after simple dilution (between 500 and 1000-fold) with 2% twice sub-boiled nitric acid. Ca concentrations were calculated by external calibration using diluted IAPSO and NASS-5 solutions.

2.4. Petrography and electron microprobe analysis of carbonate breccias
Details on the petrography and mineralogy of authigenic carbonate samples recovered at site N2-KS-44 are given in Bayon et al. (2007). Polished sections of selected samples were also examined by scanning electron microscopy (JEOL JSM-840A) and electron microprobe analyzer (JEOL JXA8800R) to provide elemental mapping of carbonate concretions and select sampling areas suitable for U-Th measurements. Authigenic carbonates recovered in the upper two meters of core N2-KS-44 sediments correspond typically to mm- to cm-size carbonate-cemented breccias (Bayon et al., 2007), similar to those reported previously in other hydrate-bearing sediments (Naehr et al., 2000; Greinert et al., 2001). Those carbonate concretions contain intraclasts (biogenic components, mudstones) cemented by aragonite and/or high-Mg calcite (Fig. 4). Some concretions exhibit large (up to ~100 μm diameter) crystals of fibrous aragonite, which have developed in open pore spaces, either between intraclasts or inside the cavities of biogenic components (Fig. 4). Botryoidal aragonite often composes carbonate cements. Numerous intraclasts consist of mudstones cemented by microcrystalline high-Mg calcite, which exhibit a darker color than the surrounding matrix and contain frambooidal pyrite. One concretion was recovered in a deeper core section (at 260 cm depth), which corresponds to a homogeneous mudstone cemented by microcrystalline high-Mg calcite (Fig. 2).

2.5. Chemical and analytical procedures for U-Th measurements

Selected areas of carbonate concretions from core N2-KS-44 were hand-drilled carefully to obtain samples having weight ranging between 50-100 mg of carbonate powder. However, carbonate breccias are highly heterogeneous and samples of this size (referred to as ‘bulk’ samples in the following text) are still significantly contaminated by detrital material, with consequences on U-Th dating. Therefore, to try to reduce such contamination, some carbonate samples were also collected using a computer-assisted microsampling device (MicroMill, New Wave Research). This system enables accurate sampling of micrometer-size areas of polished sections. For those small carbonate samples (referred to as ‘micromilled’ samples subsequently), sampling areas were selected using scanning electron microscopy and/or electron microprobe analyser (Fig. 4). Sampling areas were chosen within both aragonite- and high-Mg calcite-rich areas of
carbonate breccias. About ~ 1 mg of carbonate powders was collected for each of those micromilled samples for U-Th analysis. A total of six bulk sediment samples containing no visible carbonates were also analysed to characterize the detrital component incorporated within the carbonate concretions.

The chemical and analytical procedures used in this study largely followed those described in Bayon et al. (2009a). Briefly, each sample (i.e. bulk, micromilled, sediment) was dissolved in 7.5M HNO₃, spiked with a mixed $^{236}$U/$^{229}$Th spike, digested in concentrated HNO₃ on the hotplate, and centrifuged. At this stage, any undissolved detrital fractions were transferred into cleaned Teflon vessels and fully digested with a mixed (3:1) HF:HCl solution, before being added back into corresponding supernatants. Samples were evaporated, taken up with 7.5M HNO₃, and diluted with ultrapure water. After Fe-oxide co-precipitation, U and Th were finally separated chemically using conventional anion exchange techniques. The volumes of anion-exchange resin and acids used for separating U-Th were much smaller for micromilled samples than for bulk and sediment samples. Typical procedural blanks were $1.2 \times 10^{-10}$ g $^{238}$U and $3.0 \times 10^{-11}$ g $^{232}$Th for bulk carbonate and sediment samples, and $1.0 \times 10^{-11}$ g $^{238}$U and $1.3 \times 10^{-12}$ g $^{232}$Th for micromilled samples. Total U and Th procedural blanks were small compared to final sample concentrations. U and Th concentrations and isotope ratios were measured with a MC-ICPMS (Nu Plasma). The external reproducibility on the $^{234}$U/$^{235}$U ratio was assessed by measuring repeatedly the standard CRM-145 during each session using a standard-bracketing measurement protocol. Th was measured with $^{229}$Th and $^{230}$Th sequentially in a single ion-counter equipped with an energy filter to improve abundance sensitivity, and $^{232}$Th in a Faraday collector. Precision obtained on measured $^{229}$Th/$^{230}$Th ratios was always better than 5 ‰ for bulk and sediment samples, and 50 ‰ for micromilled samples. Blank correction on $^{230}$Th concentrations was calculated using measured $^{232}$Th/$^{230}$Th ratio and $^{232}$Th concentration for blank. For the small-size micromilled samples, blank contributions accounted for between 0.7% (N2-KS-44_75-1) to 9.3% (N2-KS-44_180-1).
3. Results

3.1. Pore-water $SO_4^{2-}$, $Cl^-$ and $Ca^{2+}$ profiles

For core N2-KS-44, pore water $SO_4^{2-}$ concentrations display seawater-like values from the surface sediment to 60 cm depth, and then decrease steadily to reach near-zero values from 260 cm depth to downcore (Fig. 2). Dissolved calcium concentrations show a relatively similar downcore profile, characterized by a significant drop from ~10 mM (i.e. seawater values) in the upper sediment layers to about 1 mM. In contrast, chloride concentrations exhibit little variation along the upper section of core N2-KS-44 (~560 ± 22 mM).

