



Tromsø, 4<sup>th</sup> of February, 2015

The Editorial Office,  
Climate of the Past

Dear Editor,

We would like to submit the revised manuscript of the paper cp-2014-127, entitled “Carbon isotope ( $\delta^{13}\text{C}$ ) excursions suggest times of major methane release during the last 14 ka in Fram Strait, the deep-water gateway to the Arctic”, authored by C. Consolaro, T. L. Rasmussen, G. Panieri, J. Mienert, S. Bünz, and K. Sztybor. All co-authors have contributed and agree with the contents of the manuscript.

We thank the two referees G. Dickens and L. J. de Nooijer very much for their very constructive reviews and greatly detailed suggestions on how to improve the manuscript. We believe we have addressed all their comments and followed their suggestions. A detailed point-by-point response is included below (reviewers’ comments in **black bold**, our answers in **blue**). Line numbering refers to the revised .pdf manuscript.

Yours sincerely,

Chiara Consolaro (corresponding author)

Chiara Consolaro  
CAGE, Department of Geology  
UiT the Arctic University of Norway,  
N-9037 Tromsø, Norway  
E-mail: [chiara.consolaro@uit.no](mailto:chiara.consolaro@uit.no), [chiara.consolaro@icloud.com](mailto:chiara.consolaro@icloud.com)

**Reply to first referee G. Dickens**

**General comment and major issues:**

**(A) The manuscript lacks an introductory conceptual framework regarding the fate of methane and the carbon isotope recorders. As a consequence, the aims of analyses and the discussion of results become confusing to follow. This will be particularly true to the broad readership of COP. I think a short new paragraph with an accompanying figure (new Figure 1) should be added to the Introduction (page 4193, between Lines 13 and 14). For this figure, I strongly suggest a cross-section from the sea surface to below the seafloor, that shows (a) a pockmark, (b) gas hydrates and the BSR, (c) variable upward CH<sub>4</sub> fluxes from the deeper CH<sub>4</sub> system, (d) the location and mode for the two potential fates of rising CH<sub>4</sub> – AOM and aerobic oxidation in the water column, and (e) the location and fate of planktic and benthic foraminifera. I have not seen such a figure before, although key components are scattered about in various works. In any case, this**

would clarify things immensely, as it would set the stage, hypothesis, and the rest of the writing.

- A new paragraph in the introduction regarding the fate of methane and the role of foraminifera as potential recorders has been added (from Page 2, line 21, to Page 3 line 21). However, we have not added the suggested figure here (Fig. 9, see comment below) but in the discussion (Section 5.2). This is because we think that the figure better pertains to the discussion/interpretation section and helps to better explain our conceptual model.

**(B) Related to the above comment, it is not obvious whether the manuscript is arguing for past times when AOM in shallow sediment was greater locally, when aerobic oxidation in the water column was greater across the North Atlantic, or something in between. At a root level, both end member processes could lead to greater carbon fluxes to the ocean, and could potentially change the d13C of benthic foraminifera, pore water DIC and even bottom water DIC at multiple locations, although much would depend on the extent and flux of methane release. For example, enhanced AOM in shallow sediment over a wide area might produce 13C-depleted HCO<sub>3</sub><sup>-</sup> that could diffuse to the seafloor.**

- In the discussion section 5.2 we discuss the different results obtained for the two depleted intervals CIE I and CIE II using the new Fig. 9. Here we suggest two different scenarios according to the different intensity of upward methane flux, using the schematic diagram modified after Borowski et al. (1996). For both scenarios the sulfate diffusion from the seawater into the sediments and sediment characteristics are considered constant.

- 1) **First scenario (Fig. 9A):** it represents CIE II, where only benthic foraminifera exhibit negative values of  $\delta^{13}\text{C}$ . This is the case where the methane flux is high and oxidized less efficiently with the consequence of lower AOM rates and higher methane fluxes into the bottom waters. In this case the sulfate-methane transition zone (SMTZ) is very close to the seafloor and the formation of carbonate crust is inhibited. This might be the situation when the negative  $\delta^{13}\text{C}$  values in the benthic foraminiferal tests are likely to be the result of calcification in presence of  $^{13}\text{C}$ -depleted DIC and probably ingestion of  $^{13}\text{C}$ -depleted methanotrophic bacteria.
- 2) **Second scenario (Fig. 9C):** it represents CIE I, where both benthic and planktonic foraminifera exhibit negative  $\delta^{13}\text{C}$  values. We have interpreted the negative values as due to secondary overgrowth precipitated after the benthic and planktonic foraminifera were buried. The bicarbonate is produced within the SMTZ through AOM precipitates as authigenic carbonate. According to Borowski et al. (1996) this scenario occurs when the fluid flow rates are low. It is also possible that the primary biogenic signal of benthic foraminifera was already negative, but the main controlling factor here is the negative signal of the AOM-derived authigenic carbonates deposited on the foraminifera tests.

