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U–Th stratigraphy of a cold seep carbonate crust

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Abstract:

On continental margins, oxidation of methane-rich fluids from the sediment often leads to formation of authigenic carbonate pavements on the seafloor. The biogeochemical processes involved during this carbonate precipitation are increasingly understood, but little is known about the duration or mode of carbonate crust formation. Here, we report uranium and thorium concentrations and isotope compositions for a set of 14 samples drilled across an authigenic carbonate pavement, which provide the first stratigraphy for a cold-seep carbonate crust. The 5.5-cm thick crust (NL7-CC2) was collected by submersible on the Nile deep-sea fan in an area of active fluid venting. U–Th analyses must be corrected for initial Th and measurement of co-existing sediments indicates the presence of both scavenged and detrital initial ^{230}Th , which must be considered during this correction. The calculated $^{230}\text{Th}/\text{U}$ age-depth profile for NL7-CC2 provides evidence for continuous downward carbonate precipitation at the studied location over the last ~ 5000 years. Three distinct phases can be distinguished from top to bottom with average growth rates of ~ 0.4, 5 and 0.8 cm/kyr, respectively, corresponding to carbonate precipitation rates ranging from ~ 7 to 92 $\mu\text{mol m}^{-2} \text{h}^{-1}$ (rates consistent with previous estimates). High-resolution $\delta^{13}\text{C}$ profiles [Gontharet, S., Pierre, C., Blanc-Valleron, M.- M., Rouchy, J.M., Fouquet, Y., Bayon, G., Foucher, J.P., Woodside, J., Mascle, J., The Nautinil Scientific Party, 2007. Nature and origin of diagenetic carbonate crusts and concretions from mud volcanoes and pockmarks of the Nile deep-sea fan (eastern Mediterranean Sea). *Deep Sea Res. II* 54, 1292–1311] and major elements across NL7-CC2 show that the variations in carbonate precipitation rates were also accompanied by changes in carbonate mineralogy and fluid composition. We suggest that these changes primarily reflect modification of the diagenetic environment, i.e. a progressive depletion of dissolved sulphate through anaerobic oxidation of methane, caused by the initial carbonate crust formation and the resulting reduction in bioirrigation. Overall, U–Th dating of cold seep carbonates offers a promising tool to bring new insights into biogeochemical processes at cold seeps and to assess the timing and duration of fluid venting on continental margins.

31 **1. Introduction**

32 Cold seep carbonates are a promising archive of past fluid flow and gas hydrate
33 dissociation on continental margins. They typically form in sub-surface sediments at
34 cold seeps, resulting from the microbial oxidation of methane-rich fluids (e.g. Ritger et
35 al., 1987; Hovland et al., 1987; Paull et al., 1992; Bohrmann et al., 1998; Aloisi et al.,
36 2000, 2002; Greinert et al., 2001; Michaelis et al., 2002; Mazzini et al., 2004; Reitner
37 et al., 2005; Stadnitskaia et al., 2005; Gontharet et al., 2007). In fluid venting areas,
38 anaerobic oxidation of methane (AOM) leads to enhanced alkalinity and dissolved
39 sulphide contents in pore waters, which favours carbonate precipitation and the
40 development of chemosynthetic communities on the seafloor.

41 In many settings, carbonate precipitation forms a hard crust at the sediment surface.
42 Numerical modelling indicate that such carbonate crusts may form within a time
43 period of several centuries (Luff and Wallmann, 2003; Luff et al., 2004, 2005), but
44 these estimates of growth rate and duration have not been confirmed with
45 chronological observations and little is known about the effect of crust growth on fluid
46 venting. To address these questions requires establishing an accurate chronology for
47 crust formation. This cannot be achieved using radiocarbon techniques because cold-
48 seep carbonates derive part of their carbon from old sources (i.e. methane). A few
49 previous studies have demonstrated that U-series could be used successfully to date
50 cold seep carbonates from modern fluid venting systems (Lalou et al., 1992; Teichert
51 et al., 2003; Watanabe et al., 2008), but there has been no detailed investigation of
52 crust formation at a single site to allow reconstruction of paleo-methane seepage
53 history at a high-resolution temporal scale.

54 The major difficulty in dating cold-seep carbonates is that they often incorporate a
55 significant fraction of detrital sediment (e.g. clays), which represents a major source of
56 initial ^{230}Th (i.e. not produced by *in situ* decay). Such detrital ^{230}Th is accompanied by
57 a much larger amount of ^{232}Th , because the $^{230}\text{Th}/^{232}\text{Th}$ ratio in most geological
58 materials is $\sim 5 \times 10^{-6}$. A typical correction procedure for dating dirty carbonates is the
59 measurement of the isotopic composition of the contaminating phase (i.e. sediment)
60 using isochron techniques (e.g. Luo and Ku, 1991; Bischoff and Fitzpatrick, 1991;
61 Edwards et al., 2003). Isochron methods consider each sample to be composed of a
62 mixture of two components and are used to separate ^{230}Th present initially (i.e. detrital
63 ^{230}Th) from that ingrown from U in the carbonate. Concern may arise however when
64 more than one component of initial thorium exists in the carbonate samples, each with

65 its own $^{230}\text{Th}/^{232}\text{Th}$ ratios (Lin et al., 1996). This is the case when carbonates contain a
66 source of ^{230}Th scavenged from seawater, in addition to detrital ^{230}Th and radiogenic
67 ^{230}Th (Lin et al., 1996; Henderson et al., 2001). Hence, the origin of initial ^{230}Th in
68 any cold seep carbonate samples must be distinguished in order to obtain reliable age
69 information with isochron methods.

70

71 In this study, we present the first high-resolution stratigraphy for a cold-seep
72 carbonate crust. U-Th carbonate age data were acquired on a series of samples drilled
73 across a carbonate pavement from the Nile deep-sea fan. The U-Th age-depth profile
74 is used together with $\delta^{13}\text{C}$ (Gontharet et al., 2007) and major element data to determine
75 carbonate precipitation rates and to provide new insights on the factors affecting crust
76 formation at cold seeps.

77

78

79 **2. Description of NL7-CC2 crust**

80

81 The carbonate crust analysed in this study was recovered offshore Egypt by
82 submersible during the Nautinil expedition (RV Atalante, 2003), on the Nile deep-sea
83 fan (Eastern Mediterranean basin; Fig. 1). Crust NL7-CC2 was collected from a large
84 ($>1\text{ km}^2$) carbonate-paved area associated with chemosynthetic vent communities at ~
85 1650 m water depth (Fig. 2A; Bayon et al., In press). It is a ~ 5.5 cm-thick, highly
86 porous, carbonate-cemented mudstone, covered by a fine layer of Fe-oxyhydroxides
87 (Fig. 2B). The bulk crust density is 1.6 g cm^3 . Gontharet et al. (2007) showed that
88 crust NL7-CC2 is dominated by aragonite, but exhibits mineralogical variability,
89 characterized by a gradual enrichment in high-Mg carbonate phases from top to bottom
90 (Fig. 2B). Examination of NL7-CC2 under optical and scanning electron microscopes
91 shows that this change from aragonite to calcite is not due to aragonite recrystallisation
92 (Gontharet et al., 2007). The ~1-cm top part of the crust is composed of various
93 fragments of chemosynthetic bivalve shells (Vesycomyidae and Thyasiridae; Bayon et
94 al., In press), cemented by aragonite (Fig. 2B). Upon recovery, numerous living
95 vestimentiferan tubeworms were observed anchored at the base of the crust, which
96 indicate that active fluid venting occurs at that site (Fig. 2A). Fibrous aragonite is
97 present typically in open pore spaces, either in cracks or inside the cavities of biogenic
98 components (e.g. foraminifers, bivalve shells).

99

100

101 **3. Analytical techniques**

102

103 **3.1. Electron microprobe analysis and XRF**

104 Polished sections of crust NL7-CC2 were examined by scanning electron
105 microscopy (JEOL JSM-840A, University of Oxford) to select sampling areas suitable
106 for U-Th measurements based on the texture of carbonate growth. To assess the bulk
107 major element composition, five ~1-cm-thick slices sampled across a section of NL7-
108 CC2 crust were analysed by wavelength-dispersive X-ray fluorescence (WD-XRF)
109 analysis of fusion beads. These analyses were performed on the same powders
110 analysed for mineralogy and $\delta^{13}\text{C}$ by Gontharet et al. (2007). In addition, high-
111 resolution abundance profiles of Ca, Mg, Sr, Si, Al, Ti, Fe, K, P, Mn, C and O were
112 measured by electron microprobe (Cameca SX50, Microsonde Ouest, IFREMER) on
113 one thin section of NL7-CC2 crust cross cut perpendicular to its growth banding.
114 Analyses were made using an accelerating voltage of 15 kV and a beam current of 10
115 nA. Spot analyses of the crusts were made at a resolution of 0.1 mm with a 20 μm
116 beam diameter. The relative error for each element is approximately 1% (1σ) for
117 concentrations in the range 10–30 wt%, but increases to about 10% (1σ) for
118 concentrations between 0.1 and 0.5 wt%. The porous nature of the crust, and the fact
119 that both C and O were measured during analysis, resulted in oxide totals mostly
120 higher than 105%. Analyses with totals more than 115% were rejected and other
121 analyses were normalized to a 100% total. For both XRF and electron microprobe data,
122 detrital contents along the crust were estimated simply by summing contents of K_2O ,
123 Fe_2O_3 , SiO_2 , TiO_2 and Al_2O_3 .

