

Response to RC1 - Major comments

Author response:

We thank Reviewer #1 for their thorough and technically informed review. We appreciate their recognition of the value of the pCO₂, temperature, and salinity profile measurements and their constructive feedback on clarifying assumptions, terminology, and methodological limitations.

We also thank the RC1 for their detailed assessment of the eddy covariance (EC) CO₂ flux measurements and for highlighting the well documented challenges associated with water vapor cross sensitivity in undried open-path NDIR sensors over marine environments. We fully agree that this cross sensitivity represents a significant limitation for the quantitative interpretation of EC CO₂ fluxes in this study. In response to this and related concerns raised during the review process, we have revised the manuscript to explicitly frame the EC CO₂ flux observations as contextual evidence complementary to the seawater profiles, rather than as definitive quantitative constraints on flux magnitude.

We emphasize that the primary objective of this study is to document pronounced near-surface stratification in carbonate system parameters during sea-ice breakup and to examine how this vertical heterogeneity challenges the assumptions underlying standard bulk air-sea CO₂ flux parameterizations. The high-resolution pCO₂, temperature, and salinity profiles form the core observational result of the manuscript. The EC measurements are retained as complementary observations that illustrate the dynamic nature of air-sea exchange during this transition period, but the revised manuscript does not rely on them to infer absolute flux magnitudes or to validate bulk flux estimates.

Upon further review of the literature describing humidity-related biases, a comparative methodological study by Landwehr et al. (2014) demonstrated that water vapor cross sensitivity can result in order-of-magnitude biases in CO₂ flux estimates from undried IRGAs. However, under conditions of low latent heat flux ($|LE| < \sim 7 \text{ W m}^{-2}$), they found agreement between sensors operating with dried and undried airstreams, concluding that humidity-related bias was negligible below this threshold. We therefore include former Fig. S7 in the main text as Fig. 8, with these thresholds indicated, to illustrate which portion of the EC dataset from Young Sound falls within this low latent heat flux regime. Within this subset ($|LE| < \sim 7 \text{ W m}^{-2}$), EC flux estimates exhibit both positive and negative values. While we cannot exclude residual systematic bias, this behavior is consistent with the expectation that near-surface stratification in the inorganic carbon system may support short-lived deviations from bulk-model flux expectations, including potential reversals in flux direction. However, robust verification of these dynamics and quantification of air-sea CO₂ exchange during sea-ice breakup will require closed-path EC systems with dried air streams. This message is also now communicated more clearly in the revised manuscript.

Response to RC1 - Minor comments

We thank the reviewer for these helpful minor comments. All suggested clarifications, wording changes, and reference additions have been implemented in the revised manuscript as detailed below.

- **Line 32:** CO₂ is now defined at first use in the abstract.
- **Line 34:** The wording has been revised to clarify that bulk models assume no vertical pCO₂ gradients within the bulk seawater below the diffusive boundary layer.
- **Lines 37-38:** Clarified that the statement refers to waters at 1 m depth.
- **Line 67:** Added the suggested reference to Miller et al. (2019).
- **Line 79:** A reference to Wanninkhof et al. (2009) has been added.
- **Line 85:** “Many” has been replaced with “most.”
- **Line 94:** The sentence has been revised following the reviewer’s suggested wording for improved rigor and precision.
- **Line 135:** The figure caption has been updated to indicate that the schematic is adapted from Liss and Slater (1974) and Wanninkhof et al. (2009).
- **Line 176:** Bracket placement and punctuation have been corrected as suggested.
- **Lines 212-213:** The text has been revised to clarify how measurements were conducted in 2017 without recommending replication of this experimental setup. Additionally, we have added text to clearly state we cannot precisely constrain CO₂ flux magnitudes.
- **Lines 253-254:** The missing reference to Sejr et al. (2011) has been added.
- **Line 268:** Figure S2 was already referenced earlier in the text (line 225 of the original manuscript).
- **Line 452:** We thank the reviewer for raising this point and agree that classical cool-skin effects (typically <0.2 K; Donlon et al., 2002) would not be expected to strongly influence bulk $\Delta p\text{CO}_2$ relative to the much larger chemical and thermal gradients observed in this study. We would like to clarify that the temperature adjustment applied here does not assume a classical cool skin. Instead, we derive a near-surface temperature that is frequently *warmer* than the temperature measured at 1 m depth due to melt-driven stratification and surface warming during ice breakup. The pCO₂ measured at 1 m is therefore adjusted from in situ conditions to this derived skin temperature. Additionally, the derived skin temperature values were already present in Table 1. However, we recognize this was not clear. We have now made this more apparent by labelling these values in the table and including the text: † Denotes skin temperatures derived from heat fluxes. ‡ Denotes pCO₂ values estimated from measurements at 1 m depth and adjusted to derived skin temperatures.

