

Biogeosciences Discuss., referee comment RC2
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Comment on bg-2021-177

Ruediger Stein (Referee)

Referee comment on "Biomarker characterization of the North Water Polynya, Baffin Bay: Implications for local sea ice and temperature proxies" by David J. Harning et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-177-RC2>, 2021

Review by R. Stein (MARUM, Bremen University & AWI Bremerhaven)

(Complete review with figures R1 and R2 is attached as pdf)

The very well paper by Harning et al. is dealing with specific biomarkers determined in surface sediments from northern Baffin Bay, with a special focus on the North Water Polynya. These biomarkers, i.e., highly-branched isoprenoids (HBIs), sterols, long-chain alkenones and archaeal GDGTs, may give information about sea-ice conditions, open-water productivity, ocean temperature, and terrigenous input, as shown in many previous studies from very different ocean regions. Although major progress in using these proxies for reconstruction of present and past environmental conditions has been obtained, more ground truth data are still needed to fully approve some of these proxies, especially the proxies dealing with the reconstruction of sea ice (for example see reviews by Stein et al., 2012; Belt and Müller, 2013; Belt, 2018). Gaps in knowledge are related to the definite identification of the source of specific biomarkers, (regional) proxy calibration to allow (semi)quantitative estimates of sea-ice extent and its seasonal variability, sea-surface temperature, salinity etc.. The missing ground truth data can be obtained by detailed studies of sediment trap material and surface sediments as well as cultural experiments, and are especially needed from the high (polar) latitudes, e.g., the Arctic Ocean and its marginal seas.

In this context, the new data set from Harning et al. may give some important insight for using these biomarkers for characterizing the modern environmental conditions in a large polynya setting, i.e., an area of reduced sea ice and increased primary productivity. Such data might be strongly relevant for using the proxies for reconstruction of the development of past polynyas. Furthermore, Harning's data set allows to directly correlate

a large variety of biomarkers (often either HBI and sterol data are produced/published from the same set of samples or alkenones or GDGTs). Despite this positive aspect, however, I have major problems with the present version of the manuscript. These concerns are related to the data set itself, the postulation of new SST calibrations for high latitudes based on a very limited data set, the missing more detailed comparison/discussion of the own data with the published biomarker data from Kolling et al. (2020), and some statements related to the interpretation of the biomarker data in terms of their origin (i.e., marine vs. terrigenous), as outlined in the following paragraphs. In my mind, a major clarification and revision of the manuscript is needed before it can be accepted for publication.

- Data base and presentation of data

The total number of data points (13 samples in total) is quite limited for the quite general statements and interpretation of data given here. Whereas for the polynya itself (eight samples) this might be ok, it is quite questionable for the area outside the polynya (five samples for the entire northern Baffin Bay). Furthermore, these five samples are from very different settings (one from the central Baffin Bay, close to Davis Strait, and three off different fjord mouths), i.e., areas with very different sea-ice conditions and sedimentation rates. Due to the latter, these 1 cm thick samples (proxy data) might represent quite different time intervals (average sea-ice condition, temperatures etc. over 10 to hundreds of years). Furthermore, a presentation of the data in terms of distribution maps (see Kolling et al., 2020) might be useful here as well. In order to allow more general statements/interpretations/conclusions, the discussion of the new data together with the data from Kolling et al. (2020) would be most helpful/important. Kolling et al. (2020) have studied samples from locations very close to those of this study (Fig. R1). Thus, data from the same biomarkers (i.e., IP25, HBIs and sterols as well as the different PIP25) are available for a detailed comparison and interpretation in terms of sea-ice extent and its seasonality, productivity etc. (see examples in Fig. R1).

- Low concentrations of HBIs and sterols

When I myself tried to roughly compare the new Harning et al. data with our Kolling et al. (2020) data, I realized a "problem", and this is one of my major concerns I have with the new data presented here. The absolute concentrations of the HBIs and the sterols are significantly lower (two orders of magnitude or so!!) than those presented by Kolling et al. (2020). What might be the cause for this? Storage of samples (fresh/deep-frozen samples vs. samples stored under room temperature), or different analytical approach? I am not a chemist. Thus, I myself cannot comment in detail the analytical approach for identification and quantification of the biomarkers that has been used here, but I know from cooperation with the chemists involved in our biomarker analyses as well as the Simon Belt group that the analytical procedure is overall significant if data from different labs will be compared. Thus, Belt et al. (2014) carried-out an inter-laboratory investigation dealing with the identification and quantification of the Arctic sea ice biomarker proxy IP25 and other HBIs in marine sediments (our lab was involved in this study as well). As final statements these authors summarized in their abstract that "data are presented that suggest that extraction of IP25 is consistent between Automated Solvent Extraction (ASE) and sonication methods and that IP25 concentrations based on 7-hexylnonadecane as an internal standard are comparable using these methods. Recoveries of some more unsaturated HBIs and the internal standard 9-octylheptadecene, however, were lower with the ASE procedure, possibly due to partial degradation of these more reactive chemicals as a result of higher temperatures employed with this method. For future measurements, we recommend the use of reference sediment material with known concentration(s) of IP25 for determining and routinely monitoring instrumental response factors."