124

125 **3.2. Sampling, chemical and analytical procedures for U-Th measurements**

126 Selected areas of carbonate crust were hand-drilled carefully to obtain samples of
127 between ~ 50-500 mg. Carbonate samples were collected at different depths across a
128 cross-cut section of NL7-CC2 crust. Carbonate crusts are typically highly
129 heterogeneous and samples of this size (referred to as ‘bulk’ samples in the following
130 text) are contaminated by detrital material, complicating U-Th dating. To try to reduce
131 such contamination, some carbonate samples were also collected using a computer-
132 assisted microsampling device (MicroMill, New Wave Research). This system

133 enables accurate sampling of sub-millimeter areas of polished sections. For those
134 small carbonate samples (referred to as 'micromilled' samples subsequently), sampling
135 areas were selected using scanning electron microscopy and/or electron microprobe
136 analyzer. Great care was taken to avoid sampling of detrital grains (i.e. quartz),
137 biogenic components and cavities (e.g. fossil emplacements of tubeworms), which
138 may be filled with late-stage aragonite (Fig. 1). About ~ 1 mg of carbonate powder
139 was collected for each of those micromilled samples for U-Th analysis.

140

141 To assess the composition of the detrital end-member and thereby allow an isochron
142 approach, two sediment samples were analysed which were collected using
143 submersible-mounted corers in the studied area, but away from active zones of fluid
144 seepage. These samples - NL14-PC1 and NL7-BC1 - were recovered at ~ 2120m and
145 1620m water depths, respectively, and are reddish-brown foraminiferal and pteropod
146 oozes. The average of their U-series composition was assumed to be representative of
147 the sediment fraction incorporated within the carbonate crust.

148

149 Each sample (i.e. bulk, micromilled, sediment) was dissolved slowly in 7.5M HNO₃
150 and spiked with a mixed ²³⁶U/²²⁹Th spike (Robinson et al., 2002). Any undissolved
151 detrital fractions were transferred into cleaned Teflon vessels and fully digested with a
152 mixed (3:1) HF:HCl solution before being added back into corresponding supernatants.
153 Samples were evaporated, taken up with 7.5M HNO₃, and diluted with ultrapure water.
154 U and Th were then co-precipitated onto Fe-oxides after addition of 5 mg (2.5 mg for
155 micromilled samples) of ultrapure Fe and precipitation with ammonia. After 24 hours,
156 Fe-oxides were centrifuged, cleaned several times in ultrapure water and dissolved in
157 7.5M HNO₃. Finally, U and Th were separated chemically using conventional anion
158 exchange techniques adapted from previous studies (Edwards et al., 1986). The
159 volumes of anion-exchange resin and acids used for separating U-Th were much
160 smaller for micromilled samples than for bulk and sediment samples. Typical
161 procedural blanks were 1.2x10⁻¹⁰ g ²³⁸U and 3.0x10⁻¹¹ g ²³²Th for bulk carbonate and
162 sediment samples, and 1.0x10⁻¹¹ g ²³⁸U and 1.3x10⁻¹² g ²³²Th for micromilled samples.
163 Total U and Th procedural blanks were small compared to final sample concentrations.

164

165 U and Th concentrations and isotope ratios were measured with a MC-ICPMS (Nu
166 Plasma). Procedures largely follow those described in Robinson et al. (2002). The

167 external reproducibility on the $^{234}\text{U}/^{235}\text{U}$ ratio was assessed by repeatedly measuring
168 the CRM-145 standard during each session using a standard-bracketing measurement
169 protocol (Robinson et al., 2002), and was 1.7 ‰ (2 s.d.) for sediment and bulk
170 carbonate samples and ranged from 2.7 to 8.3 ‰ for the mg-sized carbonate samples.
171 Th was measured with ^{229}Th and ^{230}Th sequentially in a single ion-counter equipped
172 with an energy filter to improve abundance sensitivity, and ^{232}Th in a Faraday collector.
173 Mass discrimination and ion-counter gain were assessed by bracketing Th samples
174 with CRM-145 U measurements. Internal precision obtained on measured $^{229}\text{Th}/^{230}\text{Th}$
175 ratios was always better than 5 ‰ for sediment and bulk carbonate samples, and better
176 than 50 ‰ for the smaller micromilled samples. Previous assessment of this
177 measurement approach using TIMS calibrated in-house Th standards (e.g. Robinson et
178 al. 2002) has indicated its accuracy, and that internal precisions are a reasonable
179 assessment of external repeatability at the low signal intensities used in this study.

180

181 Carbonate ages were corrected for detrital contamination by assuming that the mean
182 composition of the modern local sediment well represents the initial detrital
183 component for all samples. Ages were calculated from the measured ($^{232}\text{Th}/^{238}\text{U}$),
184 ($^{230}\text{Th}/^{238}\text{U}$), ($^{234}\text{U}/^{238}\text{U}$) of each sample and these ratios in the average sediment value
185 using a two-point isochron approach, calculated in 3D using the ISOPLOT program (v.
186 3.34, Ludwig, 2003) and half lives following Cheng et al. (2000), $\lambda_{230\text{Th}} = 9.158 \times 10^{-6}$
187 yr^{-1} , $\lambda_{232\text{Th}} = 4.95 \times 10^{-11} \text{ yr}^{-1}$, $\lambda_{234\text{U}} = 2.826 \times 10^{-6} \text{ yr}^{-1}$ and $\lambda_{238\text{U}} = 1.551 \times 10^{-10} \text{ yr}^{-1}$.
188 Uncertainty in the isotopic composition of the sediment end-member was assumed to
189 correspond to the standard deviation (2SD) of the measured ($^{232}\text{Th}/^{238}\text{U}$), ($^{230}\text{Th}/^{238}\text{U}$)
190 and ($^{234}\text{U}/^{238}\text{U}$) activity ratios for the two sediments analysed.

191

192

193 **4. Results**

194

195 **4.1. Major element data**

196 Electron microprobe Sr/Ca ratios vary from ~ 0.001 to 0.040, and Mg/Ca ratios from
197 0.0 to 0.3 (Fig. 3A,B). Down-crust variation of Sr/Ca and Mg/Ca is due to changes in
198 mineralogy, being controlled by the relative contribution of Sr-rich aragonite, Mg-rich
199 carbonate phases, low-Mg calcite, and detritus (Bayon et al., 2007). Sr/Ca ratios are
200 most typically around 0.020, which indicates the predominance of aragonite in the

201 crust (Bayon et al., 2007). Sr/Ca and Mg/Ca values are both low in the upper part of
202 the studied section (i.e. the top 0.4 cm) reflecting the presence of low-Mg calcite in the
203 bivalve shells (Fig. 3B). Below this upper layer, the frequency of high Mg/Ca values
204 increases progressively with depth, indicating enhanced contribution from high-Mg
205 carbonate phases. Detrital contents in crust NL7-CC2, inferred from both electron
206 microprobe and XRF data (Table 1), can be as high as ~ 12 wt%, increasing
207 progressively with depth (Fig. 3C).

208

209 **4.2. U-series data**

210 Uranium concentrations vary from ~ 1 to 20 ppm for carbonate samples (bulk and
211 micromilled) and average 1.3 ppm in the two sediment samples (Table 2). These
212 carbonate concentrations are comparable to those reported in the literature for other
213 cold seep carbonates (Teichert et al., 2003; Watanabe et al., 2008). The average ^{238}U
214 concentration in crust NL7-CC2 increases progressively with depth, from ~3.5 ppm for
215 the uppermost centimetre, to ~9.6 ppm for the middle part (from 1 cm to 4.3 cm-depth)
216 and ~20.8 ppm for the bottom part of the crust.

217

218 ^{232}Th concentrations range from ~30 to 2100 ppb in carbonates and are 4200 and 5000
219 ppb in the two sediments. Carbonate ($^{230}\text{Th}/^{232}\text{Th}$) ratios are low compared to many
220 natural carbonates (from 2.6 to 11.5, Table 2), due to the young age (low ^{230}Th
221 ingrowth), but also, more importantly, to detrital contamination (high initial ^{232}Th).
222 The mean ($^{238}\text{U}/^{232}\text{Th}$) value for the two sediments is 0.87 ± 0.02 , which is typical of
223 detrital sediments and river suspended particles (e.g. Vigier et al., 2001; Ludwig and
224 Paces, 2002; Dosseto et al., 2006a,b). Sediment ($^{230}\text{Th}/^{232}\text{Th}$) ratios are significantly
225 higher (~2.3) than secular equilibrium (Table 3), due to addition of excess ^{230}Th from
226 seawater.

227

228 On a ($^{230}\text{Th}/^{232}\text{Th}$) vs. ($^{238}\text{U}/^{232}\text{Th}$) isochron diagram (i.e. a Rosholt-type diagram), the
229 carbonate samples from crust NL7-CC2 plot well within the range of published data
230 for other cold seep carbonates (Fig. 4B). Micromilled carbonate samples exhibit
231 ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{238}\text{U}/^{232}\text{Th}$) ratios higher than bulk carbonate crust samples (Fig 4A)
232 indicating that micromilling has been successful, to some extent, in separating
233 carbonate phases from detrital-rich areas within carbonate crust. For all the carbonate
234 samples reported in this study, however, both major element and U-Th data clearly

235 show that detrital contamination is too high to allow calculation of simple $^{230}\text{Th}/\text{U}$ ages,
236 and a correction for initial detrital content is required.

237

238 Measured ($^{234}\text{U}/^{238}\text{U}$) ratios (Table 2) are quoted as initial $\delta^{234}\text{U}$ values, corrected for
239 detrital contamination and decay of excess ^{234}U since sample formation (Table 3),
240 where $\delta^{234}\text{U}$ represents the deviation in permil of ($^{234}\text{U}/^{238}\text{U}$) from its secular
241 equilibrium value of 1.000: $\delta^{234}\text{U} = [\{ (^{234}\text{U}/^{238}\text{U})_{\text{meas}} / (^{234}\text{U}/^{238}\text{U})_{\text{equ}} \} - 1] \times 10^3$.
242 Initial $\delta^{234}\text{U}$ values range from 130 to 153, and all samples exhibit, within error, values
243 close to modern seawater (146.6 ± 2.5 ‰; Robinson et al., 2004). This indicates that
244 the carbonate bound U is likely to be derived from seawater rather than from pore
245 waters; this latter U-pool being typically characterized by much higher $\delta^{234}\text{U}$ (Cochran
246 et al., 1986; Gariépy et al., 1993; Henderson et al., 1999).

