



## U/Th dating of cold-seep carbonates: An initial comparison

Dong Feng<sup>a,b,\*</sup>, Harry H. Roberts<sup>b</sup>, Hai Cheng<sup>c,d</sup>, Jörn Peckmann<sup>e</sup>, Gerhard Bohrmann<sup>f</sup>, R. Lawrence Edwards<sup>d</sup>, Duofu Chen<sup>a</sup>

<sup>a</sup> CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>b</sup> Coastal Studies Institute, Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803, USA

<sup>c</sup> Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

<sup>d</sup> Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455, USA

<sup>e</sup> Department of Geodynamics and Sedimentology, Center for Earth Sciences, University of Vienna, 1090 Vienna, Austria

<sup>f</sup> MARUM, University of Bremen, 28334 Bremen, Germany

### ARTICLE INFO

#### Article history:

Received 14 September 2010

Accepted 14 September 2010

Available online 17 September 2010

#### Keywords:

U/Th dating

Cold seeps

Authigenic carbonate

Gulf of Mexico

Congo Fan

Black Sea

### ABSTRACT

Authigenic carbonates from hydrocarbon seeps are unique archives of past seepage and associated environmental parameters. In order to constrain the ages of a set of seep carbonates and the time involved in carbonate formation, we applied Uranium/Thorium (U/Th) dating to samples from the Gulf of Mexico, the Congo Fan, and the Black Sea. The resulting U/Th ages indicate that environmental conditions must have been favorable for enhanced methane-rich fluid seepage during the time intervals of 53.4 to 1.7 ka BP for the Gulf of Mexico and 45.5 to 3.0 ka BP for the Congo Fan. The seep carbonates from the Black Sea formed at 1.6 to 1.1 ka BP. Our results suggest that enhanced fluid flow during these time intervals was closely related to 1) sea-level variations associated with glacial/interglacial cycles and 2) environmental alterations in the course of Late Quaternary climate change, including variations in bottom-water temperatures that affected the stability of gas hydrate reservoirs.

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### 1. Introduction

Seepage of hydrocarbon-rich fluids in marine sediments at so-called “cold seeps” is a frequently observed phenomenon worldwide (Judd and Hovland, 2007, and references therein). The precipitation of carbonates at seeps is the result of anaerobic oxidation of methane (AOM) and other hydrocarbons, which increases pore-water alkalinity (e.g., Boetius et al., 2000; Joye et al., 2004), thus favoring precipitation of authigenic carbonate minerals in subsurface sediment or at the seafloor (Bernier, 1980). Seep carbonates provide an excellent archive of past seepage and associated environmental parameters (Aharon et al., 1997; Bohrmann et al., 1998; Peckmann et al., 2001; Teichert et al., 2003; Kutterolf et al., 2008; Watanabe et al., 2008; Bayon et al., 2009a,b; Liebetrau et al., 2010).

Defining the timing and duration of fluid seepage at seeps is critical to better characterization of the geological factors that influence seepage. To address this problem, a chronometer is required that constrains the time during which seeps were active. This time constraint cannot be achieved using radiocarbon techniques because seep carbonates derive part of their carbon from fossil

sources (i.e., methane and other hydrocarbons). The  $^{14}\text{C}_{\text{carbonate}}$  ages of cold-seep carbonates consequently represent maximum ages (Paull et al., 1989; Aharon et al., 1997; Peckmann et al., 2001). A few previous studies have demonstrated that Uranium/Thorium (U/Th) dating can be used to determine the age of modern cold-seep carbonates (Aharon et al., 1997; Teichert et al., 2003; Kutterolf et al., 2008; Watanabe et al., 2008; Bayon et al., 2009a,b; Liebetrau et al., 2010). However, these studies were restricted to a single deposit or location. Here we compare the U/Th ages of seep carbonates from various cold-seep locations worldwide, including two sites from the Gulf of Mexico, Alaminos Canyon lease block 645 (AC645) and Atwater Valley lease block 340 (AT340). Data from two sites on the Congo Fan, Hydrate Hole and Diapir Field, as well as sites on the Romanian shelf (RO) and the Ukrainian slope (UKR) of the Black Sea were used to determine the timing and duration of fluid seepage in order to provide preliminary insight into probable global factors governing seepage processes along continental margins.

### 2. Materials and methods

Authigenic carbonates from six sites of hydrocarbon seepage at three distinct areas were chosen for this comparative study (Fig. 1). Location, water depth,  $\delta^{13}\text{C}_{\text{carbonate}}$  values, and mineralogy of authigenic carbonate samples analyzed are listed in Table 1. The

\* Corresponding author at: Tel.: +1 225 578 2395; fax: +1 225 578 2520

E-mail addresses: fd@gig.ac.cn, dongfeng@lsu.edu (D. Feng), hrober3@lsu.edu (H.H. Roberts), cheng021@umn.edu (H. Cheng), joern.peckmann@univie.ac.at (J. Peckmann), gbohrmann@uni-bremen.de (G. Bohrmann), edwar001@umn.edu (R. Lawrence Edwards), cdf@gig.ac.cn (D. Chen).

