Response to Reviewer #3

I have embedded specific responses to Reviewer #3's detailed and helpful comments below. Reviewer comments are in italicized text and my responses are in plain text. Excerpts from the revised text are in bold.

-Brendan and coauthors

Anonymous Referee #3

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Review of "Processes determining the marine alkalinity and carbonate mineral saturation distributions" by Carter et al.

This paper presents some interesting analysis of alkalinity and carbonate saturation. The analysis and main conclusions are on the whole (although not always) reasonable and well-founded. Some aspects of the analysis can benefit from improvement. The manuscript is generally clear and fairly well written but some sections need attention and previous work is often not acknowledged.

Overall recommendation: resubmit following revision

Main comments:

1-3, 98: The way the text is written makes it seem as if it is a benefit to have a composite tracer, one that also "highlights" river alkalinity plumes. However, the general philosophy of developing tracers is normally to subtract off as many confounding influences as possible so as to get to a variable that (ideally) traces the activity of just one biogeochemical process, or if not just one then as few as possible. The more competing influences (multiple processes) that impact on a tracer, the harder it is to deconvolve them in order to use the tracer to assess the rate of just one, and in general the less useful the tracer is. For the topic of this paper, it is less useful to have a tracer that is influenced by both carbonate cycling at sea and carbonate cycling on land (via rivers), because variation in the tracer cannot then be attributed unambiguously to either one or the other. This can be seen in, for instance, in lines 210-214. On line 3 the word "highlights" should be replaced with something more appropriate (e.g. "is also affected by"); likewise "preserves" should be changed to "is altered by" or similar wording on line 98.

We made the recommended changes (by replacing "highlights" with "is also affected by" and eliminating the portion of the sentence in which "preserves" appears. We think it is important to emphasize that *Alk** retains riverine alkalinity because earlier readers missed that point and became confused later.

52-61: there are a number of problems with the nitrogen cycle section. The chemical processes are all unidirectional rather than reversible and hence one-way arrows should be used. Ammonia (NH3) should be replaced by ammonium (NH4) because this is the dominant form (~90%) at typical seawater pH. Nitrification converts ammonium to nitrite to nitrate (in two steps); not the opposite reaction as stated in R1. Nitrogen fixation initially *creates PON from N2. It is only later following the creation of ammonium from PON (ammonification) during nitrogen fixer decay and after that nitrification to convert the ammonium to nitrate that nitrate is eventually produced.*

We originally tried to combine several reaction pathways for brevity. In this draft we decided to limit this discussion further and provide the following summary sentences, which address only the material we need to make clear:

Nitrate uptake for anaerobic denitrification and the production of amino acids occurs in an ~1:1 mole ratio with the release of molecules that increase A_T (Chen 2002). Similarly, nitrate produced by fixation of nitrogen gas and remineralization of amino nitrogen is released in a 1:1 mole ratio with acids that titrate away A_T (Wolf-Gladrow et al., 2007).

Section 3.3: This section is a little weak and not as tightly written as most of the rest of the MS. The tracer is less useful for quantification in heavily river-influenced areas because of the dual influences of in-situ calcification/dissolution and river effects, with uncertainty about how to separate the two. This section could perhaps be streamlined to include only rivers impacting on the open ocean. It would certainly help the reader follow the logic if some explanation could be given as to why Alk is calculated for rivers such as the Daugava which empties into the Baltic Sea, and the Yangtze which empties into the Yellow Sea, both of which places are blacked out (because no carbonate system data) in figure 2c.*

We cut a lot of material here, including everything having to do with the marginal seas and about half of what we had devoted to the Amazon. We did this for brevity and because this section doesn't add much, as Reviewer 3 and others pointed out.

Section 4: There is a fairly abundant although scattered literature of prior work on this topic, at least some of which should be cited. The results developed here need to be critically compared to findings from other work (for instance Orr et al 2005), including regional observational studies, for instance Yamamoto-Kawai et al 2009, Bates et al 2009, Mathis et al 2012, Shaw & McNeil 2014, Tynan et al 2014. While the results obtained from deep water seem to be broadly consistent with previous work, those from surface water are less so. In particular, the inferred importance of organic matter cycling seems very low in comparison to other work (Tynan et al 2014 in particular).

We have endeavored to add mention of some of these papers (see text below, starting with "**Despite this…**")

However, I'm not convinced that these papers are directly comparable to our discussion. The cited studies address the controls on variability at a given location over time. By contrast, we focus on why various regions throughout the world have such different baseline carbonate saturations about which they vary with time. Analogous seemingly-contradictory (but not mutually exclusive) findings would be: "Arizona has some big storms" and "Arizona is an arid place relative to the rest of the world."