3.2. Electron microprobe elemental distribution maps

The chemical maps obtained by electron microprobe analyser for one representative carbonate breccia from core N2-KS-44 (collected at 160 cm depth) are presented in Fig. 5. The Si distribution map can be used to infer the extent to which carbonate cements may be contaminated by detrital material (e.g. clays). Aragonite exhibits typically higher levels of Sr than high-Mg carbonates (Fig. 5). In Fig. 5, it is also clear that aragonite-rich areas are much less contaminated by detrital material (i.e. lower Si contents) than high-Mg calcite-rich mudclasts and cements. We showed earlier that contamination by terrigenous material in cold-seep carbonates increased as the size of crystals in the carbonate cement decreases (Bayon et al., 2007). In those carbonate-cemented breccias from core N2-KS-44, large fibrous crystals of aragonite, developed in open pore spaces and cavities, contain much less detrital material (<2 wt % Si contents) than botryoidal aragonite (<2.5 % Si), microcrystalline aragonite (<5 % Si), and microcrystalline high-Mg calcite (up to 7 % Si). In Fig. 5, this is demonstrated by the evidence that fibrous aragonite-rich areas, such as those encountered in open cavities, contain very low levels of Si. Importantly, concerning U-Th dating, this also indicates that it is best to sample well-crystallised aragonite-rich areas in order to reduce contamination by detrital material.

3.3. Uranium and thorium concentrations and isotopic ratios
U-Th data for sediments and authigenic carbonates are listed in Table 2. U concentrations vary between ~ 5-17 ppm and ~ 2-23 ppm for sediments and carbonates, respectively. $^{230}$Th concentrations range from 5 to 62 ppt (mean average of 33 ppt) in authigenic carbonates and from 80 to 105 ppt in sediments. Carbonate ($^{230}\text{Th}/^{232}\text{Th}$) ratios (brackets indicate activity ratios) are low (from 1.2 to 5.3; Table 3), due to both the young formation age of carbonates (low $^{230}$Th ingrowth) and detrital contamination (high initial $^{232}$Th). Micromilled samples for aragonite-rich concretions exhibit higher ($^{238}\text{U}/^{232}\text{Th}$) ratios (from 6.4 to 32.3; Table 2) than sediments (from 1.2 to 4.4; Table 2) and corresponding bulk carbonates (from 5.2 to 20.6; Table 2). This indicates that micromilling has been successful in sampling carbonate with lower detrital contents. In contrast, Mg-rich carbonates generally display comparatively lower ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{238}\text{U}/^{232}\text{Th}$) ratios even in micromilled subsamples, reflecting both the fact that calcite is less enriched in U compared to aragonite, and that high-Mg microcrystalline carbonate phases are more enriched in detrital components (Bayon et al., 2007).

3.4. U-Th isochron dating

Isochron dating methods consider each sample to be composed of a mixture of two components. In this case, they can be used to separate $^{230}$Th present initially from that ingrown from U in the carbonate. By analysing several subsamples of the same age but with different proportions of the two components, it is possible to calculate the age corresponding to the end-member with no initial $^{230}$Th (Edwards et al., 2003). In seep-related studies, this approach may be complicated by the fact that authigenic concretions may have recorded several discrete events of carbonate precipitation. In this case, isochron methods may also prove to be particularly useful for assessing whether studied concretions are polygenic or instead correspond to single precipitation events. In this study, we have considered a sediment end-member, assumed to be representative of the initial sediment fraction incorporated by carbonate breccias. The U-Th isotopic composition of this sediment fraction can be influenced by its mineralogical composition and the amount of incorporated hydrogenous $^{230}$Th derived from the overlying water column. Using a typical sediment end-member to correct ages is more appropriate than correcting each sample with a sediment measurement from the same core. The latter
approach would generate isochrons containing two high-precision data points, leading to unrealistically precise calculated ages which do not incorporate any uncertainty due to possible variability in the sediment. The approach of defining a typical sediment end-member for one given area circumvents this problem and leads to larger but more realistic age uncertainties, thereby allowing calculation of less precise but more accurate ages. Another possible approach would have been to consider a sediment end-member assumed to be at secular equilibrium, i.e. with activity ratios of 1.0 ± 0.5 (e.g. Bayon et al., 2013). While it may seem more appropriate to apply a regional sediment end-member for correction, note that the use of a theoretical end-member would have led to the same conclusions, yielding very similar isochron ages (always within ~25%). In this study, the sediment end-member has been defined as the average (± 1 SD) of six sediments from our study area (Table 3). All these sediments were recovered from seepage sites and hence can be considered, to a first approximation, as representative of the sediment incorporated by the studied carbonate concretions, even in the eventuality that circulation of methane-rich fluids may alter the U-Th isotopic composition of the sediment. On a \((^{230}\text{Th}/^{232}\text{Th})\) versus \((^{238}\text{U}/^{232}\text{Th})\) plot (Fig. S2), these sediments are clustered near the equiline, with typical crustal values (~ 1.0). This indicates a reasonably homogeneous source of initial Th for carbonate breccias in the studied area, and suggests that isochron dating using this sediment end-member is suitable.

Isochron diagrams and ages obtained with the sediment end-member are presented in Fig. 6 and Table 3. Isochron ages were calculated with Isoplot-Ex 3.70 (Ludwig, 2008), using measured \((^{232}\text{Th}/^{238}\text{U})\), \((^{230}\text{Th}/^{238}\text{U})\) and \((^{234}\text{U}/^{238}\text{U})\) ratios (Table 3). The \(^{230}\text{Th}/\text{U}\) age errors were calculated by a Monte Carlo simulation, rather than from the first-derivative expansion which led, in the case of this study, to unrealistically small errors. However, when the use of Monte Carlo solution was not possible, an arbitrary error of ± 25% was assigned to the obtained isochron ages. This arbitrary error corresponds to the external reproducibility on isochron ages estimated from repeated analyses of an in-house cold seep carbonate standard (Bayon et al., 2013).
In Table 3, two isochron ages are reported: 1) two-point \((n=2)\) isochron ages, which provide an age estimate for every analysed sample; and 2) pseudo-isochron ages (with \(n>2\)) that integrate, for any given concretion, all the studied sub-samples. As can be seen in Fig. 6 (Osmond isochron diagrams), except for the concretion at 75 cm depth, the distinct fractions (e.g. bulk concretion, micromilled carbonate phases, associated sediment, average composition of the local sediment) associated with carbonate breccias are remarkably well aligned along pseudo-isochron slopes, suggesting that they formed cogenetically. Importantly, this observation also provides strong support for the validity of calculated pseudo-isochron ages and indicates adequate correction of contamination from inherited Th. In contrast, the studied subsamples from the concretion at 75 cm depth are not aligned in Fig. 6, suggesting that they probably did not form contemporaneously (see discussion below). In this case, only the two-point isochron ages will hence be considered in the following discussion.