$\delta^{13}\text{C}$  values of the respective carbonate samples indicate that their carbon is derived mainly from the oxidation of hydrocarbons.

Selected samples of authigenic carbonate were chosen for U/Th dating analysis in support of this study. Selected carbonate phases of the samples were hand-drilled carefully to obtain samples with a weight of between 20 to 50 mg. Whenever possible, the microcrystalline carbonate matrix and early diagenetic aragonite cements were collected from the same sample. The microcrystalline matrix usually represents initial seepage-related precipitation, whereas the early diagenetic cements usually reflect a later phase that formed under the influence of seepage. The chemical procedures used to separate uranium and thorium for  $^{230}\text{Th}$  dating were the same as those described by Edwards et al. (1987). Dating by  $^{230}\text{Th}$  was performed at the Minnesota Isotope Laboratory on a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS, Thermo-Finnigan Neptune). Details of

instrumental approaches were explained in Cheng et al. (2000a, 2009a,b) and Shen et al. (2002). A  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio of  $4.4 \pm 2.2 \times 10^{-6}$  was used to correct for the initial  $^{230}\text{Th}$ .

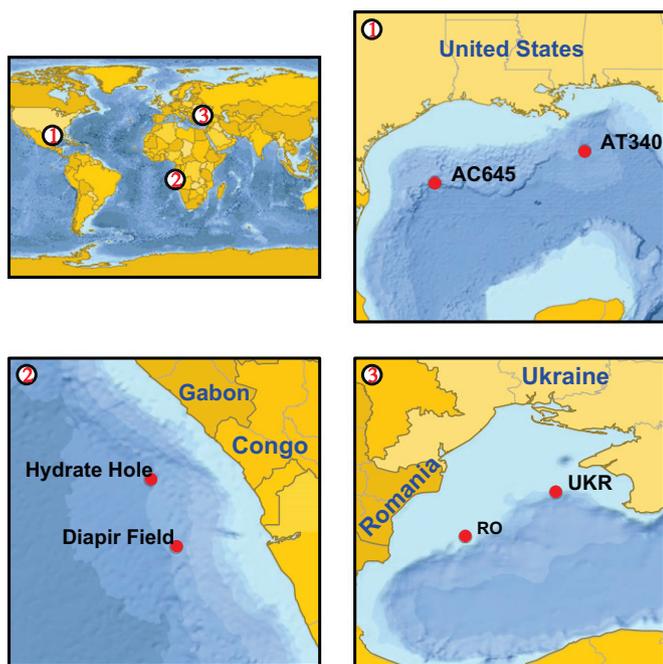
### 3. Results and discussion

#### 3.1. U/Th corrected age

All U and Th results are presented in Table 2. Uranium ( $^{238}\text{U}$ ) concentrations varied from  $\sim 4$  to 13 ppm for carbonates from AC645,  $\sim 1$  to 6 ppm for carbonates from AT340,  $\sim 2$  to 9 ppm for Congo Fan carbonates, and  $\sim 2$  to 6 ppm for Black Sea carbonates. These values are similar to those reported in the literature for other cold-seep carbonates (Aharon et al., 1997; Teichert et al., 2003; Watanabe et al., 2008; Bayon et al., 2009a). Concentrations of  $^{232}\text{Th}$  range from  $\sim 12$  to 1700 ppb in AC645 carbonates,  $\sim 1$  to 700 ppb in AT340 carbonates,  $\sim 100$  to 4800 ppb in Congo Fan carbonates, and  $\sim 1$  to 300 ppb in Black Sea carbonates. Compared to results of Aharon et al. (1997), Teichert et al. (2003), and Bayon et al. (2009a) carbonate samples from the Congo Fan have higher Th contents.

On a ( $^{230}\text{Th}/^{232}\text{Th}$ ) vs. ( $^{238}\text{U}/^{232}\text{Th}$ ) diagram (see Fig. 2), the studied samples plotted well within the range of published data for other cold-seep carbonates (cf. Bayon et al., 2009a and their Fig. 4B). The low  $^{232}\text{Th}$  concentrations measured in samples from AC645 and AT340 in the Gulf of Mexico and from the Black Sea suggested that the content of detrital minerals was low and uncertainties of  $^{230}\text{Th}$  ages were consequently small. However, the contents of detrital components of samples from the Congo Fan and two subsamples from the Black Sea were significant, as revealed by high  $^{232}\text{Th}$  concentrations, which resulted in large uncertainties on the respective  $^{230}\text{Th}$  ages. The large uncertainty of the U/Th age of the matrix was caused mainly by the high initial  $^{232}\text{Th}$  content of the enclosed detrital minerals. The diagenetic cements analyzed in this study were pure aragonite. Aragonite cements usually have small uncertainties of their U/Th ages because they contain relatively less detrital material than the matrix of the corresponding samples.

