

***Interactive comment on* “Sea-ice melt CO₂-carbonate chemistry in the western Arctic Ocean: meltwater contributions to air-sea CO₂ gas exchange, mixed layer properties and rates of net community production under sea ice” by N. R. Bates et al.**

Anonymous Referee #1

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Bates et al. “Sea-ice melt CO₂-carbonate chemistry in the western Arctic Ocean: meltwater contributions to air-sea CO₂ gas exchange, mixed layer properties and rates of net community production under sea ice”

This study describe the CO₂-carbonate chemistry of sea-ice melt (both above sea ice as “melt ponds” and below sea ice as “interface waters”) and mixed layer properties in the western Arctic Ocean in the early summer of 2010 and 2011. The partial pressure

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of CO₂ (pCO₂) in these melt ponds was found to be highly variable (< 10 to > 1500 μatm) with the majority of melt ponds acting as potentially strong sources of CO₂ to the atmosphere. The pH of melt pond waters was also highly variable ranging from mildly acidic (6.1 to 7) to slightly more alkaline than underlying seawater (8 to 10.7). All of observed melt ponds had very low (< 0.1) saturation states (Ω) for calcium carbonate (CaCO₃) minerals such as aragonite. It is suggested that sea ice generated “alkaline” or “acidic” melt pond water. Although sea-ice melt is a transient seasonal feature, above-ice melt pond coverage can be substantial (10 to > 50 %) and under-ice interface melt water is ubiquitous during this spring/summer sea-ice retreat. The authors conclude that there are growing evidence that sea-ice CO₂-carbonate chemistry is highly variable and its contribution to the complex factors that influence the balance of CO₂ sinks and sources (and thereby ocean acidification) is difficult to predict in an era of rapid warming and sea ice loss in the Arctic Ocean. The manuscript reads well, but I find pCO₂ concentrations (>1500 μatm) and rates of CO₂ fluxes record high (400 mmol/m²/d). Something must be wrong here. There must be a factor 10 or 100 wrong - where is all the carbon coming from? I would like the authors to check if there is a calculation error here – if not then the findings are exceptional. I recommend publication after considering my specific comments below.

Specific comments:

Page 1100, line 18: Low temperatures and low buffering capacity. Replace 2nd low with ‘high’.

Page 1101, line 24-16: I would be careful referring to many 1000’s μatm in bulk sea ice! In the brine it is ok, but bulk Im not so sure.

Page 1002, line 19: Sejk should be Sejr

Page 1003, line 15: ‘B(OH-)’ missing here.

Page 1104, line 6: Add how you analyzed Chl a.

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Page 1105, line 8-19: Think one should be careful when calculating $p\text{CO}_2$ and saturation indexes based on formulas for typical sea water, as we do not know the ion composition in sea ice meltwater. Do you have any data of direct $p\text{CO}_2$ measurements in melt ponds? You need to specify your assumptions here.

Page 1110, line 11: Very high $p\text{CO}_2$ values $>1500 \mu\text{atm}$. Do you have any independent measurements of this, e.g. direct measurements.

Page 1111, line 8: “Using these data, it is possible to constrain the chemical composition of sea ice”. For reasons described above (comments to 1105, line 8-19) you should be careful here.

Page 1111, line 20-23. “While there is undoubtedly some variability in CO_2 -carbonate composition in sea-ice imparted during initial formation and winter metabolism, we assume that sea-ice had a fairly uniform chemical composition before spring melt”. I do not know how you can assume this. What about difference in primary production and heterotrophic activity due to pre- and spring bloom conditions. In order to explain such large CO_2 fluxes (as indicated later) I find this highly risky business.

Page 1115, line 15. I do not understand how you can get so high values of $p\text{CO}_2$. They are much above atmospheric saturation. Melt ponds will equilibrate with the atmosphere. Could it be due to chemical composition of melt do not represent standard ocean water and thus the equations does not work? Again, do you have any direct measurements to support these calculations?

Page 1115, line 18-23: “Unlike the alkaline above-ice melt ponds, in the acidic above-ice melt ponds, meltpond water, CO_2 -equilibria dictates that carbonate species were only present in the form of dissolved CO_2 [$\text{CO}_2 + \text{H}_2\text{CO}_3$] with negligible [HCO_3^-] and [CO_3^{2-}] present. The mildly acidic pH (6.1 to 7.5) of several sea-ice melt waters sampled during the ICESCAPE expeditions (Fig. 10a) was unusual compared to typical seawater conditions.” At pH 6.1 there should still be $>40\%$ HCO_3^- left. At 7.5 $>90\%$ of the carbon should be HCO_3^- . You need to rephrase this.

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Page 1117, line 17: Again I find these $>1500 \mu\text{atm}$ difficult to understand

Page 1118, line 19: 'been' is missing before 'reported'

Page 1118, line 23: Replace Sejk with Sejr

Page 1118, line 24-28: Remember that the high pCO_2 is in the brines. Bulk pCO_2 will always be lower than the atmosphere (if rejected together with the salts) unless you have a large heterotrophic activity - but where is all the carbon coming from to provide that? Should be possible to calculate the heterotrophic activity in $\text{mmol/m}^2/\text{d}$ and compare with literature values to see if this is realistic or not. One source could be the DOM in sea ice or water, but the autotrophic and heterotrophic activities must be huge to account for this (we are talking entire annual production!). I have worked a lot in Greenland waters, and have never seen anything like this.

Page 1119, line 1-3. Any Chl a, primary production and/or bacterial production data to support this? Page 1120, line 2: Replace section 4.3 with 4.3.3

Page 1120, line 15-18: I find these rates record high ($400 \text{ mmol/m}^2/\text{d}$). Something must be wrong here. There must be a factor 10 or 100 wrong - where is all the carbon coming from. Fluxes of this magnitude for 20 d are comparable with all the carbon from the entire annual PP in the many productive arctic seas!! Also it is very difficult to figure out how this flux is calculated. More details are needed.

Page 1120, line 23-26: What are the fluxes in the alkaline above-ice melt ponds (with very low pCO_2 values? Could you provide an estimate, or make reference to previous measurements? E.g. Geilfus et al. 2012.

Page 1122, line 12: 'This approach is simplified by assumptions that sea-ice cover is a barrier to air-sea CO_2 gas exchange' – is that during winter? As I understand this you have shown that sea ice modify the carbonate system and therefore definitely do not act as a lid sealing of the air-sea CO_2 exchange.

Page 1123, line 1-3: You have to be really careful here. Calcium carbonate production

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in sea ice during winter produce CO₂ that is rejected to the underlying water column. See Rysgaard et al 2011 (Tellus paper cited in your manuscript) for the proposed mechanism. Could this CO₂ be misinterpreted as heterotrophy?

Page 1123, line 10: Where does the simulated primary production come from?

Page 1123, line 15: Given the large interval, it's hard not to be within the range observed for primary production ;-) Figure 1: Think you can combine both figures into one, and then in the legend describe the difference between autotrophy and heterotrophy

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