Harning et al. have used the ASE for extraction, and they should check their HBI and sterol data and comment on their analytical approach. For example, did you take in account the different response factors for the analytes and internal standards?

- Alkenones, high UK37', and new SST calibration

Concerning the alkenone data, I also have problems. The northern Baffin Bay is an environment with sea-surface temperatures significantly lower than 10°C (<5°C). Under such cold conditions, the C37:3 long-chain alkenones should be predominant over the C37:2 alkenones (e.g., Prahl and Wakeham, 1987). In this study, however, the C37:2 alkenones are predominant (Fig. 4 of their paper), resulting in high UK37' values of 0.7-0.9 (Fig. 7 of their paper), i.e., values that are typical for much higher temperatures. In polar and subpolar regions including Baffin Bay (!), however, UK37' values are typically between 0.2 and 0.4 (e.g., Rosell-Melé, 1998; Bendle and Rosell-Melé, 2004; Méheust et

al., 2013; Moros et al., 2016). The authors are aware about this problem and discuss that temperature, salinity and nitrate are factors that may have influenced UK37' and UK37 values. Nevertheless, they state that "given our limited dataset at this time, temperature seems to be the most important environment variable on UK37 values", and then simply have correlated the high UK37' values with the measured low SST values of Baffin Bay. As result, they obtain, of course and not surprising, a new calibration that give totally different SST values in comparison to those calculated based on Müller et al. (1998) (Fig. 7). Did the authors test their "new calibration" using the UK37' data from Moros et al. (2016), i.e., data from Baffin Bay? What SST values they would get? Furthermore, there might be another option, i.e., there might be some question mark related the data that should be clarified before postulating a new calibration (e.g., what about co-elution with other compounds that might result in too high C37:2 concentrations; see Villanueva and Grimalt; 1996). Please check!

In the introduction (Lines 55-57), some credit should be given to other studies dealing with the use and calibration of UK37 and TEX86 for SST reconstructions in high latitudes (Sikes et al., 1997; Rosell-Melé, 1998; Ho et al., 2014)

- Biomarkers (sterols) and their sources

I do not agree with the general statement that in the Arctic the abundance of brassicasterol, dinosterol, campesterol and β -sitosterol is mainly related to marine productivity. The interpretation of the sterols and their use as organic-carbon source indicator are not easy tasks and may strongly differ from region to region (e.g., Volkman, 1986; Huang and Meinschein, 1976; Fahl and Stein, 1997, 1999; Belt et al., 2013). Brassicasterol often used as "marine productivity indicator" might be ok in areas not influenced by strong terrigenous input (river discharge). In coastal areas controlled by huge river discharge, such as the Kara and Laptev seas, a large amount of brassicasterol found in surface sediments have a terrestrial (lacustrine) source (e.g., Fahl et al., 2003; Hörner et al., 2016). Furthermore, in these shallow-water coastal zones, terrestrial/lacustrine brassicasterol as well as brassicasterol produced by marine algae may be incorporated into sea ice and transported into the open central Arctic Ocean. Thus, these biomarkers not produced by sea ice may be found in the sea ice and result in erroneous interpretation of the source of this biomarker. When using brassicasterol as "open-water productivity proxy", additional information about the environmental situation should be taken into account and additional biomarkers (such as dinosterol and the HBI-III) should be used as well. When using the PIP25 approach for reconstructing sea-ice

conditions, PIP25 values based on IP25 and brassicasterol, dinosterol and HBI-III, should be calculated and discussed.