Corrected initial  $\delta^{234}\text{U}$  values ranged from 132 to 152 for samples from the Gulf of Mexico and the Congo Fan (Table 2). The average of these values was close (within error) to modern seawater ( $145.8 \pm 1.7$ ; Cheng et al., 2000b). These corresponding values indicated that the carbonate-bound U was likely derived from seawater. However, the  $\delta^{234}\text{U}$  values of the Black Sea samples were higher than those of the modern seawater ( $145.8 \pm 1.7$ ; Cheng et al., 2000b). A small variation was noted in their  $\delta^{234}\text{U}$  values, from 176 to 180. These values indicated that the carbonate-bound U was most



**Fig. 1.** Global map showing the study areas: 1) Gulf of Mexico, 2) Congo Fan, and 3) Black Sea. See Table 1 for geographical positions and water depths: Alaminos Canyon lease block 645 (AC645); Atwater Valley lease block 340 (AT340); Romanian shelf (RO); Ukrainian slope (UKR). Maps were created using Online Mapping Tool, available at [www.planiglobe.com](http://www.planiglobe.com).

**Table 1**

Location (see Fig. 1), water depth,  $\delta^{13}\text{C}_{\text{carbonate}}$  values (‰ PDB), and mineralogy of authigenic carbonate samples analyzed in this study.

Location	Water depth (m)	Morphology of carbonate precipitates	Occurrence of gas hydrate	$\delta^{13}\text{C}$ (‰, PDB)	XRD Mineral composition			Reference
					Major	Minor	Trace	
<i>Gulf of Mexico</i>								
AC645	2230	blocks, slabs, and crusts	no	−33.9 to −22.2	Ara		Cc	Feng et al., 2008a; Roberts et al., 2010
AT340	2240	blocks, concretions, slabs, crusts, and chimney rubble	no	−60.8 to −35.5	Ara	HMC	Qz, Cc	Feng and Roberts, 2010
<i>Congo Fan</i>								
Hydrate Hole	3100	nodules, crusts and slabs, tubes, and filled molds	yes	−62.5 to −46.3	Ara/HMC		Kao, Qz, Bar,	Feng et al., 2010; Haas et al., 2010
Diapir Field	2400	nodules, crusts, and slabs	yes	−40.7 to −30.7	Ara	HMC	Kao, Qz	
<i>Black Sea</i>								
Romanian shelf	120	crusts	no	−41.0 to −25.9	HMC	Ara	Qz, Cc	Peckmann et al., 2001
Ukrainian slope	180–200	crusts	no	−37.3 to −28.9	HMC	Ara	Qz, Cc	

Ara=aragonite, HMC=high-Mg calcite, Cc=Calcite, Bar=Barite, Qz=Quartz, Kao=Kaolinite.

**Table 2**<sup>230</sup>Th dating results of cold-seep carbonates from AC645, AT340 of the northern Gulf of Mexico, Congo Fan, and Black Sea.