Within error \((2s)\), most carbonate breccias display isochron corrected \(\delta^{234}\)U\(_\text{T} \) values similar to seawater values \((\delta^{234}\text{U} = 146.6 \pm 2.5 \text{‰} \) (Robinson et al., 2004; Table 3), suggesting that they formed in the near-seafloor environment. The calculated isochron ages range from 4.8 ± 1.4 to 15.6 ± 1.6 thousand years before present \((\text{ka}; \text{or ka})\). All analysed samples (bulk, micromilled, associated sediment) for the upper carbonate-rich layer at 30 cm depth yield a pseudo-isochron age of 8.5 ± 0.2 ka \((n = 4; \text{i.e. four-point isochron})\). Isochron ages of 9.4 ± 2.4 \((n = 5)\) and 10.8 ± 2.7 ka \((n = 3)\) were also obtained for carbonate breccias collected at 160 cm and 180 cm, respectively. The three carbonate samples (bulk, micromilled-1, micromilled-2) analysed for the sediment layer at 75 cm depth define two-point isochron ages of 9.3 ± 2.0 ka, 12.4 ± 1.3 ka and 4.8 ± 1.4 ka, respectively. Finally, the two bulk samples from the homogeneous nodule of high-Mg calcite at 260 cm gives a pseudo isochron age of 15.6 ± 1.6 ka \((n = 3)\).

4. Discussion

4.1. Present-day SMTZ and associated carbonate precipitation
In cold seep environments, AOM occurs typically within a localized horizon in marine sediments, called the sulphate-methane transition zone (SMTZ), where both $\text{SO}_4^{2-}$ and $\text{CH}_4$ are consumed by microbial assemblages (Reeburg, 1976; Boetius et al., 2000). Other biogeochemical processes, such as the degradation of organic matter (Froelich et al., 1979), or the consumption of $\text{C}_2$ hydrocarbon compounds (Joye et al., 2004), may also consume $\text{SO}_4^{2-}$ from pore waters in marine sediments. However, at cold seeps, AOM is generally the main process controlling sulphate depletion, leading to near-complete $\text{SO}_4^{2-}$ depletion at the SMTZ depth (Niewöhner et al., 1998; Borowski et al., 1999) and producing pseudo-linear $\text{SO}_4^{2-}$ profiles in pore-waters, similar to what can be observed at site N2-KS-44 (Fig. 2). In hydrate-bearing settings, the SMTZ depth is also often correlated with the occurrence of gas hydrate within the sediment (e.g. Borowski et al., 1999). In the study area, this feature is nicely illustrated when plotting the SMTZ depth versus the depth of occurrence of gas hydrate layers within distinct sediment cores, which both define a very good correlation (Fig. 7). Gas hydrates generally hamper the ascent of fluids and reduce their transport towards the seafloor (e.g. Sultan et al., 2010; Li et al., 2014; Crutchley et al., 2015). However, without gas supply to sustain their formation, hydrates dissolve away to stay in thermodynamic equilibrium with surrounding pore waters (e.g. Ecker et al., 1998). This dissolution process contributes to permanent supply of methane to pore waters above gas hydrate layers, acting as a driving force for the AOM reaction coupled with sulphate reduction (Sultan et al., 2010, 2014). Note that the ‘dissolution’ process that we refer to here differs from ‘dissociation’, which generally occurs whenever gas hydrates leave their temperature-pressure stability field, in response for example to a sea-level drop or a rise in bottom-water temperature.

At site N2-KS-44, the profile for pore-water $\text{Ca}^{2+}$ concentrations also shows a strong depletion at ~3.6 m depth (Fig. 2), which indicates that active carbonate precipitation is currently taking place at the depth of present-day SMTZ. This is in full agreement with evidence for the presence of dispersed high-Mg calcite phases at this depth in core N2-KS-44, inferred from modelling of bulk sediment $\text{Sr}/\text{Ca}$ and $\text{Mg}/\text{Ca}$ ratios (Bayon et al., 2007). Overall, our pore water data indicate that the present-day AOM and associated authigenic carbonate precipitation occurs at depth close to 3 m in core N2-KS-44, hence
much deeper than the overlying carbonate-rich layer of authigenic concretions encountered between ~30 and 180 cm depth.

4.2. A major event of carbonate precipitation between ~13.0 and 2.5 ka

The comparison of U-Th isochron ages for carbonate-cemented breccias with their corresponding stratigraphic age (inferred from Al/Ti tuning) can provide temporal constraints on the formation of the carbonate-rich layer located in the upper two meters of core N2-KS-44. Stratigraphically, this horizon corresponds to the approximate time interval 2.5-13.0 ka, which hence overlaps relatively well the observed range of calculated U-Th ages for carbonate breccias from 4.8 ± 1.4 to 12.4 ± 1.3 ka (Fig. 8). This observation suggests that the carbonate-breccias were formed in close proximity to the seafloor. This hypothesis is supported by the evidence that the carbonate breccias collected at 75 cm (for the micromilled-2 subsample), 160 cm and 180 cm depth provide U-Th isochron ages similar (within error) to their corresponding stratigraphic age (Fig. 8). Another argument in favor of a near-seafloor precipitation is the presence of aragonite, which is generally favored over that of calcite at high $SO_4^{2-}$ concentrations or when uprising fluids have a high velocity flow, hence whenever AOM proceeds in the near-seafloor environment (e.g. Burton, 1993; Aloisi et al., 2000; Luff and Wallman, 2003; Bayon et al., 2009a).