Vascular plants are producers of campesterol and β -sitosterol (Huang and Meinschein, 1976) but may also be produced by diatoms (Belt et al., 2013). In the Arctic Ocean characterized by strong terrigenous input into the marginal sea and – via sea ice and ocean currents – a predominantly terrigenous source of these biomarkers is most probable (e.g., Yunker et al., 1995, 2005; Stein and Macdonald, 2004; Xiao et al., 2013). Such riverine input of organic carbon onto the shelf is nicely reflected in maximum concentration of campesterol and β -sitosterol in surface sediments close to the major river mouths in the Kara and Laptev seas (Xiao et al., 2013; Fig. R2). In most part of the Arctic Ocean, thus terrigenous organic matter is predominant in surface sediments (Stein and Macdonald, 2004; Fig. R2). Thus, I. cannot agree with the authors' statement in 113/114): "In the Arctic where terrestrial biomass is low, we assume that the contribution of terrestrial-derived campesterol and β -sitosterol is minimal compared to that produced in the ocean."

References

Belt, S. T., 2018. Source-specific biomarkers as proxies for Arctic and Antarctic sea ice. *Org. Geochem.*, 125, 277-298.

Belt, S. T., and Müller, J., 2013. The Arctic sea ice biomarker IP25: A review of current understanding, recommendations for future research and applications in palaeo sea ice reconstructions. *Quaternary Science Reviews*, 79, 9–25. <https://doi.org/10.1016/j.quascirev.2012.12.001>

Belt, S. T., Brown, T. A., Ampel, L., Cabedo-Sanz, P., Fahl, K., Kocis, J. J., & Xu, Y., 2014. An inter-laboratory investigation of the Arctic sea ice biomarker proxy IP25 in marine sediments: Key outcomes and recommendations. *Climate of the Past*, 10(1), 155–166. <https://doi.org/10.5194/cp-10-155-2014>

Belt, S. T., Brown, T. A., Ringrose, A. E., Cabedo-Sanz, P., Mundy, C. J., Gosselin, M., and Poulin, M., 2013. Quantitative measurement of the sea ice diatom biomarker IP25 and sterols in Arctic sea ice and underlying sediments: further considerations for palaeo sea ice reconstruction. *Org. Geochem.*, 62, 33-45.

Bendle, J., and A. Rosell-Melé, 2004. Distributions of UK37 and UK37' in the surface waters and sediments of the Nordic Seas: Implications for paleoceanography. *Geochem. Geophys. Geosyst.* 5, Q11013, doi:10.1029/2004GC000741.

Fahl, K. and Stein, R., 1997. Modern organic-carbon-deposition in the Laptev Sea and the adjacent continental slope: Surface-water productivity vs. terrigenous input. *Org. Geochem.*, 26: 379-390.

Fahl, K. and Stein, R., 1999. Biomarkers as organic-carbon-source and environmental indicators in the Late Quaternary Arctic Ocean: Problems and perspectives. *Mar. Chem.*, 63/3-4: 293-309.

Fahl, K. and Stein, R., 2012. Modern seasonal variability and deglacial/Holocene change of central Arctic Ocean sea-ice cover: New insights from biomarker proxy records. *Earth Planet. Sci. Lett.* 351-352C, 123-133; doi:10.1016/j.epsl.2012.07.009.

Fahl, K., Stein, R., 1997. Modern organic carbon deposition in the Laptev Sea and the adjacent continental slope: Surface-water productivity vs. terrigenous input. *Organic Geochemistry* 26, 379-390.

Fahl, K., Stein, R., Gaye-Haake, B., Gebhardt, C., Kodina, L.A., Unger, D., and Ittekkot, V., 2003. Biomarkers in surface sediments from Ob and Yenisei estuaries and southern Kara Sea: Evidence for particulate organic carbon sources, pathways, and degradation. In: Stein, R., Fahl, K., Fütterer, D.K., Galimov, E. M., and Stepanets, O.V. (Eds.), *Siberian River Run-off in the Kara Sea: Characterisation, Quantification, Variability, and Environmental Significance*, Proceedings in Marine Sciences Vol.6, Elsevier, Amsterdam, 329-348.

Ho, S.L., Mollenhauer, G., Fietz, S., Martinez-Garcia, A., Lamy, F., Rueda, G., Schipper, K., Méheust, M., Rosell-Melé, A., Stein, R., Tiedemann, R., 2014. Appraisal of the TEX₈₆ and TEX₈₆^L thermometries in the subpolar and polar regions. *Geochimica et Cosmochimica Acta*, 131, pp. 213-226. doi: 10.1016/j.gca.2014.01.001.