Sample Number	Comments	<sup>238</sup> U (ppb)	<sup>232</sup> Th (ppt)	<sup>230</sup> Th/ <sup>232</sup> Th (atomic × 10 <sup>-6</sup> )	δ <sup>234</sup> U <sup>a</sup> (measured)	<sup>230</sup> Th/ <sup>238</sup> U (activity)	<sup>230</sup> Th Age (ka BP) (uncorrected)	<sup>230</sup> Th Age (ka BP) <sup>b</sup> (corrected)	δ <sup>234</sup> U <sub>Initial</sub> <sup>c</sup> (corrected)
<i>Gulf of Mexico</i>									
AC 645									
4194-1	Matrix	9030 ± 20	419800 ± 4300	158 ± 2	121.2 ± 1.7	0.4457 ± 0.0017	54.7 ± 0.3	53.4 ± 0.9	141 ± 2
4194-2	Matrix	6770 ± 20	1673000 ± 18000	18.8 ± 0.2	131.2 ± 2.1	0.2819 ± 0.0016	31.1 ± 0.2	2.55 ± 5	141 ± 3
4194-3	Matrix	8500 ± 20	500000 ± 10000	111 ± 2	122.0 ± 1.9	0.3951 ± 0.0011	46.9 ± 0.2	45 ± 1	139 ± 2
4194-4	Matrix	5910 ± 10	619000 ± 12000	29 ± 1	141.0 ± 1.9	0.1842 ± 0.0006	19.1 ± 0.1	16 ± 2	148 ± 2
4197-1	Matrix	8100 ± 10	389800 ± 7800	52 ± 1	140.9 ± 1.9	0.1516 ± 0.0005	15.5 ± 0.1	14.2 ± 0.9	147 ± 2
4197-2	Matrix	4300 ± 6	11700 ± 240	692 ± 14	143.6 ± 2.1	0.1140 ± 0.0004	11.4 ± 0.05	11.3 ± 0.1	148 ± 2
4197-3	Matrix	6020 ± 10	201000 ± 4000	50 ± 1	141.5 ± 2.0	0.1019 ± 0.0005	10.2 ± 0.1	9.3 ± 0.6	145 ± 2
4197-4	Matrix	5840 ± 9	89400 ± 1800	98 ± 2	143.6 ± 1.9	0.0913 ± 0.0003	9.1 ± 0.04	8.6 ± 0.3	147 ± 2
4197-5	Matrix	12630 ± 20	373000 ± 7500	62 ± 1	143.2 ± 1.8	0.1118 ± 0.0003	11.2 ± 0.04	10.4 ± 0.5	148 ± 2
4197-6	Matrix	7720 ± 20	230000 ± 4600	66 ± 1	142.6 ± 2.3	0.1186 ± 0.0004	11.9 ± 0.1	11.1 ± 0.5	147 ± 2
281-1	Matrix	6960 ± 10	203000 ± 4100	70 ± 1	140.7 ± 2.4	0.1243 ± 0.0004	12.5 ± 0.1	11.7 ± 0.5	145 ± 2
AT 340									
4180-1	Matrix	5780 ± 20	420600 ± 4300	27.5 ± 0.3	137.1 ± 1.6	0.1214 ± 0.0006	12.3 ± 0.1	10 ± 1	141 ± 2
4180-2	Cement	6190 ± 20	470 ± 60	17400 ± 2200	143.1 ± 1.8	0.0806 ± 0.0004	8.0 ± 0.05	7.9 ± 0.1	146 ± 2
4180-3	Cement	6240 ± 40	4100 ± 60	2040 ± 40	139.3 ± 6.8	0.0813 ± 0.0011	8.1 ± 0.1	8.0 ± 0.1	143 ± 7
4180-4	Matrix	6260 ± 30	675100 ± 7100	23 ± 1	135.0 ± 5.9	0.1489 ± 0.0053	15.3 ± 0.6	12 ± 2	139 ± 6
4180-5	Cement	4800 ± 30	490 ± 20	13300 ± 500	144.6 ± 6.4	0.0819 ± 0.0008	8.1 ± 0.1	8.0 ± 0.1	148 ± 7
4183-1	Cement	4900 ± 30	670 ± 20	12000 ± 400	140.1 ± 6.7	0.0993 ± 0.0011	9.9 ± 0.1	9.9 ± 0.1	144 ± 7
270-1	Cement	1880 ± 10	17240 ± 80	119 ± 3	141.3 ± 7.8	0.0661 ± 0.0014	6.5 ± 0.2	6.2 ± 0.2	144 ± 8
270-3	Cement	1190 ± 4	14340 ± 50	87 ± 2	149.0 ± 6.6	0.0636 ± 0.0015	6.2 ± 0.2	5.8 ± 0.2	152 ± 7
270-6	Cement	1600 ± 2	19800 ± 400	48 ± 1	143.5 ± 2.3	0.0359 ± 0.0004	3.5 ± 0.04	3.1 ± 0.2	145 ± 2
270-8	Cement	1816 ± 3	9400 ± 200	101 ± 2	148.3 ± 2.3	0.0318 ± 0.0003	3.1 ± 0.03	2.9 ± 0.1	150 ± 2
277-1	Cement	1494 ± 9	3190 ± 40	136 ± 8	150.2 ± 9.2	0.0176 ± 0.0010	1.7 ± 0.1	1.6 ± 0.1	151 ± 9
<i>Congo Fan</i>									
Hydrate Hole									
HH-2a-1-1	Cement	1780 ± 10	111100 ± 700	13.0 ± 0.8	142.9 ± 9.5	0.0479 ± 0.0029	4.7 ± 0.3	3.0 ± 0.9	144 ± 10
HH-2a-1-2	Cement	2020 ± 4	218000 ± 4000	13.1 ± 0.3	144.2 ± 2.3	0.0858 ± 0.0007	8.5 ± 0.1	6 ± 2	147 ± 2
HH-2a-2-1	Matrix	3020 ± 4	1443000 ± 29000	12.0 ± 0.3	121.4 ± 2.2	0.3590 ± 0.0013	41.8 ± 0.2	29 ± 9	132 ± 4
HH-2a-2-2	Matrix	2740 ± 7	1380000 ± 28000	12.5 ± 0.3	123.6 ± 3.3	0.3810 ± 0.0020	44.8 ± 0.3	30 ± 10	135 ± 5
HH-2a-3-1	Matrix	7160 ± 10	4050000 ± 80000	14.0 ± 0.3	123.7 ± 2.4	0.4861 ± 0.0021	61.0 ± 0.4	50 ± 10	141 ± 5
HH-2a-3-2	Matrix	8530 ± 30	4800000 ± 100000	13.8 ± 0.3	123.6 ± 2.7	0.4749 ± 0.0021	59.2 ± 0.4	40 ± 10	140 ± 5
HH-2d-1-1	Matrix	6430 ± 10	1770000 ± 40000	12.0 ± 0.3	132.9 ± 2.6	0.2058 ± 0.0011	21.8 ± 0.1	15 ± 5	138 ± 3
HH-2d-1-2	Matrix	4790 ± 10	1590000 ± 30000	12.2 ± 0.3	130.9 ± 2.6	0.2471 ± 0.0013	26.7 ± 0.2	18 ± 6	138 ± 4
HH-2d-1-3	Matrix	7810 ± 20	2430000 ± 50000	12.3 ± 0.3	133.3 ± 2.9	0.2331 ± 0.0013	25.0 ± 0.2	17 ± 6	140 ± 4
HH-2d-1-4	Matrix	5030 ± 10	1800000 ± 40000	12.9 ± 0.3	128.2 ± 2.7	0.2800 ± 0.0014	30.9 ± 0.2	21 ± 7	136 ± 4
Diapir Field									
DF-2c-1	Matrix	8300 ± 20	2220000 ± 50000	16.0 ± 0.3	136.8 ± 2.3	0.2646 ± 0.0010	28.7 ± 0.1	22 ± 5	145 ± 3
DF-2c-2	Matrix	6250 ± 10	2030000 ± 40000	15.0 ± 0.3	133.6 ± 2.2	0.2883 ± 0.0012	31.8 ± 0.2	23 ± 6	143 ± 3
DF-2c-3	Matrix	7020 ± 20	2070000 ± 40000	15.5 ± 0.3	135.4 ± 2.7	0.2784 ± 0.0014	30.5 ± 0.2	23 ± 6	144 ± 4
<i>Black Sea</i>									
Romanian shelf									
RO-1	Matrix	6170 ± 40	295000 ± 2000	11 ± 1	175.8 ± 6.9	0.0306 ± 0.0018	2.9 ± 0.2	1.6 ± 0.6	177 ± 7
RO-2	Matrix	3050 ± 20	40200 ± 200	25 ± 1	177.0 ± 6.6	0.0198 ± 0.0008	1.9 ± 0.1	1.5 ± 0.2	178 ± 7
RO-3	Cement	2560 ± 10	6720 ± 50	80 ± 4	179.7 ± 6.7	0.0128 ± 0.0006	1.2 ± 0.1	1.1 ± 0.1	180 ± 7
Ukrainian slope									
UKR-1	Matrix	4690 ± 30	338000 ± 3000	6 ± 1	176.0 ± 7.7	0.0250 ± 0.0026	2.3 ± 0.2	0.5 ± 0.9	176 ± 8
UKR-2	Matrix	3200 ± 20	14150 ± 70	43 ± 2	175.1 ± 6.9	0.0115 ± 0.0005	1.1 ± 0.05	0.9 ± 0.1	176 ± 7
UKR-3	Cement	2380 ± 10	1200 ± 20	450 ± 20	178.8 ± 6.6	0.0137 ± 0.0005	1.3 ± 0.05	1.2 ± 0.1	179 ± 7