In contrast, the two carbonate breccias from the upper carbonate-rich layer, i.e. those collected at 30 cm and 75 cm depth (with the exception of the micromilled-2 subsample), display isochron ages older than their respective stratigraphic age (Fig. 8), indicating possible sediment reworking. An interesting feature of our results is also the evidence for the presence of polygenic breccias. The two micromilled samples from the concretion collected at 75 cm depth display distinct U-Th isochron ages (12.4 ± 1.3 ka and 4.8 ± 1.4 ka), which suggests that such breccias may have recorded several precipitation events. In this context, the bulk sample (9.3 ± 2.0 ka) analysed for that particular carbonate breccia most likely corresponds to a mixture between distinct polygenic carbonate phases. For this particular concretion, the fact that the high-Mg rich micromilled sample appears to be younger than the aragonite one could possibly indicate that high-Mg carbonate phases
preferentially formed after an initial event of aragonite precipitation, perhaps after subsequent burial of concretions within the sediment. At this stage, petrographic examination does not reveal any clear succession of different carbonate precipitation events that could possibly explain the observed age/mineralogical differences in the studied breccias (Fig. 4). In fact, some high-Mg rich micro-concretions observed in the studied carbonate breccias (see Fig. 4e) even appear to be older than corresponding aragonite cement, which would go in opposite direction to what can be proposed based on our U-Th dates for the two micromilled samples at 75 cm depth. The observed complex nature of the studied carbonate breccias clearly show that a much larger U-Th investigation of additional micromilled samples from the same core would be needed to identify whether distinct carbonate precipitation events occurred during the last few thousand years. In addition, one cannot exclude that other breccias present in this core section are older or younger than those analysed in this study. Therefore, to a first approximation, and despite indications for a potentially more complex formation scenario, the comparison of U-Th isochron ages for carbonate-cemented breccias with their corresponding stratigraphic age suggest that carbonate formation at site N2-KS-44 was probably active in the near-seafloor environment during a relatively well-defined time interval, between about 13 and 2.5 ka.

### 4.3. Constraints on pockmark dynamics

As mentioned above, the evidence that a few carbonate breccias exhibit U-Th ages significantly older than their corresponding stratigraphic age suggests that sediment reworking may have taken place at site N2-KS-44. Further constraints on pockmark evolution at the studied site can also be obtained by comparing carbonate U-Th ages with the sediment accumulation rates inferred for cores N2-KS-44 and N1-KSF-39 (Fig. 8). From ~ 30 to 13 ka, the two neighbour cores were characterized by similar sedimentation rates, in the range ~ 4-10 cm/kyr, thereby suggesting a similar depositional context. However, after 13 ka, sedimentation rates at the two sites started to be decoupled. Between about 13 and 7 ka, the reference site (N1-KSF-39) experienced rapidly increasing sedimentation rates (up to ~ 23 cm/kyr), probably in relation with much higher fluvial discharges from the Niger River basin (Pastouret et al., 1978; Zabel et al., 2001),
before returning to much lower sediment accumulation after 7 ka (about 5 cm/kyr). In contrast, at site N2-KS-44, sedimentation rates remained relatively low (below 8 cm/kyr) until about 10 ka, before increasing steadily to about 18 cm/kyr for the remaining Holocene period. To account for the observed decoupling, we propose that intense circulation of methane-rich fluids near the seafloor led to highly dynamic seafloor environment at site N2-KS-44 between ~13 to 10 ka (Fig. 9b). This event would have resulted in seafloor carbonate precipitation, but also in intense fluid seepage and associated particle resuspension or sediment winnowing (Fig. 9b). Instead, from 10 ka onwards, the shift towards enhanced sedimentation rates at site N2-KS-44 could possibly be related to a second evolutionary stage of the pockmark, characterized by collapse depression (Fig. 9c). Recent studies have shown that pockmarks and other seafloor depressions are often characterized by higher sedimentation rates compared to the surrounding seafloor (e.g. Pau and Hammer, 2013; Pau et al., 2014). The same studies have also shown that sedimentation patterns at pockmarks are typically associated with deposition of coarse-grained material, transported as bedload. Based on the above consideration, one hypothesis would be that the presence of carbonate concretions older than corresponding stratigraphic ages in the upper carbonate-rich layer relates to subsequent reworking of small carbonate breccias during the period that followed intense fluid seepage. This would mean that some of the studied concretions in the upper aragonite-rich layer of core N2-KS-44 may be derived from the erosion of the surrounding seafloor, perhaps in response to the deepening of the pockmark (Fig. 9c). Another argument that would support sediment reworking after 10 ka would be the ‘sawtooth’ Al/Ti profile along core N2-KS-44, which contrasts with the much smoother Al/Ti curves observed at reference sites N1-KSF-39 and GeoB4901-8 (Fig. 3).

4.4. Evidence for fluctuating SMTZ over the last 15 ka

In contrast with the breccias from the upper carbonate-rich layer, the homogeneous nodule of high-Mg calcite collected at 260 cm depth appears to be significantly younger (15.6 ± 1.6 ka) than its corresponding estimated stratigraphic age (about 24 ka; Fig. 8). Considering the average sedimentation rate inferred from our Al-Ti-tuned age model for that section of core N2-KS-44 (~7.3 cm/kyr; Fig. 3), we can estimate that this nodule
formed at about 60 cm below the seafloor. This would explain why it is mainly composed of high-Mg calcite rather than aragonite, which more commonly precipitates at the sediment-seawater interface.

As mentioned above (section 4.1), the depth at which AOM and associated carbonate precipitation occurs in hydrate-bearing sediments of the study area is controlled primarily by the occurrence depth of gas hydrate layers (Fig. 7). Most likely, during the Holocene, both AOM and associated carbonate precipitation took place near the seafloor at site N2-KS-44, thereby explaining the formation of the aragonite-rich layer that is currently located between 30 cm and 180 cm depth. Instead, our U-Th data for the carbonate nodule at 260 cm depth suggest that the paleo-SMTZ at about 15.6 ka was probably located deeper in the sediment column (about 60 cm depth; Fig. 9a). Taken together with our pore-water analyses and inferred depth for the present-day SMTZ (i.e. about 300 cm depth), these data hence indicate methane fluxes must have fluctuated significantly over the last 15 kyr at the studied site (Fig. 9).