247

248

249 **5. Discussion**

250

251 **5.1. Detrital versus hydrogenous source of initial ^{230}Th**

252 The high ($^{230}\text{Th}/^{232}\text{Th}$) ratios measured in sediments provide clear evidence for two
253 possible sources of initial ^{230}Th : supported ^{230}Th within the detrital grains, and excess
254 ^{230}Th scavenged to the grain-surfaces from seawater. Any assumption that initial Th
255 has a typical crustal ($^{230}\text{Th}/^{232}\text{Th}$) would therefore lead to errors in calculated ages.
256 This indicates the need to measure the sediment end-member directly to improve age
257 accuracy when dating carbonate crusts.

258

259 The presence of two sources of initial ^{230}Th raises the possibility that the mixture of
260 these two sources might change with time, making the use of a constant initial
261 composition inappropriate. Changes in the ($^{230}\text{Th}/^{232}\text{Th}$) of the sediment material
262 accumulating on the seafloor may occur. However, ^{230}Th is scavenged rapidly after its
263 formation in seawater (Henderson et al. 1999), so the flux of ^{230}Th to the sediment
264 should remain largely unchanged at any one site. Significant changes in the flux of
265 detrital ^{232}Th would therefore be required to alter the sedimenting ($^{230}\text{Th}/^{232}\text{Th}$) and,
266 although these may occur on longer timescales, they are unlikely within the Holocene
267 period in which crust NL7-CC2 grew. Another issue is that after carbonate
268 precipitation and incorporation of the sediment in the crust, the ^{230}Th excess in the

269 sediment component then starts to decay towards equilibrium. Formally, this would
270 need to be corrected for the age calculation. However, because the studied carbonate
271 samples are relatively young, the decay of sediment-bound ^{230}Th is small compared to
272 the existing 2s uncertainty on the ($^{230}\text{Th}/^{232}\text{Th}$) value for the sediment end-member,
273 and hence, can be neglected.

274

275 A potentially more significant mechanism to alter the mixture of detrital and
276 scavenged Th initially present is by the direct scavenging of seawater Th to the crust
277 surface. Some assessment of the magnitude of this process can be derived by
278 considering the ^{232}Th budget of the crust samples. By assuming that ^{232}Th in each
279 sample is entirely within detrital particles, a maximum ^{232}Th concentration of the
280 detrital particles can be calculated for each sample. This calculation is performed
281 using detrital fractions calculated with the bulk chemical data for each sample (Fig. 3C)
282 and measured ^{232}Th concentrations (Table 2). The calculation indicates maximum
283 detrital ^{232}Th concentrations for all but the uppermost sample of ~ 6 to 20 ppm. This
284 range is in good agreement with the detrital Th contents of the two studied sediment
285 samples (~15 ppm, as estimated on a carbonate-free basis; Table 1), and close to
286 average shale composite Th concentrations (12.3 ppm for NASC - Condie, 1993; 14.6
287 ppm for PAAS - Taylor and McLennan, 1985). This suggests that there is negligible
288 additional scavenging of ^{232}Th directly to the crust, and that correction for seawater-
289 derived ^{232}Th is not necessary. The exception is the uppermost crust sample (0 cm)
290 which yields an estimated maximum detrital ^{232}Th concentration of ~ 175 ppm, much
291 higher than typical for crustal detritus. This suggests significant scavenging of Th to
292 the crust surface directly from seawater. Hydrogenous Fe-oxide deposits are typically
293 highly enriched in Th (e.g. Henderson and Burton 1999) and the Fe-oxide layer
294 covering NL7-CC2 probably hosts this seawater-derived Th. Using simple mass
295 balance considerations, the proportion of the hydrogenous component in the uppermost
296 carbonate sample and its Th isotopic composition can be calculated (see Appendix for
297 details of calculation). This calculation indicates that the hydrogenous Fe-oxide
298 component is characterized by a ($^{230}\text{Th}/^{232}\text{Th}$) ratio of ~ 3.1, in agreement with activity
299 ratios measured in the western Mediterranean Sea at similar water depths (Roy-
300 Barman et al., 2002). It also shows that ~ 60% of ^{232}Th in the uppermost crust sample
301 has been scavenged from seawater, whereas the remaining ~ 40% derives from
302 sediment incorporated within the carbonate matrix (see Appendix).

303

304 Clearly, the isochron age calculated for the topmost sample (9.2 ± 2.5 ka; Table 1) is
305 overestimated due to presence of initial hydrogenous ^{230}Th and, hence, is discarded in
306 the discussion below. The ^{232}Th budget calculations suggest however that other crust
307 samples have not been exposed significantly to seawater scavenging.

308

309

310 **5.2. Validity of calculated ages and age uncertainties**

311 The age calculated for the base of the NL7-CC2 crust using the high $^{230}\text{Th}/^{232}\text{Th}$
312 value of local sediment to correct for initial Th is 0.8 ± 1.3 ka (Table 3), which
313 suggests that carbonate precipitation, and hence fluid seepage, is probably still active
314 at the studied site. This agrees with evidence that dense bushes of vestimentiferan
315 tubeworms live at present underneath carbonate pavements in this area (Bayon et al.,
316 In press), providing re-assurance for the validity of the dating approach, and for the
317 suitability of the sediment end-member values used for calculations. Using an end-
318 member with typical crustal values, i.e. at secular equilibrium, would lead instead to a
319 much older age of ~ 5.2 kyr BP for the base of the carbonate crust, in contradiction
320 with in situ observation.

321

322 The two-point isochron method used in this study is convenient for acquiring a
323 high-resolution age profile for such 'complex' carbonate archives. However, the
324 uncertainty in the ages calculated with this method depends crucially on the errors
325 assigned to the sediment end-member used for calculations. In this study, the
326 uncertainty in the end-member isotopic composition was taken as the standard
327 deviation (2SD) of the isotope ratios measured for the two sediments analysed. For the
328 ($^{230}\text{Th}/^{232}\text{Th}$) sediment ratio, this corresponds to a value of 2.31 ± 0.46 . Considering a
329 less conservative error ($\pm 1\text{SD}$) on the sediment U/Th ratios would lead to smaller error
330 bars on calculated isochron ages, such as 2.12 ± 0.84 ka for the sample drilled at 1cm-
331 depth (instead of 2.1 ± 1.5 ka), and 0.84 ± 0.64 ka for the sample drilled at 5 cm-depth
332 (instead of 0.8 ± 1.3 ka).

333

334 In order to further assess the suitability of our sediment end-member for calculating
335 isochron ages, its composition was determined indirectly by performing additional 3-D
336 isochron calculations on several sets of carbonate samples drilled at similar depths of

337 NL7-CC2 crust (hence assumed to have a similar age). This approach uses the
338 intercept of each isochron to calculate the ^{232}Th -free ratios of ($^{230}\text{Th}/^{238}\text{U}$) and
339 ($^{234}\text{U}/^{238}\text{U}$) required for the age calculation, but also estimates the present-day
340 ($^{230}\text{Th}/^{232}\text{Th}$) ratio of the detrital sediment end-member. The isochron derived for the
341 two bottommost samples of the crust, drilled at 5 cm and 5.5 cm-depth, yields a
342 sediment end-member with ($^{230}\text{Th}/^{232}\text{Th}$) = 2.2 ± 0.4 (2SD). Another isochron was
343 derived for the samples drilled at 3.6 cm and 4.3 cm-depth, which provides a
344 ($^{230}\text{Th}/^{232}\text{Th}$) of 2.4 ± 1.0 . Finally, the isochron derived for the three samples collected
345 at ~2.5 cm-depth gives a detrital ($^{230}\text{Th}/^{232}\text{Th}$) of 1.92 ± 0.12 . All those independently
346 calculated ($^{230}\text{Th}/^{232}\text{Th}$) ratios agree well with the mean ($^{230}\text{Th}/^{232}\text{Th}$) \pm 2SD value
347 obtained from the analysis of our two sediments (2.31 ± 0.46), providing further
348 reassuring evidence for the suitability of the sediment end-member values and
349 associated errors used for calculations. This shows that the two-point isochron ages
350 calculated with our approach can be considered as robust.

351

352

353 **5.3. U-Th isotope stratigraphy**

354 The $^{230}\text{Th}/\text{U}$ age-depth profile for NL7-CC2 shows that the carbonate crust has
355 grown downward since about 5 ± 1 ka (Fig. 3E). Previous studies suggested on
356 theoretical grounds that carbonate crusts at cold seeps may grow downward into the
357 sediment (Paull et al., 1992; Greinert et al., 2002; Aloisi et al., 2002), but our results
358 represent the first direct evidence for this mode of formation. The average growth rate
359 for crust NL7-CC2 is ~ 1.1 cm/kyr. In detail, however, three distinct periods of
360 carbonate formation can be distinguished from top to bottom, with average growth
361 rates of ~ 0.4 cm/kyr for the upper first centimetre, ~ 5 cm/kyr for the next four cm,
362 and 0.8 cm/kyr for the bottom cm of the crust, respectively (Fig. 3E).