This is probably due to the problematic assumption in this study that surface seawater is in equilibrium with an atmosphere of 400 ppmv CO2, although the authors also calculate without this assumption. While the assumption of air-sea equilibrium is reasonable over broad swathes of the (relatively quiescent) tropical and subtropical oceans, it is often strongly violated at high latitudes, with large and long-lasting depressions in pCO2 (e.g.

>100ppmv) caused by spring phytoplankton blooms. Either the analysis should be revised to more fully explore and take account of this flawed assumption, or else the reason for the discrepancy between the findings here and in other studies should be more fully explained. The authors are doubtless correct about the strong importance of temperature, although it is not clear that the reason for the importance of temperature is understood. The underlying reason is the effect of temperature on gas solubilities (CO2 solubility) and hence CO2 gas exchange (see in particular figure 6.5 and chapter 6 of Williams and Follows 2011).

In our defense, we made this link explicitly in the abstract in the previous version… though we perhaps make it more clearly now:

We show regional differences in surface calcite saturation are due to the effect of temperature differences on CO_2 solubility and, to a lesser extent, differences in freshwater content and air-sea disequilibria.

Larger inputs of deep water to high latitude surface water may also be important (Orr et al., 2005). These should be mentioned. Again previous work on the topic should be acknowledged and the findings of this study related to (and explained in the context of) previous findings.

Regarding Tynan et al. 2014, they have a nearly opposite finding to our own… specifically they find organic matter formation is important and the effects of temperature changes are negligible. However, this is because their calculations presume that all saturation change from organic matter formation occurs without the opportunity for re-equilibration. Similarly, they do not account for the changes in equilibrium C_T with changes in temperature. They therefore essentially use a calculation equivalent to our poorly-equilibrated-seawater calculation. Casual inspection of their data suggests that the temporal variability in carbonate saturation could be reasonably well explained by temperature variability if they allowed for the influence of temperature on equilibrium C_T. I do not mean to imply they are wrong, merely that presuming no gas exchange is just as perilous as presuming complete gas exchange. We try to presume neither. Instead, we try to make it clear here that our two calculations represent extreme cases and that the appropriate calculation will depend on the timescale considered. We've added the following text to highlight this distinction:

Despite this, it is important to recognize that air-sea equilibration following a process is not instantaneous, and that the S_{R_i} value estimates in section 4.1 will be better for estimating short term changes following fast acting processes such as spring blooms (e.g. Tynan et al., 2014) or upwelling events (e.g. Feely et al., 1988).

Appendix A: this is very hard to follow. The analysis is over-elaborate and could probably be simplified without loss of rigour. It is not clear why so many steps are required for what is seemingly quite a simple calculation. Example calculations should be shown to make the explanations more concrete.

We have tried to simplify this further several times. We tried again with this draft (see our response to Reviewer 2), but most more invasive options that we came up with do require some loss of rigor.

Detailed comments:

6-7: according to Fig 2c, net carbonate precipitation lowers Alk" across the low latitudes in all basins, not just the Indian and Atlantic.

We were originally referring to the mean values, which by themselves do not support this correct statement (due to upwelling in the North Pacific). We still emphasize the Indian and the Atlantic in the Abstract because these two oceans had lower mean *Alk**, even when only considering the subtropics. We rewrote portions of the basin mean value discussions to make this clear, and changed this portion of the abstract to read:

Strong net carbonate precipitation results in low *Alk in subtropical gyres, especially in the Indian and Atlantic Oceans.**

24: why work with gridded rather than bottle data? A reason should be given.

We now give our reason:

We use our gridded dataset to limit sampling biases and to enable us to make volume-weighted mean property estimates.

72: potential alkalinity usually also includes salinity normalisation. The definition here is unusual.

The original potential alkalinity from Brewer et al. 1975 did not normalize to salinity, though Reviewer 3 is correct that there have been papers that refer to it as though it did.

106-107, fig 1: Jiang et al 2014 discusses the non-linearity of NTA and the consequence thereof. It is done in greater detail and with greater rigour, and can be cited for this point. Fig 1 could be deleted.

This very recent paper did help simplify the discussion of this topic. We now refer to Jiang et al. (2014) in the discussion, and we have moved most of our calculations to supplementary materials.

In Supplementary Materials document SC we demonstrate that *Alk mixes conservatively, and briefly contrast *Alk** to traditionally normalized potential alkalinity which does not mix conservatively (Jiang et al., 2014).**

137: is the physical process always upwelling?

If I understand the question correctly, then I believe yes.

154: presumably "Net precipitation in the tropics and net evaporation in the subtropics..."