The error is 2σ error. U and Th decay constants are as same as those described in Cheng et al. (2009a,b).

Corrected <sup>230</sup>Th ages assume the initial <sup>230</sup>Th/<sup>232</sup>Th atomic ratio of 4.4 ± 2.2 × 10<sup>-6</sup>. Those are the values for a material at secular equilibrium, with the bulk earth <sup>232</sup>Th/<sup>238</sup>U value of 3.8. The errors are arbitrarily assumed to be 50%

<sup>a</sup> δ<sup>234</sup>U = ((<sup>234</sup>U/<sup>238</sup>U)<sub>activity</sub> - 1) × 1000.

<sup>b</sup> B.P. stands for "Before Present" where the "Present" is defined as the year 1950 A.D.

<sup>c</sup> δ<sup>234</sup>U<sub>initial</sub> was calculated based on <sup>230</sup>Th age (T), i.e., δ<sup>234</sup>U<sub>initial</sub> = δ<sup>234</sup>U<sub>measured</sub> × e<sup>1234 × T</sup>.

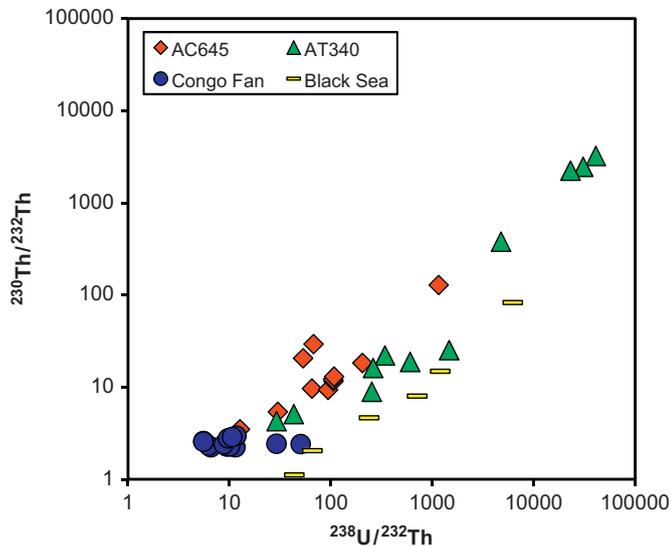
likely derived from pore waters rather than from seawater; this former U-pool was typically characterized by much higher δ<sup>234</sup>U values (cf. Cochran et al., 1986; Teichert et al., 2003).