363

364 As discussed earlier, the relatively large error bars associated to calculated
365 carbonate ages (on average ± 1.3 kyr; Table 3), reflect the large uncertainty on the
366 sediment end-member composition. However, although the ($^{230}\text{Th}/^{232}\text{Th}$) of the
367 sediment end-member is not known with accuracy, it is not likely to vary much on the
368 small spatial scale involved in the studied crust. Instead, the detritus at this particular
369 site is most probably characterized by a more constant composition. This suggests that
370 the age of one piece of the crust relative to another is much better known in relative

371 terms that by taking the difference in the two absolute ages. Hence, we are confident
372 that the changes in growth rate in the crust reported above and discussed below
373 (section 5.5) are robust, at least when described in relative terms.

374

375

376 **5.4. A record of progressive sulphate depletion**

377 The age-depth profile is compared to profiles for carbonate $\delta^{13}\text{C}$ and carbonate
378 mineralogy (Gontharet et al., 2007), Sr/Ca and Mg/Ca (Fig. 2). Sr/Ca and Mg/Ca ratios
379 show opposite vertical trends, indicating a gradual downward change from aragonite to
380 high-Mg-rich carbonate phases. A similar mineralogical trend was reported for a
381 carbonate crust collected from the Amsterdam mud volcano in the eastern
382 Mediterranean basin (Aloisi et al., 2002). In the absence of any microscopic evidence
383 for re-crystallisation of aragonite into high-Mg calcite, this trend is best explained by a
384 change in chemical conditions (Aloisi et al., 2002). Previous studies have shown that
385 aragonite precipitation is favoured over that of high-Mg calcite at high SO_4^{2-}
386 concentrations (e.g. Burton and Walker, 1987; Burton, 1993), whereas high-Mg
387 carbonates generally precipitate from pore waters with low dissolved SO_4^{2-} contents,
388 typically at the interface between methane and sulphate (Luff and Wallman, 2003; Luff
389 et al., 2004; Gieskes et al., 2005). Our geochemical data therefore suggest that the
390 mineralogical trend from aragonite to high-Mg carbonates in crust NL7-CC2 was
391 induced by a progressive depletion in dissolved sulphate.

392 In anoxic or suboxic conditions, it is well known that U is reduced from its
393 hexavalent to its tetravalent state and becomes insoluble. The depth profile for U
394 concentrations across NL7-CC2 (see Table 2), indicating increasing U concentrations
395 from top to bottom, therefore would also suggest that a gradual change in chemical
396 conditions occurred during the formation of the crust. This is further supported by the
397 down-crust $\delta^{13}\text{C}$ profile (Fig. 3D). Methane-rich fluids on continental margins are
398 characterized by $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}$ from ~ -110 to -30 ‰) much lower than seawater
399 ($\delta^{13}\text{C} \sim 1$ ‰). Hence, the progressive downward depletion in carbonate ^{13}C in crust
400 NL7-CC2 indicates an increasing contribution from AOM-derived versus seawater-
401 derived carbon in the lower part of the crust (Gontharet et al., 2007). Overall, these
402 data point clearly toward a progressive isolation of the growing crust from seawater

403 through time. This is consistent with the downward growth of the crust indicated by
404 the U/Th chronology.

405

406 **5.5. Carbonate precipitation rates**

407 Interestingly, variations in mineralogy across crust NL7-CC2 coincide relatively
408 well with the changes in growth rates determined from the age-depth profile (Fig. 3).
409 In particular, the transition between aragonite and high-Mg calcite in the lower part of
410 the crust corresponds to a shift from fast (~ 5 cm/kyr) to slow (~ 0.8 cm/kyr) period of
411 carbonate formation (Fig. 3E). Growth rates can be converted into carbonate
412 precipitation rates using the bulk crust density (1.6 g cm^3). The carbonate precipitation
413 rates corresponding to the three growth periods in NL7-CC2 average $\sim 6 \mu\text{mol cm}^2 \text{ a}^{-1}$
414 for the topmost part of the crust, $\sim 80 \mu\text{mol cm}^2 \text{ a}^{-1}$ for the middle part, and $\sim 12 \mu\text{mol}$
415 $\text{cm}^2 \text{ a}^{-1}$ for the high-Mg carbonate part of the crust. Using dimensions commonly used
416 in experimental studies ($\mu\text{mol m}^2 \text{ h}^{-1}$), those carbonate precipitation rates yield ~ 7 , 92
417 and $14 \mu\text{mol m}^2 \text{ h}^{-1}$, respectively. The average rate of precipitation estimated for the
418 high-Mg carbonate layer ($14 \mu\text{mol m}^2 \text{ h}^{-1}$) is consistent with rates determined
419 previously from laboratory experiments ($1\text{-}14 \mu\text{mol m}^2 \text{ h}^{-1}$; Burton and Walter, 1987;
420 Zhong and Mucci, 1993) and numerical modeling of biogeochemical processes at cold
421 seeps ($11 \mu\text{mol m}^2 \text{ h}^{-1}$; Luff and Wallmann, 2003). The average aragonite
422 precipitation rate calculated for the middle part of the crust ($\sim 92 \mu\text{mol m}^2 \text{ h}^{-1}$) is in
423 agreement with the kinetic constant derived from modeling by Luff and Wallmann
424 ($114 \mu\text{mol m}^2 \text{ h}^{-1}$), but higher than experimental values ($22\text{-}41 \mu\text{mol m}^2 \text{ h}^{-1}$; Burton
425 and Walter, 1987). This finding hence would confirm the existing literature
426 indications that aragonite precipitates much faster at cold seeps than during abiotic
427 laboratory experiments.

428

429 **5.6. Controls on carbonate crust formation at cold seeps**

430 Several parameters are known to affect carbonate formation at cold seeps, including
431 sedimentation rates, bioturbation, bioirrigation, and upward methane fluxes (see Luff
432 et al., 2004; Luff and Wallmann, 2004). The fact that the ~ 5000 year-old NL7-CC2
433 crust is still exposed on the seafloor at present suggests that particles sedimenting on
434 the seafloor at the studied location have been eroded with time, and hence that changes
435 in sedimentation rates have not played a significant role in controlling the formation of
436 the crust.

437

438 At the onset of fluid seepage, an initial cm-thick layer of aragonite may precipitate
439 relatively rapidly, in just a few hundred years (Luff et al., 2005). The same authors
440 have suggested that subsequent development of carbonate crust is limited by high
441 bioturbation activity. The presence of large fragments of chemosynthetic bivalves in
442 the topmost part of NL7-CC2 crust suggests that bioturbation was active ~ 5 kyr ago,
443 during the initial stage of carbonate precipitation (Fig. 5A). At that time, the initiation
444 of fluid venting probably led to development of vent communities and associated
445 bioturbation processes in the near-seafloor environment. Most likely, this initial stage
446 of carbonate crust formation led to pore space clogging, reduced fluid venting and
447 associated development of macro-benthos communities supported by chemosynthesis,
448 all of which would have resulted in a significant drop of bioturbation at the studied
449 location (Fig. 5B). It is possible that the absence of bioturbation resulted in enhanced
450 carbonate precipitation, thereby explaining the differences in aragonite growth rates
451 observed in the topmost layer of crust NL7-CC2, from slow (average $7 \mu\text{mol m}^2 \text{h}^{-1}$) to
452 fast ($\sim 92 \mu\text{mol m}^2 \text{h}^{-1}$) rates.

453

454 Certainly, the development of an aragonite crust near the sediment surface would
455 have affected the exchange of dissolved species between sediment and bottom water,
456 leading to reduced supply of CH_4 and lower AOM rates. As a consequence, as less
457 bicarbonate is supplied to pore water via AOM, dissolution of aragonite may start after
458 the initial stage of carbonate crust formation. Using numerical simulations, Luff et al.
459 (2005) suggested that aragonite dissolution may prevail over precipitation at this stage,
460 at least temporarily. Then, after the initial aragonite layer has become thinner, higher
461 flow velocity allows again for enhanced upward transport of methane, inducing in turn
462 precipitation of aragonite and calcite at the base of the initial aragonite crust (Luff et
463 al., 2005). A new maximum in AOM rates and aragonite precipitation can hence be
464 attained, which leads to the formation of a new aragonite-rich layer, about 2000 yrs
465 after the initial stage of carbonate precipitation (Fig. 5B). Those results from
466 numerical modeling agree well with the mineralogical and geochemical downward
467 changes observed in crust NL7-CC2. Therefore, the lower rates of carbonate
468 precipitation observed for the top part of the crust could also reflect, at least to some
469 degree, a temporary episode of aragonite dissolution that followed the initial stage of
470 carbonate crust formation ~ 5000 years ago.

471

472 One of the most prominent results of this study is the gradual SO_4^{2-} depletion at the
473 studied location inferred from $\delta^{13}\text{C}$, Sr/Ca and Mg/Ca data, which could result either
474 from enhanced upward methane fluxes and/or a reduction of the dissolved sulphate
475 transport to the base of the crust. Although a change in the upward CH_4 flux is
476 possible, it is very likely that the downward flux of seawater sulphate has dropped with
477 time. In carbonate-paved areas, bioirrigation is an important factor controlling the
478 solute exchange between bottom-waters and underlying sediments, in which
479 macrobenthic organisms actively pump water into the sediment. At the studied
480 location, the presence of dense bushes of vestimentiferan tubeworms must have
481 sustained an active and continuous inflow of seawater sulphate over the last thousand
482 years, which allowed high AOM turnover and fast aragonite precipitation at the base of
483 crust (Fig. 5B). However, with time, it is likely that the efficiency of this biological
484 pump has decreased, most probably in response to progressive clogging due to intense
485 carbonate formation (Fig. 5C).