**(C) The manuscript lacks a compelling demonstration and discussion of its true significance. More specifically, are the negative d13C excursions really similar in age and magnitude to those at sites shown in Figure 1? In general, I do not like paleoceanographic interpretations based on results from a single piston core. This is because most things of significance can and should be reproducible in multiple cores. In the present manuscript, comparison to other cores in the North Atlantic arises (page 4203), which is good. However, this is not rigorously demonstrated or discussed. An additional last figure, one showing and detailing the correlation, would be very welcome; indeed, I will suggest this is almost mandatory. If the correlation of benthic d13C excursions is correct, then much of the discussion should be condensed and modified, as local processes are not the answer. Such correlation also should include**

**cores away from pockmarks, to assess the alternative possibilities: (i) there are multiple locations with local carbon isotope perturbations at the same time (perhaps in pore waters); (ii) the deep water of the North Atlantic has had significant short-term changes in its stable carbon isotope composition.**

- In order to better explain the correlation to other sites and the apparent correlation between methane events and climatic events at global or regional scale climatic events in the North Atlantic, a new figure (Fig. 10) and short new paragraphs have been added to the discussion (Section 5.3 ‘North Atlantic deglacial CIEs’).

Fig. 10 shows the correlation of the Vestnesa Ridge record with the Greenland record of Smith et al. (2001), together with the NorthGRIP ice core  $\delta^{18}\text{O}$  record (North Greenland Ice Core Project Members, 2004), the Greenland Ice Sheet Project 2 (GISP2) atmospheric  $\text{CH}_4$  record (Brook et al., 2000), and the melt water pulse mwp-1A and mwp-1B (Peltier and Fairbanks, 2006; Stanford et al., 2011) (moved from Fig. 4 to Fig. 10).

However, the correlation with methane measured in ice core is speculative, and our paper does not aim to prove that methane emissions from Svalbard margin contribute to the global carbon cycle or climate change. We present data from a “local site”. The sum of contributions from local sites might provide a more global record, but the data available so far is not conclusive and this is considered speculative at this stage.

According to the data published so far on the isotope records of planktonic foraminifera (most of them cited for comparison in the paper) there are no anomalies in the North Atlantic deep water during the same time intervals. Therefore, these regional events likely consist of local carbon isotope perturbations at different locations, which presumably have been triggered by local processes, but with a similar timing during the last deglaciation.

Further work is necessary to test these hypotheses and to understand the possible triggering mechanisms. At the Centre for Arctic Gas Hydrate, Environment and Climate in Tromsø we are working on several cores from the Vestnesa ridge with the main goal to define the timing of methane events and to understand if the negative anomalies recorded by benthic foraminifera (and planktic) are due to local or global processes.

#### **Other comments:**

**Page 4193 – Line 14 Rewrite because the grammar is incorrect.**

**Lines 15-17: This needs expansion and rewriting. The various studies suggest incorporation of  $^{13}\text{C}$ -depleted carbon, but it needs to be presented if this is through pore water or through overlying seawater (See also Comment A).**

- The whole paragraph has been modified and rewritten (now Page 3 – Lines 6-10).

**Page 4194 – Line 24: think this is past tense – “has occurred”.**

- Changed to “occur” (now in introduction section 1, Page 2– Line 24).

**Page 4195 – Lines 5-8: Rewrite because awkward, including an odd verb.**

- This sentence has been rewritten. The last sentence has been deleted (now Page 5– Lines 2-3).

**Page 4199 – Line 21: Rewrite because the grammar is incorrect.**

- The sentence has been changed (now Page 9 – Line 24).

**Page 4201 – Line 14-22: This section does not make sense to me. Why would AOM lead a coating dominated by  $\text{SiO}_2$ ?**

- We have introduced a figure with the EDS spectra (Fig. 7) showing the composition of the coating enriched in Si, Mg and traces of FeS. We have also introduced a new paragraph where

we have explained why this coating on the *N. pachyderma* (s) test has been interpreted as a result of diagenetic effects connected with AOM-derived processes (now Page 10– Lines 21-28).

**Page 4202 – Line 3: Something seems incorrect here. AOM (CH<sub>4</sub> + SO<sub>4</sub><sup>2-</sup> → HCO<sub>3</sub><sup>-</sup> + HS) generates bicarbonate (and consequently alkalinity) not CO<sub>2</sub>. This process favors authigenic carbonate precipitation, as abundantly clear at many locations. I suppose one might suggest that AOM drove FeS precipitation, and subsequent oxidation of these sulfides caused carbonate dissolution. All sites that I have looked at where AOM is occurring have significant amounts of FeS minerals.**

- According to Sun and Turchyn (2014), another reaction that occurs at the SMTZ is  $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ , which indeed produces CO<sub>2</sub>. This is now well explained in the introduction paragraph (Section 1), here is only cited the reference paper (now Page 11– Lines 6-7). A short paragraph about FeS minerals has been added (Page 10 – Lines 30-33).