4.5. Factors controlling gas hydrate dynamics and associated CH$_4$ fluxes in Niger Delta sediments

Field observations and measurements have shown that the distribution of gas hydrates within sediments is highly heterogeneous in hydrate-bearing areas, both at small (meter) and regional scales (Tréhu et al., 2004; Sultan et al., 2007). Gas hydrates are found typically in meter-thick patchy zones in marine sediments (Kvenvolden and Lorenson, 2001; Tréhu et al., 2004). In Niger Delta sediments, such a large heterogeneity for gas hydrate distribution was confirmed by geophysical surveying and coring during the NERIS expeditions (Sultan et al., 2007) and subsequent cruises (Sultan et al., 2010; Sultan et al., 2014; Wei et al., 2015). It is likely, therefore, that variations in upward methane fluxes from one site to another are controlled primarily by the heterogeneous distribution of gas hydrates within sediments, or the presence of faults acting as a major methane conduit. Considering a given hydrate-bearing site (e.g. Site N2-KS-44), however, it is expected that changes in the CH$_4$ flux over time are caused by parameters affecting the dynamic of gas-hydrate deposits, such as changes in e.g. hydrostatic
pressure, bottom-water temperature, slope stability, and *in situ* \( \text{CH}_4 \) flux and/or concentration at the base of the gas-hydrate occurrence zone (GHOZ) within the sediment. Below, we investigate whether each of those four different factors may have accounted for the inferred fluctuations of the SMTZ depth (and associated methane fluxes) at site N2-KS-44.

Sea-level rise since the last 15,000 years is unlikely to have led to gas-hydrate dissociation in Niger Delta sediments. Instead, increasing hydrostatic pressure at that time contributed most probably to an opposite effect, i.e. greater gas hydrate stability in sediments. Alternatively, reorganization of intermediate-water circulation during the Holocene period could have induced an increase in bottom-water temperatures, leading to partial dissociation of hydrate layers in sediments (see Fig. S1). This would need to be tested in future studies, but at present, to the best of our knowledge, there is no evidence for deep-sea temperature changes over glacial-interglacial timescales in the Tropical Atlantic for the water depth considered in this study. Sedimentation rates were apparently higher on the Niger deep-sea fan between 13 to 10 ka, as shown by our own data (Table 1) and in agreement with previous studies (Pastouret et al., 1978; Zabel et al., 2001). This was due probably to high fluvial discharges at the onset of the so-called Holocene thermal maximum (~ 11-6 ka) in subtropical Africa, i.e. a progressive climatic shift towards warmer and wetter conditions related to maximum summer insolation. This could have possibly triggered slope failures and, in turn, to destabilization of gas hydrate reservoirs within sediments. However, in absence of any evidence for sediment instabilities in the studied area, higher sedimentation rates at that time led most likely to even greater hydrate stability instead.

Based on the above, we argue that the inferred variation of methane fluxes at site N2-KS-44 has not been driven by external parameters during the last 15,000 years, but instead by internal processes. Previous studies have already suggested that local fluid flow dynamics was likely to explain both the evolution of gas-hydrate reservoirs and associated pockmarks (Cathles et al., 2010; Sultan et al., 2010; Sultan et al., 2014). In this area, the occurrence of gas hydrate reservoirs in sub-surface sediments is related to
high fluid pressure in the deeper sedimentary column, and associated migration of both
free gas and methane-rich fluids along fractures (Sultan et al., 2014). Periodically, as a
consequence of enhanced fluid flow, gas hydrate fronts can move both upwards and
laterally in shallower sediments. Therefore, at site N2-KS-44, the period of intense fluid
activity after 13 ka inferred from our data hence probably corresponds to a particular
episode of high free gas and fluid pressure at the base of the GHOZ, which led to gas-
hydrate formation near the seafloor.

4.6. Implications on the evolution of hydrate-bearing pockmarks through time

The timing of pockmark formation has been often discussed in previous studies, in
particular through the application of U-Th dating to cold seep carbonates. Carbonate U-
Th investigations conducted at various seeps worldwide (e.g. Gulf of Mexico, Japan Sea,
Black Sea, Congo margin, Hikurangi margin, South China Sea) have led to the
suggestion that pockmark formation often took place during low sea-level stands in the
past (Watanabe et al., 2008; Feng et al., 2010; Liebetrau et al., 2010; Tong et al., 2013;
Han et al., 2014). The reduced hydrostatic pressure that has accompanied previous sea-
level falls is thought to have resulted in both enhanced fluid flow and hydrate
dissociation, which ultimately led to pockmark formation and authigenic carbonate
precipitation. Other factors have been also evoked as possible mechanisms accounting
for past hydrate destabilisation events and/or pockmark formation, which include e.g.
changes in bottom water temperatures (Mienert et al., 2005; Ménot and Bard, 2010;
Berndt et al., 2014; Pau et al., 2014), dissolved sulfate contents (Crémière et al., 2013),
seismic activity (Liebetrau et al., 2010; Fischer et al., 2013). In our study, as discussed
above and in agreement with earlier works (Sultan et al., 2010; Sultan et al., 2014), gas
hydrate and pockmark dynamics have been probably mainly driven by internal factors, at
least over the last few thousand years. At a longer time scale, of course, one cannot
exclude that external parameters such as sea-level changes also played an important role
in controlling fluid seepage intensity in the Niger delta area, especially at seep sites
located at shallower water depths.
In marked contrast, very little information exists about the evolution of hydrate-bearing pockmarks through time. This is simply because such information can only be derived from numerical modeling (e.g. Sultan et al., 2010) or analytically challenging high-resolution U-Th investigations of authigenic carbonate deposits or buried concretions along sediment cores (Watanabe et al., 2008; Crémière et al., 2013). In this regard, our study provides interesting constraints about the duration and evolution of hydrate-bearing pockmark at margins.

Our results first suggest that the presence of gas hydrate reservoirs near the seafloor can sustain continuous methane seepage and associated carbonate precipitation for several thousand year long periods of time. Interestingly, at site N2-KS-44, the duration of this event of enhanced seepage activity and gas-hydrate growth, associated carbonate precipitation, and subsequent hydrate dissolution inferred from our results (i.e. about 10,000 years) agrees relatively well with estimates obtained by numerical modeling for the same study area (about 8,000 years; Sultan et al., 2010). In this latter work, the calculated duration corresponded to the period of gas hydrate dissolution that followed a sudden theoretical cessation of methane supply from the underlying sediment column.

