AC1: Response to reviewers' comments

Colors:

Reviewer comments

Author response

Changed manuscript

Response to Reviewer #1: RC1

(Comment on egusphere-2025-5089) by Joseph B. Novak

Reviewer #1

SUMMARY

Viola et al. present a very nice study that explores the potential of mass spectrometry imaging to capture interannual climate variability in sedimentary archives. The data presented here probe the extent to which sedimentary processes may obscure these high-frequency climate signals. This study is an important contribution to the cutting edge of our field – particularly because of the profoundly important climate processes the MSI technique could be used to investigate. The writing and figure design are excellent. My main comment relates to the mass spectrometry techniques used. I am not familiar with the statistical techniques used in this manuscript and leave their evaluation to the other reviewers. I look forward to the publication of this work after my comments are addressed.

We thank the reviewer for helpful and constructive comments. As detailed below, we now have expanded the method section with further details on the analytical aspects of MSI based Uk'37 and their comparison to other approaches.

Reviewer #1:

MAJOR COMMENTS

Methods:

Is there any reason for concern about potential differences in the ionization efficiency of the C37:3 vs. C37:2 alkenones influencing your results? This is an issue for other mass spectrometer techniques (e.g., GC-MS and HPLC-MS, see (Chaler et al., 2000, 2003; Liao et al., 2023)). If steps were taken to account for this on the analytical side, some additional text outlining that procedure would be helpful to better understand the data.

Thank you for raising this point, as differences in the ionization efficiency between the alkenones would in fact have the potential to bias MSI derived Uk'37 series and reconstructed temperatures. This comment is related to general comments #2&#4 of reviewer #2 and we changed the section according to both comments.

As the reviewer pointed out, issues regarding the ionization efficiencies of C37 alkenones are reported for several mass spectrometry approaches (Chaler et al., 2000, 2003; Liao et al., 2023). Unfortunately, to our knowledge, systematic studies addressing this for (MA)LDI FT-ICR MS workflows are currently lacking. Studies in warm SST areas (Napier et al., 2022; Obreht et al., 2022a; Wörmer et al., 2022) reported systematic offsets between GC-FID and MSI results and introduced site specific correction factors. Most likely these effects are due to a bias towards individual measurement spots ("shots") representing relatively colder temperatures. Shots with very high temperatures would lead to C37:3 more likely falling below the detection limit, and hence being excluded. In general, the potential influence of data processing choices is part of an ongoing project by the author. An alternative explanation could be related to lower alkenone concentrations at these areas in an effect similar to the "injection amount-effect" described in Liao et al. (Liao et al., 2023), especially given the still open questions around ion formation and matrix effects in (MA)LDI (Fuchs et al., 2010; Knochenmuss, 2006).

In the temperate Santa Barbara Basin, none of these biases would in principle play a big role, as both alkenone species are similarly abundant and concentrations are generally high. In fact, the comparisons to GC-FID data in sediments from the SBB showed high agreement between MSI and GC-FID based Uk'37 values (Alfken et al., 2020) (see Fig. R1 below). The MSI results for SBB sediments were additionally verified with instrumental SST data. The temporal overlap of boxcore SPR0901-05BC utilized by Alfken et al. 2020 and CalCOFI buoy station data (California State Department of Fish and Game; NOAA Fisheries; Scripps Institution of Oceanography, 2001) allowed to estimate the correlation between sediment MSI uk'37 based temperature reconstructions and buoy SST data of the modern era. On interannual timescale estimated from 1984 to 2009 the MSI based temperatures resulted in spearman's rank correlations of up to ~0.6 with upper 0-30m water column data at the closest CalCOFI station 81.8 46.9. Similar average temperatures for this period (MSI ~0.3C warmer) lead us to believe that differences in ionization efficiencies are not influential or relevant compared to the overall uncertainties and that MSI based uk37 in the middle of the Uk'37 temperature range and especially in SBB to be robust recorders of SST variability.