**Page 4202 – Line 12-27: This section needs rewriting. It is supposedly on methane release, which I would assume means to the water column; however, the section discusses AOM, which at least in my mind is the consumption of methane before it escapes to the water column. (See also comment A).**

- The whole paragraph has been rewritten (now Section 5.1.2) with the discussion about the two different scenarios described in Fig. 9 (see reply to point (B)).

**Reply to second referee L. J. de Nooijer**

**Main comments:**

**EDS is not a common tool to quantitatively analyze element concentrations in (carbonate) samples. Accuracy of obtained concentrations could have been ok by using a set of reference materials. The Methods section (page 7, lines 8-15) is very brief on this topic and does not mention such a strategy. Table 2 summarized the EDS results and suggest a level of accuracy that is unrealistic (and it is confusing that the wt% of the recorded elements apparently does not refer to the real wt% in the material, which is for example 40 wt% for Ca in any piece of calcite). In short, the EDS measurements only allow distinction between mineral phases on a broad level (e.g. between CaCO<sub>3</sub> and SiO<sub>2</sub>).**

**Mapping the elements (e.g. Mn) on embedded, sectioned and polished specimens would have allowed detection of (contaminant) surface phases. Spatial recognition of a contaminant phase throughout the chamber wall would make a valuable addition to the discussion of overgrowths and potential distortion of the primary signal. I hope the authors can include such maps (e.g. using ion microprobe) to replace the EDS-results which should either completely be removed or used only to show that the outer surface of some foraminifera is covered by something rich in Si.**

- We agree with L. de Nooijer that the EDS it is not a common tool to quantitatively analyse element concentration. Our purpose was to show that the outer surface of *Neogloboquadrina pachyderma* (s) in CIE I interval is covered by a thin coating rich in Si, Mg and traces of FeS. Therefore we have deleted the Table 2 with EDS results and added two spectra (Fig. 7), showing the composition of the carbonate test of the foraminifera (rich in Ca) and the composition of the layer covering the *N. pachyderma* (s) (rich in Si). Fig. 6 (SEM pictures of *N. pachyderma* s) and Fig. 8 (SEM pictures of *C. neoteretis*, previously Fig. 7) have been modified accordingly.

**Part of section 5.2 should be in the Results rather than in the Discussion.**

- The sentences with the results of SEM analyses have been moved from section 5.2 (Discussion) to section 4.2 (Results) as suggested. And the remaining paragraphs of the previous section 5.2 'SEM investigations' have been moved to the previous section 5.1.

**Minor comments:**

**Page 3, line 14: 'that lives' should be 'living'.**

- This sentence has been changed completely (now Page 3, lines 6-10), but this suggestion has been used in another section (Page 12, line 6).

**Page 4, line 8: 'warm, saline water' should be 'relatively warm, saline water'.**

- "Relatively" was added to the sentence (now Page 4, line 6).

**Page 5, line 5: 'at' may better be replaced by 'from'.**

- "At" has been replaced with "from" (now Page 4, line 31).

**Page 5, lines 22-23: approximately how much of the total number of foraminifera were specimens of *N. pachyderma* and *T. quinqueloba*?**

- *N. pachyderma* (s) and *T. quinqueloba* represents together the 88–98% of the assemblage, this information has been added to this sentence (now Page 5, lines 10-11).

**Page 6, lines 10-14: difficult to understand this sentence: please rewrite.**

- The whole sentence has been changed (now Page 5, lines 24-32).

**Page 6, line 15 and 17 afterwards: what standards were used and how were the carbonate results corrected? I assume all values are expressed relative to VPDB.**

- The standard used has been specified (NBS-19) and it has been specified that the isotope values are expressed relative to VPDB (now Page 6, lines 6-7 and 14-15). The size fraction of 100  $\mu\text{m}$  has been specified (line 3).

**Page 9, line 6 and 10: 'lighter' should be 'more depleted'.**

- "Lighter" has been substituted with "more depleted" (now Page 8, lines 17-18 and 21).

**Throughout 5.2 and in the (caption of) figures 6 and 7, the authors state that specimens from certain intervals are 'altered', whilst others are not. Figure 6a-c nicely shows that this alteration is likely confined to the very surface: most of the inner parts of the shell wall looks just like that of the other specimens (d-f and g-i). Therefore, please refer to this alteration as a 'surface alteration' or something: by far most of the shell does not appear altered.**

- The alterations of the foraminiferal tests are now referred to as 'surface alteration' in the text and in the figure caption (now Figs. 6 and 8).

**Page 12, line 14: 'strong enough and long enough' reads better as something like 'prolonged and sufficiently high'.**

- The whole section (now 5.2) has been rewritten completely.