Hörner, T., Stein, R., Fahl, K., Birgel, D., 2016. Post-glacial variability of sea ice cover, river run-off and biological production in the western Laptev Sea (Arctic Ocean) - A high-resolution biomarker study. *Quaternary Science Reviews* 143, 133-149. <http://dx.doi.org/10.1016/j.quascirev.2016.04.011>

Huang, W. Y., and Meinschein, W. G., 1976. Sterols as source indicators of organic materials in sediments. *Geochem. Cosmochim. Acta* 40, 323-330.

Kolling, H. M., Stein, R., Fahl, K., Sadatzki, H., de Vernal, A., Xiao, X., 2020. Biomarker distributions in (sub)Arctic surface sediments and their potential for sea ice reconstructions. *Geochemistry, Geophysics, Geosystems* 21, e2019GC00862. <https://doi.org/10.1029/2019GC008629>

Méheust, M., Fahl, K., Stein, R., 2013. Variability in modern sea-surface temperature, sea ice and terrigenous input in the sub-polar North Pacific and Bering Sea: Reconstruction from biomarker data. *Org. Geochemistry* 57, 54-64.

Moros, M., Lloyd, J.M., Perner, K., Krawczyk, D., Blanz, T., de Vernal, A., Ouellet-Bernier, M.-M., Kuijpers, A., Jennings, A.E., Witkowski, A., Schneider, R., Jansen, E., 2016. Surface and sub-surface multi-proxy reconstruction of middle to late Holocene palaeoceanographic changes in Disko Bugt, West Greenland. *Quaternary Science Reviews* 132, 146-160.

Muñer, P. J., Kirst, G., Ruhland, G., von Storch, I., and Rosell-Mel, A., 1998. Calibration of the alkenone paleotemperature index UK'37 based on core-tops from the eastern South Atlantic and the global ocean (60°N-60°S). *Geochim. Cosmochim. Acta* 62, 1757-1772, 1998.

Prahl, F. G., and Wakeham, S. G., 1987. Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessment. *Nature*, 330, 533-537.

Rosell-Mel, A., 1998. Interhemispheric appraisal of the value of alkenone indices as temperature and salinity proxies in high latitude locations. *Paleoceanography* 13, 694.

Sikes, E.L., Volkman, J.K., Robertson, L.G., Pichon, J.-J., 1997. Alkenones and alkenes in surface waters and sediments of the Southern Ocean: Implications for paleotemperature estimation in polar regions. *Geochimica et Cosmochimica Acta* 61, 1495-1505

Stein, R. and Macdonald, R.W. (Eds.), 2004. *The Organic Carbon Cycle in the Arctic Ocean*, Springer-Verlag, Berlin, 363 pp.

Stein, R., 2008. *Arctic Ocean Sediments: Processes, Proxies, and Palaeoenvironment*. *Developments in Marine Geology*, Vol. 2, Elsevier, Amsterdam, 587 pp..

Stein, R., Fahl, K., and Müller, J., 2012. Proxy reconstruction of Arctic Ocean sea ice history: „From IRD to IP₂₅“. *Polarforschung* 82, 37-71, hdl:10013/epic.40432.d001

Villanueva, J. and Grimmalt, J.O., 1996. Pitfalls in the chromatographic determination of the alkenone UK37 index for paleotemperature estimation. *Journal of Chromatography A* 723, 285-291.

Volkman, J. K., 1986. A review of sterol markers for marine and terrigenous organic matter. *Org. Geochem.*, 9, 83-99.

Xiao, X., Fahl, K., and Stein, R., 2013. Biomarker distributions in surface sediments from the Kara and Laptev Seas (Arctic Ocean): Indicators for organic-carbon sources and sea-ice coverage. *Quat. Sci. Rev.*, doi.org/10.1016/j.quascirev.2012.11.028.

Yunker, M.B., Belicka, L.L., Harvey, H.R., Macdonald, R.W., 2005. Tracing the inputs and fate of marine and terrigenous organic matter in Arctic Ocean sediments: a multivariate analysis of lipid biomarkers. *Deep-Sea Research II* 52, 3478-3508.

Yunker, M.B., Macdonald, R.W., Veltkamp, D.J., Cretney, W.J., 1995. Terrestrial and marine biomarkers in a seasonally ice-covered Arctic estuary-integration of multivariate and biomarker approaches. *Marine Chemistry* 49, 1-50.

Please also note the supplement to this comment:

<https://bg.copernicus.org/preprints/bg-2021-177/bg-2021-177-RC2-supplement.pdf>