## Anonymous Referee #1

Received and published: 5 March 2014

**Author Response:** We sincerely thank Referre #1 for their thoughtful and thorough comments that have improved the paper. We have added statements in **blue** below that detail our response to each comment. All the comments and their corrections were minor in nature, and we have added a few clarifying statements in the introduction, method and discussion

Referee comments:

Bates et al. "Sea-ice melt $CO_2$-carbonate chemistry in the western Arctic Ocean: meltwater contributions to air-sea $CO_2$ gas exchange, mixed layer properties and rates of net community production under sea ice" This study describe the $CO_2$-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 of $CO_2$ ($pCO_2$) 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 $CO_2$ 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 ($CaCO_3$) 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 $CO_2$-carbonate chemistry is highly variable and its contribution to the complex factors that influence the balance of $CO_2$ 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 $pCO_2$ concentrations (>1500 µatm) and rates of $CO_2$ fluxes record high (400 mmol/m$^2$/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.

We thank the reviewer for their very helpful comments. We have rechecked the computations again and find high $pCO_2$ (as stated in the original submission) for the Canada basin melt ponds. As we discuss below, the increase in [$CO_2$] is about 15-20 µmol so it is possible that the melt ponds in this particular location can manifest high levels from contributions of $CO_2$ from sea-ice. At the highest end, one might get very high rates of gas exchange, but we provide additional caveats in the revised paper. Most of the melt ponds we sampled had much lower $pCO_2$ and a substantial number may have taken up $CO_2$. There are other locations with similarly high $pCO_2$ in the East Siberian Sea (e.g., Tiksi bay) although different processes are at play.

Specific comments:

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

This is corrected in revised text.

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.

We have clarified this in the text. If you take the few carbonate chemistry data reported for sea-ice cores, some of the computed $pCO_2$ values exceed tens of thousands. This is face-value use of other peoples' data, and there could be problems with analytical techniques for sea-ice analysis.

Page 1002, line 19: Sejk should be Sejr

This is corrected in revised text.

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

This is corrected in revised text.

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

This is added to in the methods section.. Chl a was determined both with fluorometry and HPLC.

Page 1105, line 8-19: Think one should be careful when calculating $pCO_2$ 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 $pCO_2$ measurements in melt ponds? You need to specify your assumptions here.

We have added statements about this. We have to assume that the ionic strength of melt water is proportionate to seawater and that brine rejection and melting have not substantially altered the contributions of $Ca^{2+,}$ $Mg^{2+}$, etc, and if they have, these processes have also proportionately altered carbonate and bicarbonate. Unfortunately, we did not have $pCO_2$ sensors for the melt ponds, but hopefully the "fet"s might be reliable in future studies.

Page 1110, line 11: Very high $pCO_2$ values >1500 µatm. Do you have any independent measurements of this, e.g. direct measurements.

We did not have direct measurements of $pCO_2$. However, such high $pCO_2$ would be expected in lower pH environments (especially at pH of <7 where due to $CO_2$ equilibria, there would be an absence of $[CO_3^{2-}]$ and smaller amounts of $[HCO_3^-]$). The concentration of $[CO_2]_{aq}$ in the melt pond water would be small (~20-45 µM), but $pCO_2$ or fugacity will be high relative to what we would expect to see in surface waters. Such high $pCO_2$ values are not uncommon in the Arctic (>1500 µatm in Tiksi Bay waters of the East Siberian Sea; >900 µatm in Long Strait in the Siberian Sea current in surface waters). There is a different cause and set of circumstances behind these observations though (i.e., high respiration rates of allochthonous and autochthonous derived DOM/POM in the river/estuaries of these Siberian Sea shelves).

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.

We have restated the caveats in the revised paper.

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.
We have added a caveat that brine reduction, pre-conditioning, etc would add variability. However, our previous early spring surface and water-column water data has indicated that the winter water on the Chukchi Sea shelf has a relatively constrained range of DIC and TA relative to salinity, and we use this observation to constrain the source water for winter sea-ice.

Page 1115, line 15. I do not understand how you can get so high values of $pCO_2$.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?
Please see our comments earlier about $CO_2$ equilibration in lower pH waters.