While gas hydrates may form rapidly, their long-term preservation in sub-surface sediments is indeed ultimately controlled by the sustainability of methane inputs from deeper sediments (Sultan et al., 2014). Gas-hydrate dissolution occurs whenever the methane flux and/or concentration at the base of the GHOZ decreases. The upper layers of gas hydrate reservoirs are generally those that start dissolving first in response to a local decrease of methane fluxes (Sultan et al., 2010). Hydrate dissolution generally leads to an increase of pore-water pressure and, in turn, to sediment collapse and pockmark formation (Sultan et al., 2010; Sultan et al., 2014). In this context, the inferred mode of gas hydrate evolution can be referred to as rapid hydrate growth versus slow hydrate dissolution (Sultan et al., 2014). This latter model that links hydrate dynamics and the evolution of pockmark through time agrees very well with our own observations based on carbonate U-Th dating and inferred sedimentation rates (Fig. 9). Based on our data alone, however, it would remain difficult to argue whether the observed pockmark
evolution at site N2-KS-44 and the recent deepening the SMTZ inferred from our pore-water data are related to a sudden, or instead a progressive, decrease of methane fluxes.

5. Concluding remarks

In this study, we have been able to reconstruct the temporal evolution of gas hydrate deposits and associated methane fluxes at a pockmark on the Niger Delta margin, using an original approach based on: 1) U-Th dating of methane-derived carbonate breccias collected at various depths along a sediment core, 2) the determination of corresponding stratigraphic ages and inferred sedimentation rates, and 3) acquisition of pore water data. At the studied location, a major episode of carbonate precipitation occurred between about 13.0 and 2.5 ka, probably triggered by the upward migration of gas hydrate reservoirs to near the seafloor. Enhanced methane fluxes in the upper sediment layers were probably first accompanied with intense fluid seepage and sediment winnowing at the seafloor. After this initial phase, we propose that hydrate dissolution prevailed in sub-surface sediments, probably in response to decreasing methane fluxes at the base of the local gas hydrate occurrence zone. Presumably, this would have led to pockmark formation and the deepening of the sulphate-methane transition zone, in agreement with evidence from present-day pore-water data. This would also be supported by evidence for rapidly increasing sedimentation rates at the same time and the presence of carbonate concretions older than corresponding stratigraphic ages, which both suggest sediment erosion and/or reworking.

Similarly to what has been previously proposed for the same area based on numerical modeling, our results suggest that the activity of pockmarks in the Niger Delta area is strongly related to gas hydrate dynamics. In future work, the methodology developed in this study could provide interesting insights into the co-evolution of gas hydrate reservoirs and pockmarks at margins. In particular, high-resolution U-Th studies of cold seep carbonates from hydrate-bearing areas should aim at further investigating the resilience of gas hydrate reservoirs and associated pockmark activity to past
environmental changes, especially in the context of ongoing global warming and its potential impact on submarine gas hydrate reservoirs.

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**Figure Captions**

**Figure 1:** Bathymetric map of the studied area with position of the studied cores. This area corresponds to the collapsed summit of an anticline, which is delimited by two deep-rooted normal faults. Note that core N1-KSF-39 is located about 3 km south-west of core N2-KS-44.

**Figure 2:** Lithological description of core N2-KS-44 and corresponding pore-water sulphate, calcium and chloride profiles. Analytical uncertainties are within the size of the symbols. Note that original photographs of the studied carbonate concretions can be found in Bayon et al. (2007).

**Figure 3:** Downcore profiles of Al/Ti ratios for GeoB4901-8 (Zabel et al., 2001), N1-KSF-39 and N2-KS-44 (this study), and corresponding age control points. The chronology for core N1-KSF-39 relies on nine 14C-AMS radiocarbon analyses of mixed planktonic foraminifera fractions (Table 1), and tuning of its Al/Ti profile to the Al/Ti curve of core GeoB4901-8 (dashed lines); a well-dated sediment record also recovered in the Niger Delta deep province (Zabel et al., 2001). The age model for core N2-KS-44 was established by tuning its downcore Al/Ti profile to the nearby reference core N1-KSF-39 (dashed lines).

**Figure 4:** Backscatter electron (BSE) images of polished sections of carbonate-cemented breccias. (a,b) N2-KS-44_30 cm. (c,d) N2-KS-44_160 cm-1. (e) N2-KS-44_160 cm -2. HMg: microcrystalline high-Mg calcite-cemented mudstones; Fib: Radial fibrous crystals of aragonite; Btr: Botryoidal aragonite; Pyr: Framboidal pyrite; Bio: shell fragments (e.g. bivalves, foraminifera).

**Figure 5:** Backscatter electron (BSE) image and electron microprobe chemical maps for a carbonate-cemented breccia (N2-KS-44_75cm). HMg: microcrystalline high-Mg...
calcite-cemented mudstones; Fib: Radial fibrous crystals of aragonite; Btr: Botryoidal aragonite; Bio: shell fragments.

**Figure 6.** Osmond isochron diagram for carbonate concretions and sediments at Site C (core N2-KS-44). Isochron ages are calculated from the slope of the isochrons. The sediment end-member (defined in Fig. 6) is used in all isochrons. The sediment associated with authigenic carbonates at 30 cm is also used in the isochron. Analytical errors are within the size of symbols.

**Figure 7:** Relationship between the depth of the sulphate-methane transition zone (SMTZ) and the depth of occurrence of gas hydrate nodules in the study area. The plot was constructed using data for core N2-KS-44 (this study) and previously published data (Rongemaille, 2011; Ruffine et al., 2013; Sultan et al., 2014; de Prunelé et al., 2015).