486

487

488 **6. Concluding remarks**

489 The application of U-series to methane-derived authigenic carbonates adds unique
490 temporal information to the study of biogeochemical processes related to anaerobic
491 oxidation of methane (AOM) on continental margins. U-Th ages require correction for
492 appreciable initial Th content, and we have shown that this is more appropriately
493 performed using the U-Th composition of local sediment containing excess ^{230}Th from
494 seawater, than with typical crustal U-Th values. Dating of a crust from the Nile deep-
495 sea fan demonstrates clearly something previously suspected – that crusts grow
496 downwards with time from the sediment surface – in this case over a period of ~ 5kyr.
497 This chronology also allows carbonate precipitation rates to be estimated. Calculated
498 rates for average aragonite formation are about six-time higher than for high-Mg
499 calcite. In agreement with numerical studies, aragonite precipitates much faster at cold
500 seeps than during abiotic laboratory experiments, due most probably to microbial
501 catalysis. Our results also highlight the role played by chemosynthetic macro-benthos
502 at cold seeps in the formation of cold seep carbonates, through transport of seawater
503 sulphate available for AOM (i.e. bioirrigation). Comparison of $^{230}\text{Th}/\text{U}$ ages with
504 other data (mineralogy, $\delta^{13}\text{C}$, Sr/Ca, Mg/Ca) suggests that both carbonate mineralogy

505 and precipitation rates are closely related to the efficiency of this biological pump
506 through time.

507

508

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518

519 **Appendix: Calculation of the proportion of the hydrogenous component in the**
520 **uppermost carbonate crust sample and of its ($^{230}\text{Th}/^{232}\text{Th}$) composition**

521
522 The ^{232}Th , ^{230}Th and ^{238}U budgets in the uppermost crust sample follow the mass
523 balance equations:

524
525
$$^{232}\text{Th}_{\text{total}} = ^{232}\text{Th}_{\text{sediment}} \cdot x + ^{232}\text{Th}_{\text{hydrogenous}} \cdot y + ^{232}\text{Th}_{\text{carbonate}} \cdot z \quad (1)$$

526
527
$$^{230}\text{Th}_{\text{total}} = ^{230}\text{Th}_{\text{sediment}} \cdot x + ^{230}\text{Th}_{\text{hydrogenous}} \cdot y + ^{230}\text{Th}_{\text{carbonate}} \cdot z \quad (2)$$

528
529
$$^{238}\text{U}_{\text{total}} = ^{238}\text{U}_{\text{sediment}} \cdot x + ^{238}\text{U}_{\text{hydrogenous}} \cdot y + ^{238}\text{U}_{\text{carbonate}} \cdot z \quad (3)$$

530
531 where $^{230}\text{Th}_{\text{carbonate}}$ refers to the ^{230}Th accumulated by decay of U since the authigenic
532 carbonate sample formed. The subscripts *sediment* and *hydrogenous* refer to the
533 sediment and water-derived contributions, respectively, of ^{232}Th , ^{230}Th and ^{238}U .
534 Sediment values for ^{232}Th (4.68 ppm), ^{230}Th (58 ppt) and ^{238}U (1.33 ppm) are derived
535 from the analyses of the two studied sediments. The subscript *total* refers to the
536 measured concentrations of ^{232}Th (0.86 ppm), ^{230}Th (17.6 ppt) and ^{238}U (4.85 ppm) in
537 the bulk carbonate sample. x , y and z represents the proportions of sediment,
538 hydrogenous (Fe-oxides) and authigenic carbonate fractions, respectively. Microprobe
539 measurements of the detritus content in the uppermost carbonate sample indicate that x
540 ~ 0.005 (0.5 wt%).

541
542 Assuming that $^{232}\text{Th}_{\text{hydrogenous}} = 100$ ppm (Henderson and Burton, 1999) and $^{232}\text{Th}_{\text{carbonate}} = 0$,
543 the proportion y of the hydrogenous component incorporated in the
544 uppermost carbonate sample can be calculated from Eqn. 1: $y \sim 0.008$ (0.8 wt%). This
545 shows that $\sim 60\%$ of ^{232}Th in this uppermost crust sample derives from the
546 hydrogenous component (most probably associated to the Fe-oxide coating), whereas
547 the remaining $\sim 40\%$ of ^{232}Th derived from the sediment incorporated within the
548 carbonate matrix.

549
550 Then, assuming that $^{238}\text{U}_{\text{hydrogenous}} = 13$ ppm (Henderson and Burton, 1999), $^{238}\text{U}_{\text{carbonate}}$
551 can be inferred using Eqn. 3: $^{238}\text{U}_{\text{carbonate}} \sim 4.80$ ppm.

552
553 Based on the $^{230}\text{Th}/\text{U}$ age profile for crust NL7-CC2, it can be reasonably argued that
554 the uppermost part of the crust formed about 5000 years ago. Using this age, one can
555 use the ^{230}Th age equation (Eqn. 4) to deduce $^{230}\text{Th}_{\text{carbonate}} \sim 4.2$ ppt.

556
557
$$\left(^{230}\text{Th}_{\text{carbonate}} / ^{238}\text{U}_{\text{carbonate}} \right) = 1 - e^{-\lambda_{230}t} + (\delta^{234}\text{U}_m / 1000) \cdot (\lambda_{230} / (\lambda_{230} - \lambda_{234})) \cdot (1 - e^{-(\lambda_{230} - \lambda_{234})t})$$

558 (4)

559
560 The value obtained for $^{230}\text{Th}_{\text{carbonate}}$ can be inserted in Eqn. 2 to infer $^{230}\text{Th}_{\text{hydrogenous}} \sim$
561 1650 ppt, and finally, $(^{230}\text{Th}/^{232}\text{Th})_{\text{hydrogenous}} = 3.1$.

562
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566

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714 **Table captions**

715

716 **Table 1**

717 <DL means concentration lower than the instrumental detection limit.

718

719 **Table 2**

720 Depths indicated for samples correspond to centimetres below the surface of the crust.

721 Round brackets denote activity ratio. All calculations have used the half-lives
722 measured by Cheng et al. (2000).

723

724 **Table 3**

725 Depths indicated for samples correspond to centimetres below the top of the crust.

726 Initial $\delta^{234}\text{U}$ represents the deviation in permil of ($^{234}\text{U}/^{238}\text{U}$) from its secular
727 equilibrium value of 1.000, at the time T of carbonate precipitation, with initial $\delta^{234}\text{U} =$
728 $[\{(^{234}\text{U}/^{238}\text{U})_{\text{T}} / (^{234}\text{U}/^{238}\text{U})_{\text{equ}}\} - 1] \times 10^3$. Measured values (see Table 2) are corrected
729 for detrital contamination and decay of excess ^{234}U since sample formation. One
730 sample (0.0cm) is rejected as meaningful age based on the presence of significant
731 seawater ^{230}Th (see text for details), and is shown in italics. Other calculated ages are
732 considered reliable. All calculations have used the half-lives measured by Cheng et al.
733 (2000).

734

735 **Figure captions**

736

737 **Figure 1**

738 Shaded bathymetric map of the Central Nile deep-sea fan (Loncke et al., 2006), and
739 location of the studied carbonate crust. Crust NL7-CC2 was collected from a
740 carbonate-paved area, at an active zone of fluid venting located at ~ 1650 m water
741 depth.

742

743 **Figure 2**

744 Description of carbonate crust NL7-CC2. (A) Seafloor bottom photograph showing
745 sampling with the *Nautilie* submersible. Upon recovery, numerous living
746 vestimentiferan tubeworms were observed anchored at the base of the crust. (B)
747 Cross-section. Crust NL7-CC2 is a highly porous carbonate-cemented mudstone
748 covered by a fine layer of Fe-oxyhydroxides. Numerous fragments of bivalve shells
749 are observed in the upper ~1-cm of the crust. Fibrous aragonite is present in open pore
750 spaces, either in cracks or inside the cavities of biogenic components. Crust NL7-CC2
751 is dominated by aragonite, but exhibits mineralogical variability, characterized by a
752 gradual enrichment in high-Mg carbonate phases from top to bottom (Gontharet et al.,
753 2007). The areas of the crust sampled for U-Th analysis are shown as white-filled
754 squares (hand-drilled samples), green-filled rectangles (micromilled samples). The
755 micromilled sample at 0.0 cm (crossed red-filled rectangle) was rejected as meaningful
756 age based on the presence of significant seawater ^{230}Th (see text for details).

757

758 **Figure 3**

759 High-resolution profiles for A) Sr/Ca ratios; B) Mg/Ca ratios; C) detritus contents
760 (wt%); D) $\delta^{13}\text{C}$ (‰ PDB), Gontharet et al. (2007); and E) $^{230}\text{Th}/\text{U}$ ages (kyr BP) across
761 NL7-CC2 crust. A), B), C) The small empty squares correspond to electron
762 microprobe data, and the larger infilled squares to XRF analyses of bulk carbonate
763 crust samples. Detrital contents were calculated by summing contents (wt %) of XRF
764 data for K_2O , Fe_2O_3 , SiO_2 , TiO_2 and Al_2O_3 (see Table 1). Below the aragonite-rich
765 upper crust layer, the frequency of high Mg/Ca values increases progressively with
766 depth, indicating enhanced contribution from high-Mg carbonate phases. Detrital
767 contents in crust NL7-CC2 can be as high as ~ 12 wt%, increasing progressively with
768 depth. D) The progressive downward depletion in carbonate ^{13}C in crust NL7-CC2
769 indicates an increasing contribution from AOM-derived versus seawater-derived
770 carbon in the lower part of the crust (Gontharet et al., 2007). E) The $^{230}\text{Th}/\text{U}$ ages vary
771 from $\sim 4.9 \pm 1.2$ ka in the topmost part of the crust to $\sim 0.8 \pm 1.3$ ka at its base,
772 indicating that the crust has grown downward. Three growth periods can be
773 distinguished from top to bottom (dashed lines), with average growth rates of ~ 0.4, 5
774 and 0.8 cm/kyr, respectively (thick lines). Those growth variations are accompanied
775 by changes in carbonate mineralogy (see Sr/Ca and Mg/Ca profiles) and fluid
776 composition (see $\delta^{13}\text{C}$ values). The vertical error bars shown in panels D) and E)

777 correspond to sample thickness. The horizontal error bars are 2sd uncertainties on
778 isochron ages.