### 3.2. Timing of seep activity and potential driving processes

#### 3.2.1. Gulf of Mexico

The seep carbonate samples from AC645 (Gulf of Mexico) showed U/Th ages of between 53.4 and 8.6 ka (Table 2). The ages indicated two time intervals of enhanced carbonate precipitation.

One relatively recent period ranged from 24.5 to 8.6 ka BP, and an earlier period, from 53.4 to 45.3 ka BP. The U/Th ages of seep carbonate samples from AT340 varied between 12.4 and 1.6 ka (Table 2). Most samples of AC645 seep carbonate formed at about 12 ka (Fig. 3), and, remarkably, carbonate precipitation started at almost the same time interval as AT340 (Gulf of Mexico; 12.4 ka BP). Because carbonate precipitation at seeps depends on the flux of ascending methane (Luff and Wallmann, 2003; Peckmann et al., 2009), the environmental conditions during these two time intervals must have been favorable for enhanced rates of seepage. The obtained U/Th ages revealed that carbonate precipitation



**Fig. 2.** Comparison of ( $^{230}\text{Th}/^{232}\text{Th}$ ) vs. ( $^{238}\text{U}/^{232}\text{Th}$ ) ratios of cold seep carbonates from AC645 and AT340 of the northern Gulf of Mexico, Congo Fan, and Black Sea. The decrease of  $^{238}\text{U}/^{232}\text{Th}$  ratios of carbonate samples (AT340 from  $\sim 29$  to 40952; AC645 from  $\sim 13$  to 1155; Black Sea from  $\sim 44$  to 6208; Congo Fan from  $\sim 6$  to 50) may partly reflect an increasing content of detrital minerals (cf. Bayon et al., 2009a).

occurred episodically, suggesting that seepage was not a continuous process but was amplified during distinct intervals (see Fig. 3). A similar scenario has been put forward by Teichert et al. (2003), who observed that U/Th ages of seep carbonates from Hydrate Ridge cluster in certain periods. Similarly, a recent study on carbonate nodules enclosed in hydrate-bearing sediments at methane seeps off Joetsu, Japan Sea, indicated that carbonate precipitation was restricted to distinct intervals (12.8 to 15.8 ka, 20.6 to 25.3 ka; 35.8 ka, and 62.4 ka; see Watanabe et al., 2008, for details). The short life spans of seepage activity at all those localities were probably controlled by interim exhaustion of hydrocarbon sources, possibly amplified by the clogging of the plumbing system as a result of extensive carbonate formation and/or hydrate accumulation. On a geological time scale, eustatic sea-level fluctuation is presumed to be the main influence on seepage intensity (Kiel, 2009). Roberts and Carney (1997) proposed a general relationship between sea level, sediment loading of the continental slope, salt movement, and expulsion of fluids and gas to the seafloor. It is suggested from their study that major episodes of sediment delivery to the slope are related to fluvial entrenchment of the shelf and delta building at the shelf edge during periods of lowered sea level, areas downslope of these zones of sedimentation undergo sediment loading. Shelf-edge depocenters shift through time; therefore, sectors of the slope loaded by this process also shift with time. Thus, for the lower continental slope of the Gulf of Mexico (sites AC645 and AT340), we suggest that the current phase of vigorous seepage was induced by increased sedimentary loading and associated salt diapirism that activated fault conduits at approximately 12.4 ka BP at the end of the last deglaciation. Because of an increase in sediment loading during deglaciation, salt movement and fluid-gas expulsion (perhaps warm fluids), and warming of the water column, destabilization of gas hydrates may have been consequently enhanced during these periods. Similar to our findings, Aharon et al. (1997) suggested that vigorous seepage at mid-bathyal and abyssal depth began at 12.3 ka and continues until today. Maslin et al. (2004) proposed that 70% of the landslides in the North Atlantic of the last 45 ka occurred during two meltwater peaks 15–13 and 11–8 ka ago.

### 3.2.2. Congo Fan

The U/Th ages of carbonate samples from the Congo Fan span a long time interval (Table 2; Fig. 3). Especially, carbonate samples from Hydrate Hole show a wide range with U/Th ages, between 45.5 and 3.0 ka. In contrast, carbonate samples from Diapir Field reveal U/Th ages of between 23.2 and 21.7 ka (Table 2). The studied carbonate samples have positive  $\delta^{18}\text{O}$  isotopic signatures, presumably caused by hydrate dissociation (cf. Feng et al., 2010; Haas et al., 2010). Destabilization of gas hydrates in marine settings may result from 1) decreased pressure, linked to falling sea level, 2) increased temperature of bottom waters, or 3) increased salinity of interstitial waters (e.g., Sloan, 1998). The water depth of the gas hydrates occurrences at the studied seeps in the lower Congo Basin is deeper than 2400 m. These sites are located within the gas hydrate stability zone, which makes them less likely to be sensitive to small sea-level perturbations. However, most of our carbonate samples revealed U/Th ages that point to formation during sea level lowstand. Sea level was  $\sim 60$  m lower than today around 45 ka BP and almost 120 m lower than today during the glacial maximum (cf. Labeyrie et al., 1987). Destabilization of gas hydrates in the Congo Fan seep sites from pressure decrease, linked with a drop in sea level, cannot be ruled out. Accordingly, recent studies show that during Pleistocene glacial-interglacial cycles the occurrence of seep carbonate appears to correlate with sea-level low stands (Teichert et al., 2003; Watanabe et al., 2008). Kiel (2009) further suggested that this correlation also exists on a much larger time-scale from the Late Jurassic to the Recent. On the other hand, the Congo Fan seeps are situated in pockmarks, which are associated with underlying tectonic structures, such as fault zones, salt diapirs, and polygonal faults (Gay et al., 2007). Gay et al. (2007) proposed that fluid migration in the Lower Congo Basin depends mainly on two factors: 1) the gas hydrate system, which inhibits fluid and gas migration, and 2) the polygonal fault systems, which favor fluid migration when faults move and fluids are periodically released. Notably, supply of hot fluids from deeper sources and focused flow along the margins of salt diapirs can produce fluids that are capable of destabilizing gas hydrates in the shallow subsurface of the study sites.