Page 1115, line 18-23: “Unlike the alkaline above-ice melt ponds, in the acidic above ice melt ponds, meltpond water, CO2-equilibria dictates that carbonate species were only present in the form of dissolved CO2 [CO2 + H2CO3] with negligible [HCO-] and [CO2-] 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% HCO3 left. At 7.5 > 90% of the carbon should be HCO3-. You need to rephrase this.
Please see our comments earlier about $CO_2$ equilibration in lower pH waters. The text is corrected to illustrate the proportion of $[HCO_3^-]$ at pH of 6.1 for example (i.e., 35%).

Page 1117, line 17: Again I find these >1500 µatm difficult to understand
Please see our comments earlier about $CO_2$ equilibration in lower pH waters

Page 1118, line 19: ‘been’ is missing before ‘reported’
This is corrected in revised text.

Page 1118, line 23: Replace Sejk with Sejr
This is corrected in revised text.

Page 1118, line 24-28: Remember that the high $pCO_2$ is in the brines. Bulk pCO2 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 mmol/m2/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.
In the more acidic melt ponds, the concentration of $[CO_2]_{aq}$ in the melt pond water is

about ~20-45 µM, compared to mixed layer values of ~10 to 18 µM. One source of $CO_2$ could be DOM as you have indicated. The Sogaard et al 2013 paper, which came out after the submission of this paper, was very helpful and shows a build up of DOC in sea-ice of 40-60 µM, for example. In the western Arctic, the seasonal water column production on the Chukchi Shelf does not produce much DOC (POC instead), while the river influenced surface waters transported from the East Siberian Sea to the Chukchi Sea has higher DOC (by up to 40 µM compared to "Pacific" water). The interesting feature for the melt ponds studied here, is that the relatively high $pCO_2$ was only observed over the Canada Basin, and not over the Chukchi Sea (which seems more like the Greenland and Canadian Archipelago studies). The Gosselin et al 1997 data showed rates of up to 310 mg C $m^{-2}$ $d^{-1}$ total sea-ice algal production suggesting that there is sufficient OM to generate $CO_2$ in the melt ponds. The melt pond water in the Canada Basin, we sampled were probably also earlier in their NEM sequence which might argue against net heterotrophy. But $CaCO_3$ formation (e.g., Ikaite) seems low in the Greenland sea-ice (~2 to 4 µmol $l^{-1}$; Fig. 5; Sogaard et al.). We don't have sea-ice $CaCO_3$ concentrations from the environs of the melt ponds unfortunately.

Page 1119, line 1-3. Any Chl a, primary production and/or bacterial production data to support this?
We have chlorophyll a data from 2011 which will be referred to in the text.

Page 1120, line 2: Replace section 4.3 with 4.3.3
This is corrected in revised text.

Page 1120, line 15-18: I find these rates 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. 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.
This has been expanded upon, and a caveat to the highest flux rate (from Wanninkhof 1992 issues). Rapid remineralization of sea-ice OM (if production rates in sea-ice are 50 to 300 mg C $m^{-2}$ $d^{-1}$) could contribute to the maximum efflux of 35 mg $m^{-2}$ $d^{-1}$ (i.e., converted from 400 mmoles $m^2$ $d^{-1}$). We agree that the highest rate of efflux (again observed over the Canada Basin) are highly unlikely, and we discuss these caveats (including the barriers to effective gas exchange) in the revised paper. The PP or NCP of the Chukchi Sea euphotic zone can also get up to 2 to 4 g C $m^{-2}$ $d^{-1}$, so even the highest efflux would be

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.
Again there would be caveats to this but one might estimate maximum influx rates of 100 mmoles $m^2$ $d^{-1}$ (i.e., based on $\Delta pCO_2$ of ~300 µatm and winds of 10 m $s^{-1}$)

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 no contact 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 in sea ice during winter produce $CO_2$ 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 $CO_2$ be misinterpreted as heterotrophy?
Yes, but we don't know how much $CaCO_3$ was produced. If we have similar build up of ~4 µmol $L^{-1}$ of $CaCO_3$ in sea-ice over the winter/early spring season (as in the Sogaard et al., study in Greenland), the production of $CO_2$ would be relatively small to the difference in [$CO_2$] between the most acidic melt pond water and their underlying mixed layer. $CaCO_3$ production rates don't seem sufficient to explain the build up of $CO_2$, but of course, the Canada Basin sea-ice scenario "could" be different.

Page 1123, line 10: Where does the simulated primary production come from?
The PP data comes from Manizza et al., 2013's paper on the western Arctic.

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
We have re-thought this figure as suggested.