779

780 **Figure 4**

781 A) Rosholt isochron diagram for bulk and micromilled carbonate samples (crust NL7-
782 CC2). Isochron ages are calculated from the slope of the isochrons, using a sediment
783 end-member defined as the average of the two studied sediments. The values for the
784 sediment end-member are $(^{230}\text{Th}/^{232}\text{Th}) = 2.30 \pm 0.47$ (2SD) and $(^{238}\text{U}/^{232}\text{Th}) = 0.87 \pm$
785 0.02 (2SD). The dashed line represents the equiline. Note the large error bars on
786 $(^{238}\text{U}/^{232}\text{Th})$ ratios for samples drilled at 0.4 cm, 0.9 cm and 2.8 cm depth below the
787 crust surface, which prevent calculation of reliable ages. B) Comparison of
788 $(^{230}\text{Th}/^{232}\text{Th})$ vs. $(^{238}\text{U}/^{232}\text{Th})$ ratios of cold seep carbonates from different settings,
789 including our carbonate crust samples from the Nile deep-sea fan, carbonate nodules
790 collected in hydrate-bearing sediments from methane seeps off Joetsu (Eastern Margin
791 of Japan Sea; Watanabe et al., 2008), and aragonite chemoherms recovered on the
792 seafloor at the Hydrate Ridge (Cascadia Margin; Teichert et al., 2003). Note that the
793 $(^{238}\text{U}/^{232}\text{Th})$ ratios decrease from the Hydrate Ridge chemoherm carbonates (from ~
794 100 to 10000), the crust samples from the Nile margin (from ~ 15 to 175; this study),
795 and the carbonate nodules from the Japan Sea (from ~ 4 to 16), which may reflect, at
796 least partly, an increasing contamination by detrital material during carbonate
797 precipitation.

798

799 **Figure 5**

800 Schematic diagram for the mode of formation of the studied carbonate crust,
801 integrating mineralogical and geochemical data, and calculated $^{230}\text{Th}/\text{U}$ ages. A)
802 Stage 1 (from $\sim 5 \pm 1$ to 3 ± 1 kyr BP) - onset of fluid venting at the studied location
803 leading to development of chemosynthetic communities on the seafloor and aragonite
804 precipitation. Aragonite precipitates near the seafloor, cementing shell fragments of
805 chemosynthetic bivalves. At this stage, the formation of a cm-thick aragonite crust can
806 reduce the exchange of dissolved species between sediment and bottom water, leading
807 to reduced AOM rates and, possibly, to partial aragonite dissolution. B) Stage 2 (from
808 $\sim 3 \pm 1$ to 2 ± 1 kyr BP) – rapid growth of the carbonate crust. The absence of
809 significant bioturbation and an efficient supply of seawater sulphate at the base of the

810 crust via vestimentiferan tubeworms (bioirrigation), lead to high rates of AOM
811 (anaerobic oxidation of methane) turnover promoting fast carbonate precipitation
812 (mainly aragonite). C) Stage 3 (from $\sim 2 \pm 1$ kyr BP to present) – reduced rates of
813 carbonate formation. The bottom part of the crust becomes isolated from seawater,
814 leading to reduced supply of sulphate by bioirrigation. The sulphate depletion at the
815 base of the crust induces lower AOM rates and preferential precipitation of high-Mg
816 calcite over aragonite.

Table 1. XRF major element composition of bulk carbonate and sediment samples

Sample	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MnO %	MgO %	CaO %	Na ₂ O %	K ₂ O %	TiO ₂ %	P ₂ O ₅ %	SO ₄ %	LOI %	Sr ppm	Total
NL7-CC2 crust (N32°31.61', E30°21.16', 1686 m water depth)														
0-1cm	1.73	0.74	0.31	0.004	0.49	50.73	0.33	0.03	0.05	0.01	0.17	43.69	5708	98.84
1-2 cm	3.13	1.21	0.44	<DL	0.53	49.22	0.44	0.06	0.08	0.04	0.24	42.80	6382	98.82
2-3 cm	3.84	1.55	0.65	<DL	1.07	48.20	0.44	0.08	0.09	0.03	0.61	41.89	6584	99.12
3-4 cm	4.27	1.73	0.73	<DL	1.39	47.26	0.40	0.09	0.10	0.03	0.65	41.57	6343	98.86
4-5.5 cm	7.55	3.14	1.54	<DL	3.06	41.94	0.46	0.17	0.19	0.01	1.36	38.96	5497	98.92
NL7-BC1 sediment (N32°30.50', E30°23.09', 1623 m water depth)														
	20.56	7.00	3.11	0.10	3.43	31.95	0.71	0.26	0.41	0.10	0.90	30.97	1248	99.51
NL14-PC1 sediment (N32°38.33', E29°55.80', 2116 m water depth)														
	24.21	8.21	4.28	0.07	2.96	27.69	1.19	0.32	0.54	0.13	0.54	29.67	1132	99.81

Table 2. Measured U-Th data for sediment and carbonate samples

Sample	Description	Weight (mg)	^{238}U (ppm) $\pm 2\sigma$	^{232}Th (ppb) $\pm 2\sigma$	$(^{234}\text{U}/^{238}\text{U})$ $\pm 2\sigma$	$(^{230}\text{Th}/^{232}\text{Th})$ $\pm 2\sigma$	$(^{238}\text{U}/^{232}\text{Th})$ $\pm 2\sigma$
<u>Sediments</u>							
NL14-PC1		51.43	1.420 ± 0.002	4939.5 ± 18.5	1.025 ± 0.002	2.48 ± 0.01	0.878 ± 0.003
NL7-BC1		50.82	1.261 ± 0.002	4214.1 ± 13.1	1.041 ± 0.002	2.17 ± 0.01	0.914 ± 0.003
'	replicate	327.7	1.239 ± 0.002	4634.0 ± 17.2	1.053 ± 0.002	2.12 ± 0.02	0.817 ± 0.003
<u>NL7-CC2 carbonate crust</u>							
0.0 cm	bulk	166.6	4.85 ± 0.01	861.3 ± 2.2	1.143 ± 0.002	3.83 ± 0.01	17.20 ± 0.05
0.1 cm	micromilled	1.14	4.05 ± 0.07	228.5 ± 29.4	1.138 ± 0.003	5.47 ± 0.17	54.2 ± 7.0
0.4 cm	micromilled	1.06	3.29 ± 0.06	115.8 ± 44.9	1.128 ± 0.009	6.49 ± 0.55	86.9 ± 33.7
0.9 cm	micromilled	1.06	1.67 ± 0.03	29.1 ± 4.1	1.132 ± 0.009	11.54 ± 0.41	174.9 ± 24.7
1.0 cm	bulk	43.48	8.40 ± 0.01	885.7 ± 3.7	1.141 ± 0.002	3.10 ± 0.01	28.96 ± 0.13
2.2 cm	micromilled	0.95	10.44 ± 0.22	697.0 ± 4.0	1.142 ± 0.003	3.88 ± 0.05	45.73 ± 1.00
2.5 cm	micromilled	0.56	8.79 ± 0.31	689.1 ± 8.1	1.137 ± 0.005	3.53 ± 0.05	38.95 ± 1.47
2.5 cm	bulk	111.0	12.85 ± 0.02	1323.6 ± 4.6	1.144 ± 0.002	2.91 ± 0.01	29.65 ± 0.11
'	replicate	466.1	12.29 ± 0.02	1383.7 ± 4.3	1.144 ± 0.002	2.81 ± 0.04	27.12 ± 0.09
2.8 cm	micromilled	0.82	5.37 ± 0.13	202.0 ± 69.6	1.129 ± 0.009	5.25 ± 0.25	81.2 ± 28.0
3.6 cm	micromilled	1.50	8.31 ± 0.11	583.9 ± 8.4	1.140 ± 0.003	3.37 ± 0.12	43.46 ± 0.85
4.3 cm	micromilled	1.37	10.62 ± 0.16	956.8 ± 40.0	1.142 ± 0.003	3.14 ± 0.08	33.89 ± 1.50
5.0 cm	bulk	502.8	20.85 ± 0.03	2141.9 ± 4.8	1.147 ± 0.002	2.58 ± 0.04	31.14 ± 0.10
5.5 cm	bulk	103.0	20.82 ± 0.03	2044.6 ± 5.8	1.144 ± 0.002	2.57 ± 0.01	29.69 ± 0.08

Table3

[Click here to download Table: Table3.pdf](#)

Table 3. Activity ratios used for age calculation and U-Th ages for carbonate samples