### 3.2.3. Black Sea

The U/Th ages of carbonate samples from RO of the Black Sea ranged from 1.6 to 1.1 ka (Table 2 and Fig. 3). The U/Th age for the matrix of carbonate sample from UKR of the Black Sea is  $0.5 \pm 0.9$  ka (Table 2) leading to uncertainty as to the real age of the sample. However, the U/Th age of the aragonite cement in the same sample was  $1.2 \pm 0.1$  ka. The microcrystalline matrix of seep carbonates usually represents initial precipitation, whereas early diagenetic cements tend to reflect the last phase of carbonate formation related to seepage. Hence, it is most likely that the matrix of the UKR carbonate sample is older than 1.2 ka. The Black Sea represents the world's largest anoxic water mass, and numerous methane seeps have been recognized from shallow depth to below 2000 m (Gulin et al., 2003, and references therein). Feng et al. (2008b), investigating the rare earth element patterns of the samples studied here, suggested that they formed under both oxic and anoxic conditions. The change of age of seep carbonates with signatures of oxic conditions at different depths on the continental slope may reflect the rise of the oxic/anoxic interface in the water column. Likewise, the oxic–anoxic interface may have fluctuated between the depth of the sites on the Romanian shelf (120 m water depth) and the sites on the Ukrainian slope (180 to 200 m water depth) during formation of the studied seep carbonates. The obtained U/Th ages consequently suggest that bottom waters were oxic until at least 1.2 ka BP on the Ukrainian slope and 1.1 ka BP on the Romanian shelf.