Response to RC2 - Major comments

We thank Reviewer #2 for their careful, constructive, and encouraging assessment of our manuscript. We appreciate their recognition that the high-resolution near-surface $p\text{CO}_2$, salinity, and temperature profiles provide a compelling and chemically plausible explanation for how melt-driven stratification can bias bulk air-sea CO_2 flux estimates during the sea-ice breakup period. We also thank the reviewer for their clear guidance on how the eddy covariance (EC) data should be framed to strengthen the manuscript.

We fully agree that the quantitative robustness of open-path EC CO_2 fluxes in marine environments is limited by water vapor cross sensitivity. In response to these concerns, we have revised the manuscript as recommended by RC2 to explicitly acknowledge the EC limitations and reframe the EC observations as qualitative context rather than as definitive quantitative constraints.

In the revised manuscript, the primary conclusions are now based on the independently measured near-surface carbonate system structure, which robustly demonstrates strong vertical $p\text{CO}_2$ heterogeneity during sea-ice breakup. This results in varying flux magnitudes depending upon the depth chosen in the bulk parameterization. The EC data are retained to illustrate the high variability of air-sea CO_2 flux estimates during this period and discuss the possibility for oversaturation during seasonal sea-ice transition as a result of heightened stratification.

Response to RC2 - Specific comments

We thank the reviewer for the following specific and helpful comments, all of which have been addressed in the revised manuscript.

- **Line 34** The text has been revised to clarify that bulk flux models assume no vertical $p\text{CO}_2$ gradients within the bulk seawater below the diffusive boundary layer
- **Lines 167 & 404** We have removed the discussion of potential physical disequilibrium after recognizing that it is not relevant for the conclusions of the manuscript. The mismatch between calculated and measured $p\text{CO}_2$ noted by the reviewer is already described in the Methods section.
- **Lines 206 & 495** In line with the reviewer's recommendation, we have reframed the EC data as qualitative context supporting the possibility that air-sea exchange during ice breakup may differ in sign, while explicitly acknowledging that open-path cross sensitivity likely inflates flux magnitudes. The revised manuscript does not rely on EC data to establish quantitative flux constraints.
- **Lines 450** We thank the reviewer for raising this point and agree that classical cool-skin effects (typically <0.2 K; Donlon et al., 2002) would not be expected to strongly influence bulk $\Delta p\text{CO}_2$ relative to the much larger chemical and thermal gradients observed in this study. We would like to clarify that the temperature adjustment applied

here does not assume a classical cool skin. Instead, we derive a near-surface temperature from the measured heat fluxes that is frequently *warmer* than the temperature measured at 1 m depth due to melt-driven stratification and surface warming during ice breakup. The pCO₂ measured at 1 m is then adjusted from in situ conditions to pCO₂ at the derived skin temperature. Furthermore, the derived skin temperature values were already present in Table 1. However, we recognize that this was not obvious. We have now made this more apparent by labelling these values in the table and including the text: † Denotes skin temperatures derived from heat fluxes. ‡ Denotes pCO₂ values estimated from measurements at 1 m depth and adjusted to derived skin temperatures.

- **Figure S7 (now Figure 8):** As suggested, this figure has been moved to the main text and is now referenced when discussing the reliability and uncertainty of the EC flux estimates.