Sample	$(^{232}\text{Th}/^{238}\text{U})$ $\pm 2\sigma$	$(^{230}\text{Th}/^{238}\text{U})$ $\pm 2\sigma$	$(^{234}\text{U}/^{238}\text{U})$ $\pm 2\sigma$	Corrected U-Th age (ka) $\pm 2\sigma$	Initial $\delta^{234}\text{U}$ (‰) $\pm 2\sigma$
<u>Sediment end-member</u>					
	1.149 \pm 0.029	2.65 \pm 0.47	1.036 \pm 0.030		
<u>NL7-CC2 carbonate crust</u>					
0.0 cm	0.0581 \pm 0.0002	0.2224 \pm 0.0010	1.143 \pm 0.002	9.1 \pm 2.5	153 \pm 2
0.1 cm	0.0185 \pm 0.0024	0.0917 \pm 0.0083	1.138 \pm 0.003	4.9 \pm 1.2	142 \pm 2
0.4 cm	0.0115 \pm 0.0045	0.0624 \pm 0.0181	1.128 \pm 0.005	3.5 \pm 2.1	130 \pm 9
0.9 cm	0.0057 \pm 0.0017	0.0423 \pm 0.0124	1.132 \pm 0.005	2.8 \pm 1.3	134 \pm 9
1.0 cm	0.0345 \pm 0.0001	0.1053 \pm 0.0005	1.141 \pm 0.002	2.5 \pm 1.4	145 \pm 2
2.2 cm	0.0219 \pm 0.0001	0.0805 \pm 0.0009	1.142 \pm 0.003	2.95 \pm 0.88	145 \pm 3
2.5 cm	0.0257 \pm 0.0003	0.0817 \pm 0.0013	1.137 \pm 0.005	2.2 \pm 1.0	140 \pm 5
2.5 cm	0.0337 \pm 0.0001	0.0976 \pm 0.0003	1.144 \pm 0.002	2.0 \pm 1.4	148 \pm 2
replicate	0.0369 \pm 0.0001	0.1034 \pm 0.0004	1.144 \pm 0.002	1.8 \pm 1.5	148 \pm 2
2.8 cm	0.0123 \pm 0.0042	0.0548 \pm 0.0085	1.129 \pm 0.005	2.6 \pm 1.4	131 \pm 9
3.6 cm	0.0230 \pm 0.0004	0.0741 \pm 0.0012	1.140 \pm 0.003	2.06 \pm 0.93	142 \pm 3
4.3 cm	0.0295 \pm 0.0013	0.0896 \pm 0.0054	1.142 \pm 0.003	2.1 \pm 1.3	144 \pm 3
5.0 cm	0.0337 \pm 0.0001	0.0862 \pm 0.0004	1.144 \pm 0.002	0.8 \pm 1.3	150 \pm 2
5.5 cm	0.0321 \pm 0.0001	0.0827 \pm 0.0003	1.147 \pm 0.002	0.8 \pm 1.3	148 \pm 2

Figure1

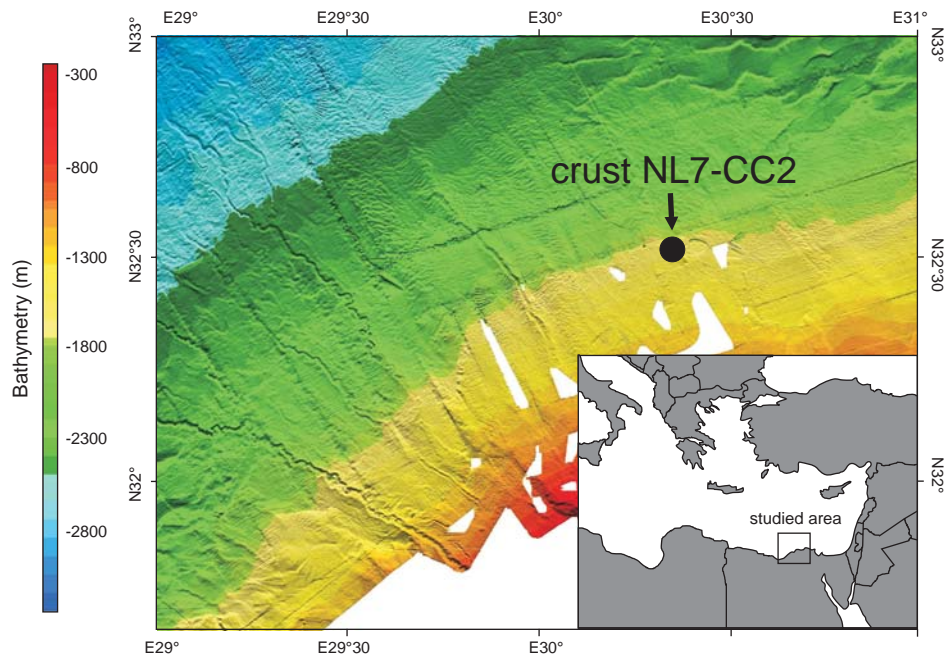
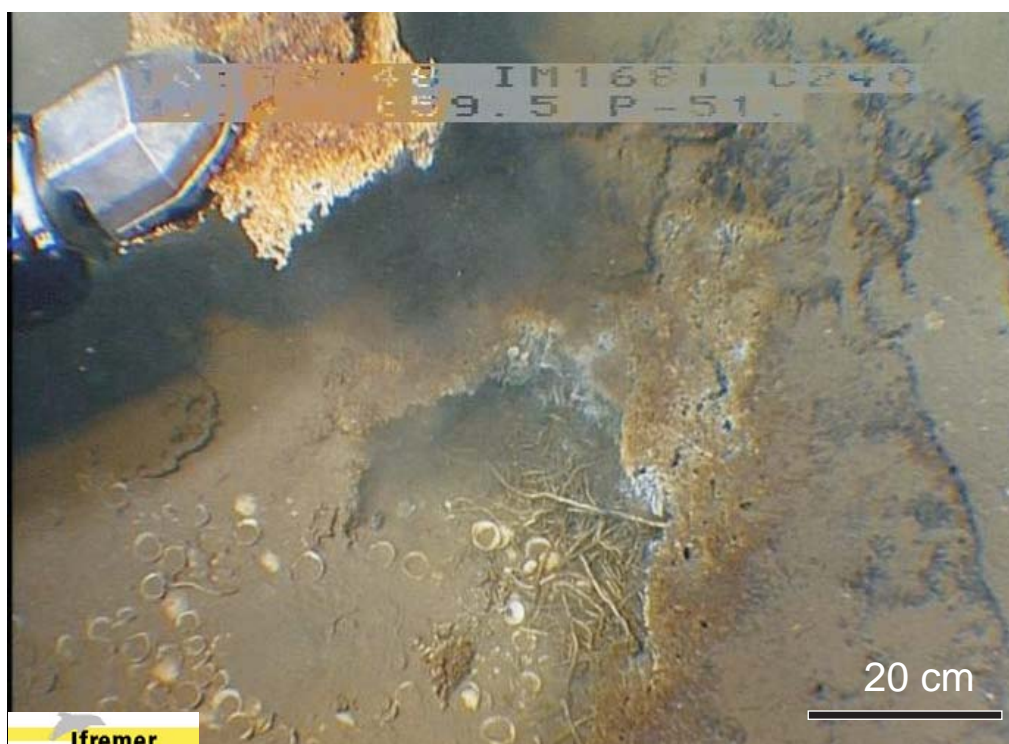


Fig1 (in colour)

A)



B)

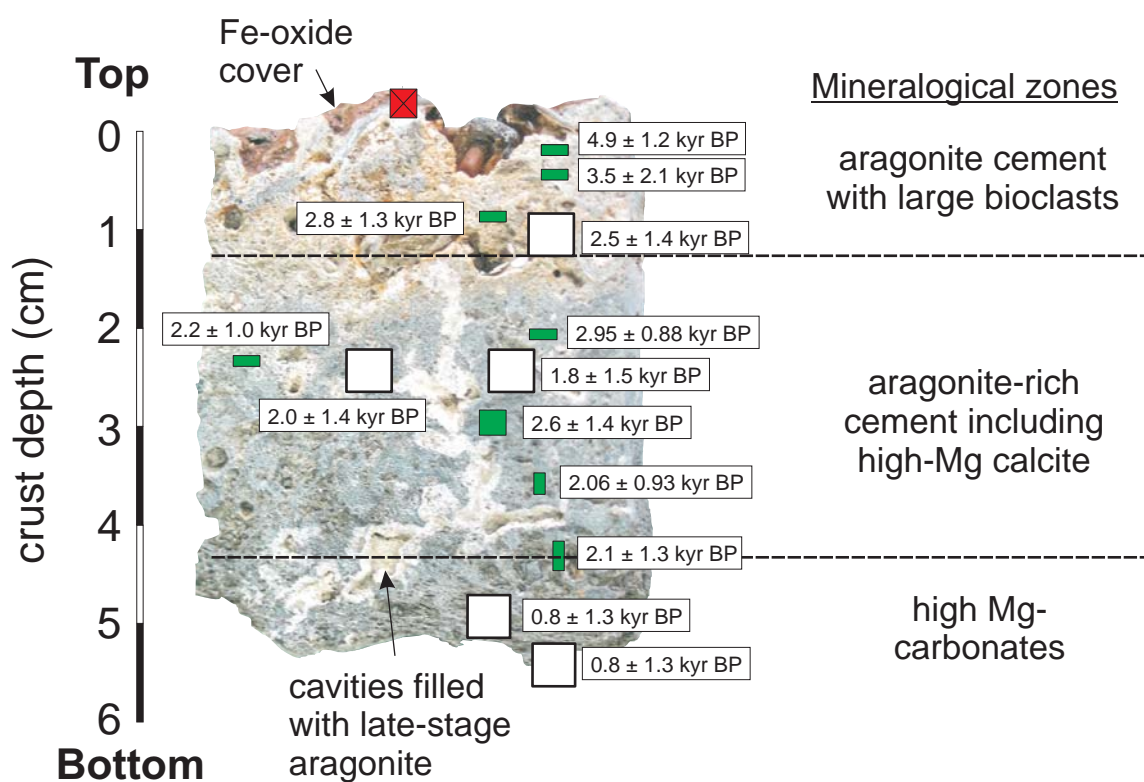


Fig. 2 (in colour in print)