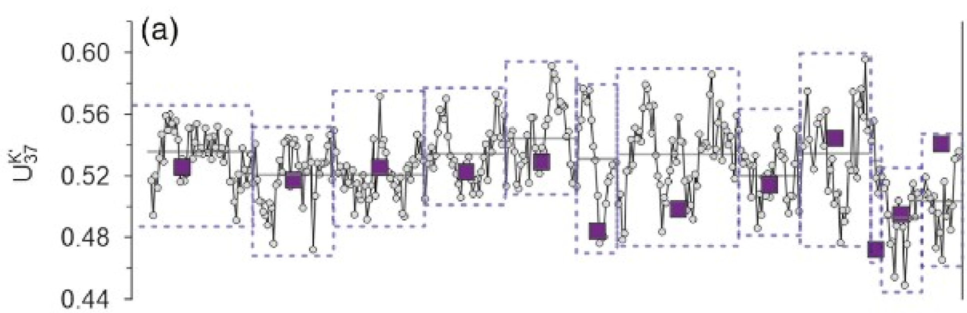

Fig. R1: Comparison of MSI-based and conventional extraction-based data of Uk'37. Grey points and line are MSI derived Uk'37 estimates, purple squares are GC-FID based estimates. Dotted rectangles indicate the corresponding depth range averaged for one sample used for extraction and horizontal lines display the corresponding mean value of the MSI data. Based on fig. 2 of Alfken et al. (2020).

The section now reads as:

During the development of the MSI workflow by Wörmer et al, (Wörmer et al., 2014) and in subsequent studies, the resulting $U^{K'}_{37}$ values were verified using GC-FID measurements (Alfken et al., 2020; Napier et al., 2022; Obreht et al., 2022a, b). Differences in $U^{K'}_{37}$ values obtained by different mass spectrometry techniques have been reported and attributed to varying ionization efficiencies of alkenones, the co-elution of other compounds, and additional factors (Chaler et al., 2000, 2003; Liao et al., 2023; Rama-Corredor et al., 2018). Notably, data derived from MSI in warm SST regions have shown a cold bias compared to GC-FID data, leading to the introduction of site-specific correction factors. However, in the temperate SST regime of SBB, MSI and GC-FID data did not exhibit significant differences and correlated well with CalCOFI buoy SST data at the site (Alfken et al., 2020; California State Department of Fish and Game; NOAA Fisheries; Scripps Institution of Oceanography, 2001).

Reviewer #1:

MINOR COMMENTS

L29–32: Another important aspect of paleoclimate archives is that they allow climate scientists to understand climate processes in warmer-than-present climate states. It may be worthwhile to add a comment to this effect.

Thank you, this aspect improves the rationale behind our study and was added accordingly.

The section now reads as:
Understanding past climate and its dynamics is crucial for contextualizing recent climate change and processes in warmer-than-present climate states under projected future conditions.

Reviewer #1:

L40: a comma is needed after "however."
L42: remove space between "carries" and the period at the end of the sentence.
L55: "export productivity" is a more appropriate term here than "primary productivity" because the sediments only preserve the proportion of the biological products that are exported from the surface and buried.
L150–151: I think there is a typo or missing word here.

Thank you for catching these errors and the suggestion, which clarifies what we are reconstructing with the pyropheophorbide α data.

The changes have been made accordingly, L150-151 now read as:
Given a regional cluster of n proxy records with a similar climate between sites, the mean power spectrum, M, averaged across all individual records' spectra, will yield a precise estimate of the proxy spectrum P.

Reviewer #1:

Figure 2 caption: an explanation of the black “Xs” in panel A would be nice.

Thank you for this suggestion as it makes the figure much easier to understand, especially when viewed in isolation.

The caption now reads as:
Figure 2: Maps and time-series of the sediment section KC1. (A) X-ray density map with black crosses or rectangles where material was removed as markers for orientation of the samples, (B) exemplary swUk (spotwise $U_{37}^{K'}$) maps of one replicate per depth interval. Maps are shown as measured, on the MSI coordinate grid, before affine transformation onto Xray coordinates, values below 1% and above 99% quantiles were removed for optimal color scaling during plotting. (C) Scaled density plots of the spatial swUk maps per replicate, and (D) the resulting $U_{37}^{K'}$ time-series per replicate and depth interval. Note that the area corresponding to the 1761 AD floodlayer in depth interval 0-5 cm was removed prior to analyses.

Reviewer #1:

L220: need a subscript on “C0”
L230: C37:3 needs a subscript

Thank you for catching these.

The lines have been changed accordingly.

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