**Figure 8:** Al/Ti, weight proportion of aragonite (Bayon et al., 2007), sediment accumulation rates, and methane-derived carbonate U-Th ages *versus* stratigraphic age of sediment core N2-KS-44. The grey band represents the aragonite-rich layer between 30 cm and 180 cm depth, which corresponds stratigraphically to the time interval 13.0 – 2.5 ka. The dashed black line represents the isochrone connecting carbonate and sediment samples that have the same age. Note that carbonate concretions below 160 cm depth are characterized by carbonate U-Th ages younger than corresponding stratigraphic ages, while carbonate-cemented breccias from the upper sediment layer display carbonate U-Th ages similar or older than stratigraphic ages.

**Figure 9:** (a to d) Conceptual model for gas hydrate dynamics and pockmark evolution at the studied site (see text for details).
Figure 2

- Clay-bearing foraminiferal diatomaceous ooze
- Gas-hydrate-bearing sediments
- Small (mm- to cm-size) carbonate-cemented breccias
- Homogeneous carbonate nodule

Fig. 2
Al/Ti Al/Ti Al/Ti

Depth (cm)

17.4 cm/kyr
14.9 cm/kyr
7.8 cm/kyr
3.6 cm/kyr
9.2 cm/kyr
7.3 cm/kyr

GeoB4901-8 N1-KSF-39 N2-KS-44

AMS 14-C dates
Tuning points to GeoB4901-8
Tuning points to N1-KSF-39

Fig. 3
Fig. 4
Fig. 5
Fig. 6
Figure 7

Gas hydrate upper layer depth (m)

SMTZ depth (m)

$y = 0.88x - 0.32$

$R^2 = 1.00$

Fig. 7
SMTZ (~60 cm)

Gas hydrate dissolution

Seafloor carbonate precipitation (aragonite-rich breccias)

Increased CH₄ flux

Pockmark formation

Sediment reworking

Decreased CH₄ flux

Present-day

Fig. 9
Table 1. Radiocarbon dates (mixed planktonic foraminifera) and age control points for core N1-KSF-39

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<th>Core depth (cm)</th>
<th>Lab code</th>
<th>(^{14}\text{C age}) (yr BP)</th>
<th>Error ((^{14}\text{C age BP}))</th>
<th>Cal. age range (1 (\sigma)) (yr BP)</th>
<th>Cal. age (yr BP)</th>
<th>Sedimentation rates (cm/kyr)</th>
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<tr>
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<td>(238^U/232^Th)</td>
<td>(230^Th) (ppt)</td>
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<td></td>
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<td></td>
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<td>6.50 ± 0.01</td>
<td>11.47 ± 0.01</td>
<td>2.20 ± 0.01</td>
<td>11.94 ± 0.03</td>
</tr>
<tr>
<td>N1-KSF-23_155 cm</td>
<td>52.5</td>
<td></td>
<td>8.88 ± 0.01</td>
<td>34.5 ± 0.1</td>
<td>2.20 ± 0.01</td>
<td>11.94 ± 0.03</td>
</tr>
<tr>
<td>N1-KSF-23_160 cm</td>
<td>109.9</td>
<td></td>
<td>22.46 ± 0.03</td>
<td>54.0 ± 0.2</td>
<td>3.30 ± 0.01</td>
<td>22.46 ± 0.07</td>
</tr>
<tr>
<td>N1-KSF-23_180 cm</td>
<td>50.3</td>
<td></td>
<td>7.13 ± 0.01</td>
<td>29.5 ± 0.2</td>
<td>1.72 ± 0.01</td>
<td>6.83 ± 0.03</td>
</tr>
<tr>
<td>N1-KSF-23_190 cm</td>
<td>0.91</td>
<td></td>
<td>2.28 ± 0.06</td>
<td>5.2 ± 0.3</td>
<td>4.41 ± 0.22</td>
<td>27.35 ± 0.90</td>
</tr>
<tr>
<td>N1-KSF-23_200 cm</td>
<td>0.91</td>
<td></td>
<td>1.83 ± 0.04</td>
<td>17.7 ± 0.5</td>
<td>1.16 ± 0.02</td>
<td>1.87 ± 0.06</td>
</tr>
<tr>
<td><strong>Carbonate-cemented breccias</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2-KS-44_30 cm</td>
<td>41.1</td>
<td>Aragonite</td>
<td>11.47 ± 0.01</td>
<td>34.5 ± 0.1</td>
<td>2.20 ± 0.01</td>
<td>11.94 ± 0.03</td>
</tr>
<tr>
<td>micromilled-1</td>
<td>1.00</td>
<td>Aragonite</td>
<td>8.88 ± 0.18</td>
<td>27.2 ± 1.0</td>
<td>2.42 ± 0.08</td>
<td>12.59 ± 0.37</td>
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<tr>
<td>N2-KS-44_75 cm</td>
<td>109.9</td>
<td>Aragonite</td>
<td>22.46 ± 0.03</td>
<td>54.0 ± 0.2</td>
<td>3.30 ± 0.01</td>
<td>22.46 ± 0.07</td>
</tr>
<tr>
<td>micromilled-1</td>
<td>1.09</td>
<td>Aragonite</td>
<td>23.52 ± 0.44</td>
<td>62.4 ± 1.5</td>
<td>5.28 ± 0.07</td>
<td>32.26 ± 0.85</td>
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<tr>
<td>micromilled-2</td>
<td>1.19</td>
<td>HMg</td>
<td>21.56 ± 0.37</td>
<td>33.8 ± 0.9</td>
<td>2.74 ± 0.06</td>
<td>28.16 ± 0.68</td>
</tr>
<tr>
<td>N2-KS-44_160 cm</td>
<td>50.3</td>
<td>Aragonite / HMg</td>
<td>7.13 ± 0.01</td>
<td>29.5 ± 0.2</td>
<td>1.72 ± 0.01</td>
<td>6.83 ± 0.03</td>
</tr>
<tr>
<td>micromilled-1</td>
<td>1.15</td>
<td>Aragonite</td>
<td>9.04 ± 0.16</td>
<td>25.9 ± 0.8</td>
<td>2.67 ± 0.06</td>
<td>14.90 ± 0.37</td>
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<tr>
<td>micromilled-2</td>
<td>1.29</td>
<td>Aragonite</td>
<td>5.92 ± 0.10</td>
<td>29.9 ± 0.8</td>
<td>2.01 ± 0.04</td>
<td>6.39 ± 0.15</td>
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<td>micromilled-3</td>
<td>1.10</td>
<td>HMg</td>
<td>4.77 ± 0.09</td>
<td>31.3 ± 0.7</td>
<td>1.57 ± 0.02</td>
<td>3.83 ± 0.10</td>
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<td>N2-KS-44_180 cm</td>
<td>0.91</td>
<td>Aragonite</td>
<td>2.28 ± 0.06</td>
<td>5.2 ± 0.3</td>
<td>4.41 ± 0.22</td>
<td>27.35 ± 0.90</td>
</tr>
<tr>
<td>micromilled-1</td>
<td>0.91</td>
<td>HMg</td>
<td>1.83 ± 0.04</td>
<td>17.7 ± 0.5</td>
<td>1.16 ± 0.02</td>
<td>1.87 ± 0.06</td>
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<tr>
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<td>HMg</td>
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<td>24.5 ± 0.1</td>
<td>1.76 ± 0.01</td>
<td>5.21 ± 0.01</td>
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<td></td>
</tr>
<tr>
<td>N2-KS-44_260 cm</td>
<td>104.2</td>
<td>HMg</td>
<td>4.44 ± 0.01</td>
<td>24.5 ± 0.1</td>
<td>1.76 ± 0.01</td>
<td>5.21 ± 0.01</td>
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<td>bulk-2</td>
<td>116.8</td>
<td>HMg</td>
<td>9.68 ± 0.01</td>
<td>49.9 ± 0.2</td>
<td>1.87 ± 0.01</td>
<td>5.94 ± 0.01</td>
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Table 3. Activity ratios used for age calculation and isochron U-Th ages