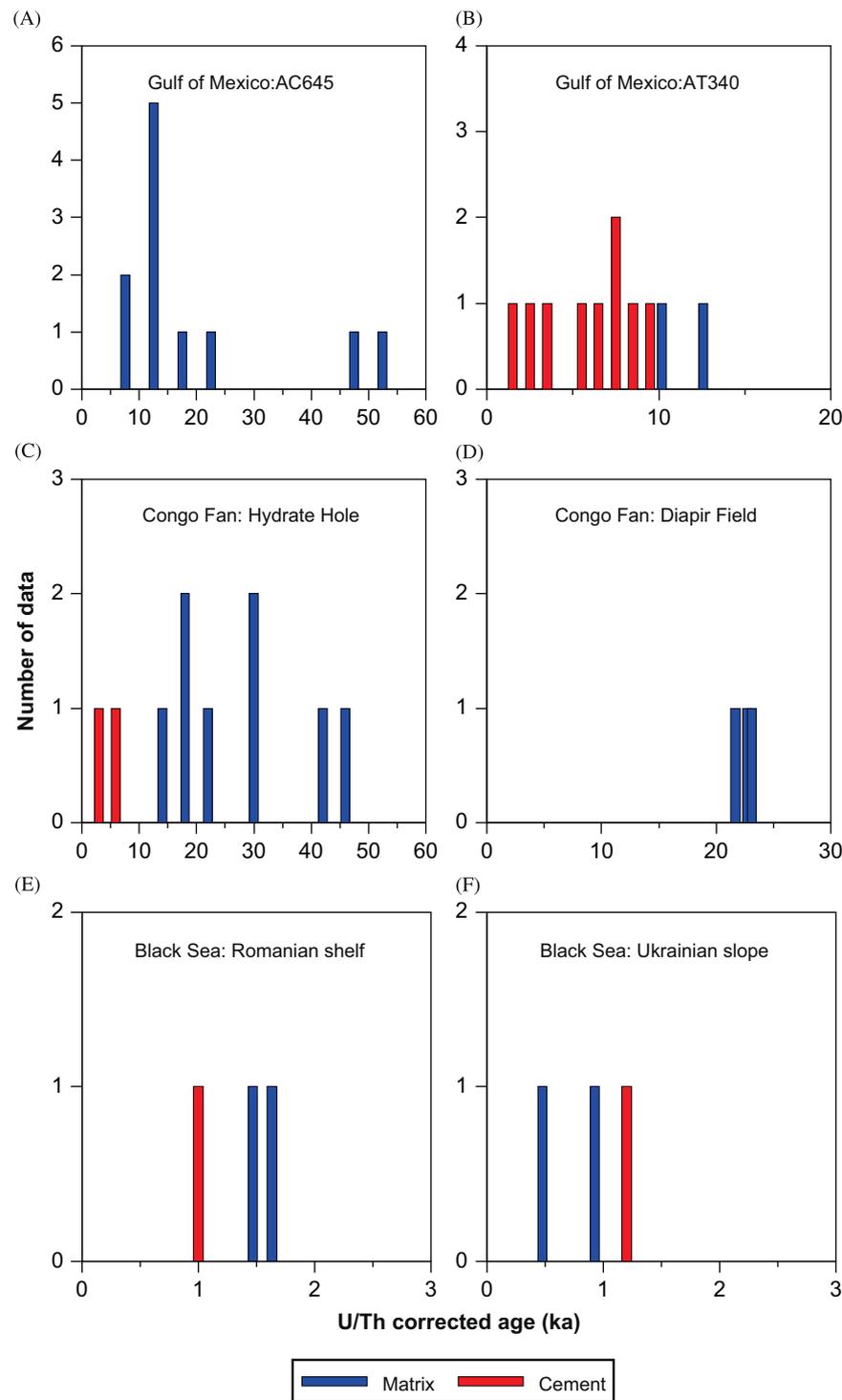


Fig. 3. (A–F) Histogram of corrected U/Th ages of samples of the microcrystalline carbonate matrix and carbonate cement (data from Table 2).

#### 4. Summary

The ages of seep carbonates determined to date allow a first estimation of the chronology of seepage along a variety of continental margins (Aharon et al., 1997; Teichert et al., 2003; Kutterolf et al., 2008; Watanabe et al., 2008; Bayon et al., 2009a,b; Liebetrau et al., 2010; this study). These ages suggest that periods of enhanced hydrocarbon seepage occurred from the late Pleistocene and continues today. Factors governing the episodic intensification of seepage are 1) the decomposition of gas hydrate and/or the ascent of methane gas triggered by the decrease of hydraulic pressure induced

by a falling sea level (e.g., Teichert et al., 2003; Watanabe et al., 2008), 2) the decomposition of gas hydrate induced by warming of bottom seawater (e.g., Congo Fan; Marmara Sea by Ménot and Bard, 2010), 3) the increase of sedimentary load (e.g., Gulf of Mexico), and 4) active salt diapirism (e.g., Gulf of Mexico; Congo Fan). Although some scenarios describing the long-term dynamics of fluid flow at seeps have been suggested (e.g., Aharon et al., 1997; Teichert et al., 2003; Watanabe et al., 2008; this study), the relationship between climatically driven sea level and/or bottom water temperature changes and enhanced carbonate precipitation at cold seeps cannot be considered proven and must await further confirmation. Therefore,

more U/Th measurements are required for better constraining the chronology of the formation of seep carbonates and to adjust the interpretation of processes governing the long-term dynamics of seepage along continental margins.

The application of U/Th dating to authigenic seep carbonates from a variety of geologic settings, including the northern Gulf of Mexico, the Congo Fan, and the Black Sea, adds new information on the timing and the factors governing cold-seep activity along continental margins. Dating of carbonates from the northern Gulf of Mexico show that the current phase of vigorous seepage at the lower continental slope began at approximately 12.4 ka BP, possibly reflecting a time of increased sedimentary loading and associated salt diapirism that activated fault conduits to the seafloor at the end of the last deglaciation. Dating by the U/Th method indicated that long-term intensity of hydrocarbon seepage was not constant but fluctuated and has durations with distinct intervals. The apparently short life span of seepage at a particular locality is probably controlled by the exhaustion of the hydrocarbon sources, possibly amplified by clogging of the plumbing system due to extensive carbonate formation. Precipitation of seep carbonates from 45.5 to 3.0 ka BP in the Congo Fan suggests thermally induced destabilization from subsurface sources of the local gas hydrate reservoirs as an additional factor that enhanced seepage activity apart from low sea level. Both U/Th dating (this study) and rare earth elements patterns (cf. Feng et al., 2008b) suggest that Black Sea bottom waters were oxic until at least 1.2 ka BP on the Ukrainian slope in 180 to 200 m water depth and 1.1 ka BP on the Romanian shelf in 120 m water depth.

## Acknowledgments

This study was funded by Bureau of Ocean Energy Management, Regulation and Enforcement (BOEMRE) Contract no. 1435-01-05-39187 and partially supported by the NSFC (40906031, 40725011, and U0733003) and 973 Program (2009CB219506). Additional financial support was provided by the “Deutsche Forschungsgemeinschaft” through the DFG-Excellence Cluster MARUM, Bremen. The Gulf of Mexico seep carbonate samples were obtained from cruises sponsored by the MMS through cooperative agreements with LSU. We appreciate the thoughtful and constructive comments provided by Dr. G. Bayon (Ifremer), which improved the manuscript. This paper is contribution No. IS-1218 from GIGCAS.

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