

## Response to RC3, William Rush

We thank William Rush for his considered comments on the manuscript. In addition to some minor comments, RC3 expressed their major concern that that more discussion of anaerobic oxidation of methane was required, as there is extensive literature on the formation of thermogenic methane in the North Atlantic during the PETM, the anaerobic oxidation of which could have influenced the formation of ikaite. This is a valid point, and we will accordingly add a discussion of the possible source and role of methane in ikaite precipitation to the manuscript (see response to comment on Lines 340-341 and Line 438. As the review lists the major and minor points in order they appear in the manuscript, we will answer the line-by-line comments in order also, in order to orient the reader.

Lines 48-49: specify °C when saying “temperatures approaching zero”.

- We can add a bracket with the temperature as follows “*cold water* temperatures (< 10 °C) are much more favourable for the precipitation, growth, and longevity of this mineral.”

Lines 62-63: explain why the glendonites are a topic of controversy, there should be more discussion on these previous studies that are referenced.

- We will clarify this by adding “have been a topic of controversy in the paleoclimate community *due to the apparent mismatch with concurrent paleotemperature proxies* (Huggett et al., 2005; Spielhagen and Tripathi, 2009)”

Lines 78-80: “Whether these cooling events reflect a localised as well as short-lived cooling is not understood, nor the mechanism by which such cooling could occur, although these have been speculated upon” discuss how these have been speculated upon and what some of the proposed mechanisms have been.

- As the one of the main points of this paper is to discuss the evidence for and proposed mechanisms of cooling in this region, we would rather keep this as an introduction of the problem which is later discussed in detail (see section 4.3 ‘Timing and conceptual model for ikaite growth’). We propose to change this sentence to “*While the potential drivers of intermittent cooling episodes have been touched upon by previous studies (Schoon et al., 2015; Stokke et al., 2020a; Vickers et al., 2020), the causes, spatial extent, and recurrence times of such events remains unresolved.*”

Line 244: Somewhat minor, but I believe there could be a better word choice than “mush”, perhaps mixture or amalgam?

- We will change the word “mush” to “*amalgam*”.

Lines 296, 310: Again, I believe there is a better word choice than “blebs”. I will leave that choice to the author, as I’m not exactly certain what is meant by blebs.

- We have added the following definition of the word to improve clarity: “Notably, areas of calcite blebs (bubble-like mineral inclusions)...”

Line 311: there is a space missing between “localised” and “increase”.

- We will add this missing space in.

Line 340-341: This is my major concern with the paper. The authors reference anaerobic oxidation of methane as playing a key role in ikaite precipitation, yet do not discuss the extensive literature on the thermogenic methane production in the North Atlantic during the PETM associated with North

Atlantic Igneous Province volcanism. There are many papers on this topic, including Jones et al., 2019 and Frieling et al., 2016 among others. At the very least, there should be discussion as to the possibility that anaerobic oxidation of methane could have played a role in the formation of ikaite as an alternative to the volcanic ash hypothesis, why this methane could not have played a role, or the potential that these mechanisms could have worked in conjunction.

- This is a good point, and we will accordingly expand the discussion to include the methane-ikaite link hypothesis. Here, we will add a section as follows: “The breakdown of sedimentary  $C_{org}$  via sulphate reduction, and/or the anaerobic oxidation of methane (AOM) are thought to play a key role in ikaite precipitation, largely because the low  $\delta^{13}C$  values measured in ikaites and glendonites suggest an organic or methanogenic source of carbon (e.g. *Rogov et al., 2023 and references therein*), and also because these organic matter decomposition processes generate DIC (*Hiruta and Matsumoto, 2022; Whiticar et al. 2022*). *Methane has been linked to ikaite/glendonite formation due to their frequent proximity to methane seeps (Greinert and Derkachev, 2004; Teichert and Luppold, 2013; Hiruta and Matsumoto, 2022) and gas inclusions containing methane and other hydrocarbons in glendonite specimens from the Jurassic of Siberia (Morales et al., 2017). However, other studies which examined sedimentary biomarker evidence for AOM in Oligocene and Eocene-aged glendonite-bearing strata did not find evidence for significantly elevated rates of AOM and support an organic matter source for the examined glendonites (Qu et al., 2017; Vickers et al., 2020).*” For ikaite to be precipitated over the more stable  $CaCO_3$  polymorphs, factors inhibiting calcite and promoting ikaite precipitation are also required. These may include high alkalinity, high concentrations of phosphate and/or  $Mg^{2+}$ , and low temperatures (Rickaby et al., 2006; Zhou et al., 2015; Purgstaller et al., 2017; Stockmann et al., 2018). *The explosive NAIP emplacement may have played a key role in generating just such conditions for  $CaCO_3$  precipitation and the precipitated polymorph being ikaite. Hydrothermal venting of methane and other gases occurred at sites proximal to the NAIP (Svensen et al., 2004; Frieling et al., 2016; Jones et al., 2019; Berndt et al., 2023); and the explosive nature of the NAIP eruptive volcanism could have driven short-term climate cooling (‘volcanic winters’, e.g. Robock et al., 2000; Schmidt et al., 2016; Stokke et al., 2020a). Furthermore, the large amounts of volcanic ash deposited in the sediments likely underwent rapid diagenesis, generating the chemical conditions in the pore waters that could have inhibited calcite precipitation and therefore promoted ikaite precipitation (e.g. Gislason and Oelkers, 2011; Olsson et al., 2014; Murray et al., 2018). Indeed, ikaite and other carbonates were discovered as travertine in the Hvanná river in the vicinity of the Eyjafjallajökull volcano shortly after eruptive activity began in Spring of 2010 (Olsson et al., 2014).*” We will further discuss the evidence for methane in the 396 cores and Nordic Seas region a little later on in the manuscript (see response to comment Line 438).

Line 393: there is a missing space between “ $CaCO_3$ ” and “in”.

- We will add this missing space in.

Line 438: Again, here the influence of methane should be discussed in addition to the rapid diagenesis of ash.

- We will change this to “For sediments such as those encountered in Modgunn and Mimir, the primary driver of DIC was likely AOM (rather than bacterial sulphate reduction of organic matter), since TOC in the sediments is low (generally < 1.5 wt %; *Planke et al., 2023b,c*) and there was much methane venting in the area (*Svensen et al., 2004; Berndt et al., 2023*)”.

Lines 449-450: A recent paper in this journal (Rush et al., 2023) found transient cooling associated with ETM2 in the Mid-Atlantic of the United States. This would not have been an enclosed basin but provides evidence of another region that experienced cooling during an Eocene hyperthermal and may be worth a citation.

- Very exciting. Also Meckler et al. 2022 found variable temperatures at odds with global for the North Atlantic. We will edit this section to include these new findings:  
*“Paleotemperature estimates for the PETM and early Eocene from both biomarkers and stable and clumped isotope thermometry for the North Atlantic and Nordic Seas region show variable temperatures and intervals of cooling which are apparently at odds with global records (Schoon et al., 2015; Stokke et al., 2020; Vickers et al., 2020; Meckler et al., 2022; Rush et al., 2023).”*