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Dominant mineral</th>
<th>Activity ratios</th>
<th>Two-point isochron age (kyr ± 2s)</th>
<th>Pseudo-isochron age (kyr ± 2s)</th>
<th>δ²³⁴U (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment end-member (±1s)</td>
<td></td>
<td></td>
<td>0.676 ± 0.124</td>
<td>0.939 ± 0.196</td>
<td>1.117 ± 0.016</td>
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<tr>
<td>Carbonate-cemented breccias (±2s)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>N2-KS-44_30 cm</td>
<td>sediment</td>
<td></td>
<td>0.228 ± 0.001</td>
<td>0.370 ± 0.002</td>
<td>1.141 ± 0.002</td>
<td>n.d.</td>
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<tr>
<td></td>
<td>bulk Ara</td>
<td></td>
<td>0.087 ± 0.000</td>
<td>0.195 ± 0.001</td>
<td>1.144 ± 0.002</td>
<td>8.3 ± 3.8</td>
</tr>
<tr>
<td></td>
<td>micromilled-1 Ara</td>
<td></td>
<td>0.079 ± 0.004</td>
<td>0.187 ± 0.010</td>
<td>1.144 ± 0.005</td>
<td>8.6 ± 3.7</td>
</tr>
<tr>
<td>N2-KS-44_75 cm</td>
<td>bulk Ara</td>
<td></td>
<td>0.049 ± 0.000</td>
<td>0.155 ± 0.001</td>
<td>1.149 ± 0.002</td>
<td>9.3 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>micromilled-1 Ara</td>
<td></td>
<td>0.031 ± 0.001</td>
<td>0.162 ± 0.004</td>
<td>1.156 ± 0.005</td>
<td>12.4 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>micromilled-2 HMg</td>
<td></td>
<td>0.036 ± 0.001</td>
<td>0.096 ± 0.003</td>
<td>1.140 ± 0.009</td>
<td>4.8 ± 1.4</td>
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<tr>
<td></td>
<td>sediment</td>
<td></td>
<td>0.325 ± 0.001</td>
<td>0.422 ± 0.002</td>
<td>1.133 ± 0.002</td>
<td>n.d.</td>
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<tr>
<td>N2-KS-44_160 cm</td>
<td>bulk Ara/1 HMg</td>
<td></td>
<td>0.150 ± 0.001</td>
<td>0.265 ± 0.001</td>
<td>1.133 ± 0.002</td>
<td>7 ± 8</td>
</tr>
<tr>
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<td>micromilled-1 Ara</td>
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<td>0.067 ± 0.001</td>
<td>0.175 ± 0.005</td>
<td>1.133 ± 0.009</td>
<td>9.0 ± 2.8</td>
</tr>
<tr>
<td></td>
<td>micromilled-2 Ara</td>
<td></td>
<td>0.156 ± 0.003</td>
<td>0.309 ± 0.009</td>
<td>1.130 ± 0.009</td>
<td>12 ± 8</td>
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<tr>
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<td>micromilled-3 HMg</td>
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<td>0.261 ± 0.007</td>
<td>0.401 ± 0.013</td>
<td>1.124 ± 0.009</td>
<td>n.d.</td>
</tr>
<tr>
<td>N2-KS-44_180 cm</td>
<td>micromilled-1 Ara</td>
<td></td>
<td>0.037 ± 0.001</td>
<td>0.140 ± 0.008</td>
<td>1.126 ± 0.009</td>
<td>9.5 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>micromilled-2 HMg</td>
<td></td>
<td>0.534 ± 0.029</td>
<td>0.590 ± 0.033</td>
<td>1.098 ± 0.009</td>
<td>n.d.</td>
</tr>
<tr>
<td>Homogeneous carbonate nodule (±2s)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>N2-KS-44_260 cm</td>
<td>bulk-1 HMg</td>
<td></td>
<td>0.192 ± 0.000</td>
<td>0.337 ± 0.002</td>
<td>1.127 ± 0.002</td>
<td>11 ± 10</td>
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<td></td>
<td>bulk-2 HMg</td>
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<td>0.168 ± 0.000</td>
<td>0.315 ± 0.001</td>
<td>1.129 ± 0.002</td>
<td>11 ± 9</td>
</tr>
</tbody>
</table>

Table3
Click here to download Table: Table3.pdf