Figure3

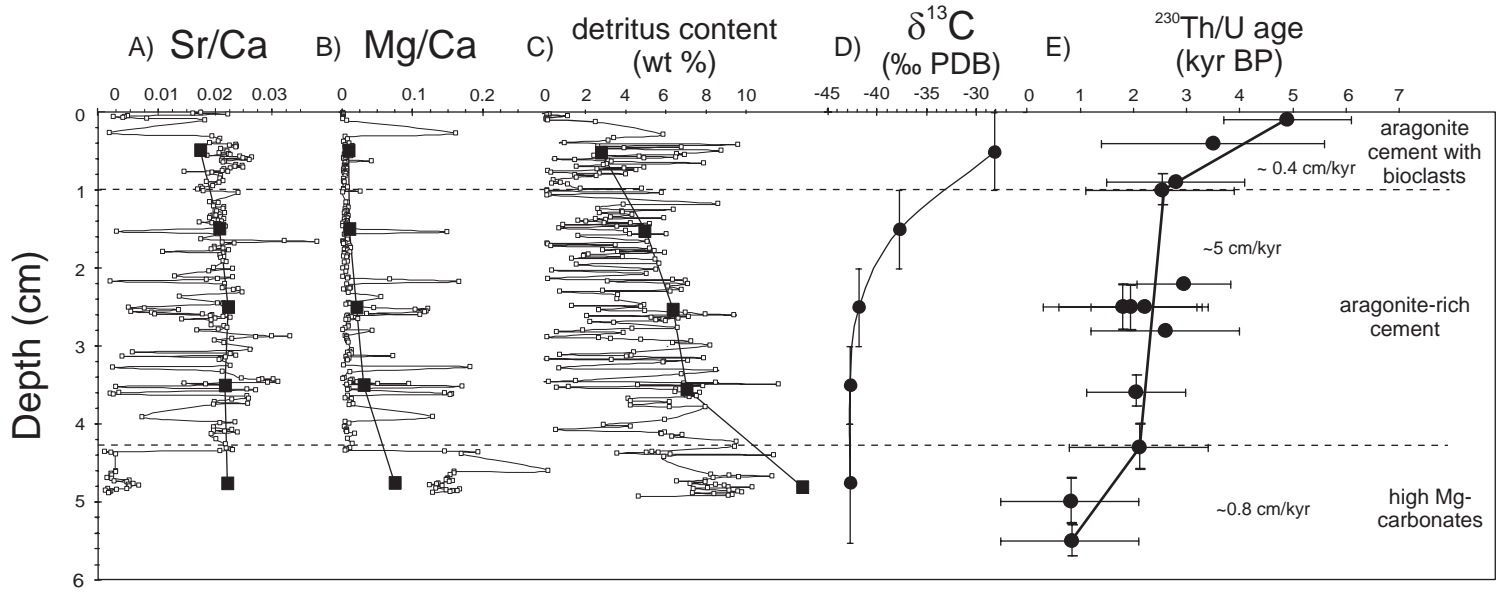


Fig. 3

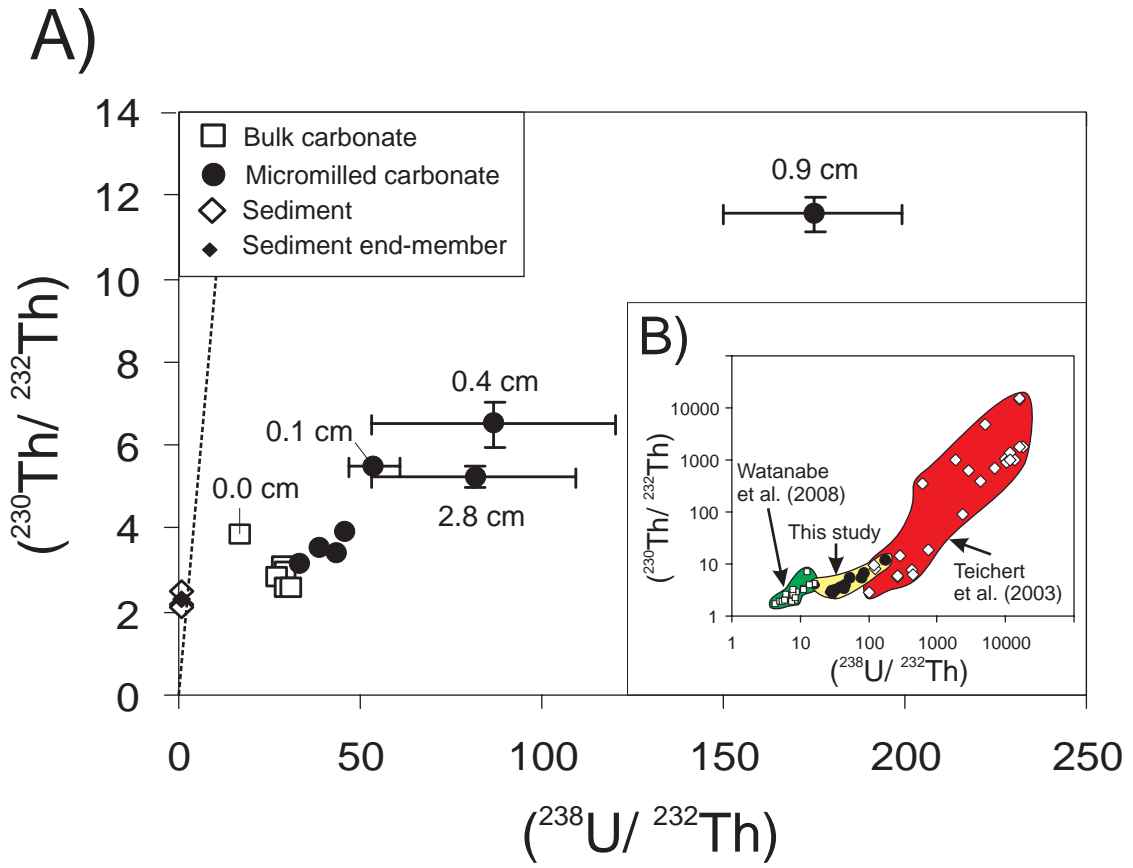


Fig. 4

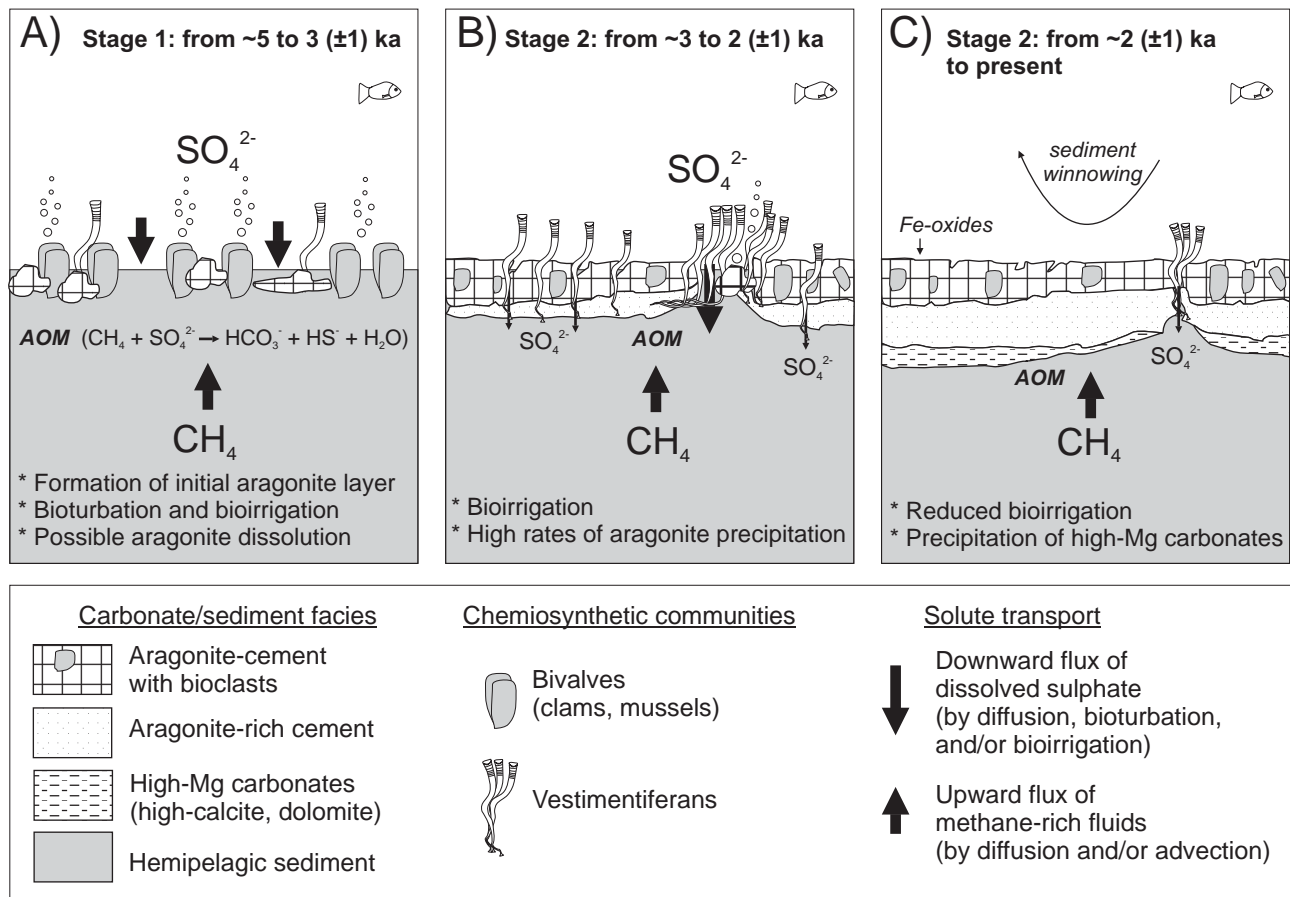


Fig. 5