Correct. We changed the text in this draft to read as presumed.

180-187: which of these differences are statistically significant?

This is a tough question to answer well, and an even harder one to answer in few words. Uncertainty on the gridded *Alk** values can be estimated from the differences between measurements and the gridded values at each measured location. However, this is likely an uncertainty overestimate because measurements and the gridded data can disagree without either being wrong… simply because they represent different quantities (one is averaged in time and space and the other is not). Nevertheless, using this approach suggests our gridded estimates have a standard uncertainty of ~10 $\mu\text{mol kg}^{-1}$. When we consider that we are averaging a large number of these gridded values (6092 for the Atlantic) the uncertainty on the mean value becomes quite small (~0.1) if we presume (almost certainly incorrectly) that the errors in the gridded values are uncorrelated. Given the many caveats to this assessment, I am not confident saying that the Atlantic and the Indian have different mean *Alk** values. I am confident that all other oceans are different, as defined, however. This thinking motivates the language we use to frame this discussion.

182: Alk" cannot be measured directly. This should be reworded, for instance: "The Atlantic has the highest measured TA in the open-ocean surface but the lowest Alk" and..."

Good point. We removed the word "measured" here and elsewhere.

185-187: A near-zero mean value does not imply balance. All basins must be balanced unless the authors are making the unlikely suggestion that mean values are changing over time where Alk" is high.

We clarified our meaning in this version:

Considering the weak Pacific riverine input, this suggests that, relative to other ocean basins, there are either larger *Alk inputs from exchange with other basins and deeper waters or smaller Pacific basin mean net calcium carbonate.**

203-214, 354-355: This section should be deleted (along with figure 7?) unless anything new can be said compared to the papers by Cooley et al (2006; 2007), which should be cited. The conclusion is not new.

We truncated this section and cited the Cooley et al. (2007) paper.

However, the influence of the Amazon on *Alk can be seen in the seasonal *Alk** cycle in the Amazon plume. Figure 7 provides a map of *Alk** for this region scaled to show the influence of this low *Alk** river in the Northern Hemisphere (a) winter and (b) summer months. The higher *Alk** found for summer months is consistent with Amazon discharge and A_T seasonality (Cooley et al., 2007) and Moore et al.'s (1986) radium isotope based finding that Amazon River outflow comprises 20-34% of surface water in this region in July compared to only 5-9% in December.**

251: Jiang et al 2014 should be cited for low alkalinity values in the Red Sea, and calcification as the reason. They carry out a more thorough separation of salinity and calcification effects, reaching the same conclusion. It could be noted that the analysis is stronger for Red Sea than for elsewhere because no sizeable rivers flow into the Red Sea and so decreases in Alk" can be attributed straightforwardly to calcification.

We tried to keep out discussion brief:

Like Jiang et al. (2014), we attribute low Red Sea *Alk to exceptionally active calcium carbonate formation.**

268: better in what way?

We have clarified that we are referring to the fact that the magnitude of the feature could not be explained by ikaite cycling.

However, riverine A_T inputs better explain the magnitude of the feature:

280-281: delete "are". Reword "depth changes of seawater".

We changed this to "pressure changes of seawater" for clarity.

337: salinity is not normally expressed in units of g/kg.

Fixed

339: the sentence should be reworded to explain that it is not the current (deep) temperature that ensures high 52, but rather the warm temperature when it last left the surface (which would have ensured CO2 outgassing until the surface seawater was driven to a low [CO2(aq)] commensurate with a CO2 partial pressure of ~400 ppm at low solubility; when low CO2 concentration is achieved through gas exchange then it drives carbonate ion concentration to high values).

We struggled with how to (and whether to) clarify our meaning here in the last draft as well. In this draft we say:

The deep Red Sea is also unusual for having deep water that was warm when it last left contact with the atmosphere (the Red Sea is >20 °C at >1000 m depth). This provides high initial deep calcite saturation that—combined with decreased influence of pressure changes at higher temperatures—keeps deep Red Sea Ω_C > 3.

362-364: temperature has little direct effect on 52 (table 1.1.6 of Zeebe & Wolf-Gladrow 2001) so it is confusing to include both temperature and air-sea gas exchange in this sentence. A high rate of primary production (to be expected in river plumes) is a more common way of inducing a strong increase in 52.

We got rid of this sentence during our pruning of the conclusions section.

367-368: calcium carbonate cycling is also usually less important to 52 than organic matter cycling, even in coral reef lagoons.

Interesting!

372-373: this sentence should be reworded – Alk" is not a process. The meaning of the term "lower cocnentrations of recently-upwelled remineralized CT" is not clear.

We got rid of this sentence during our pruning of the conclusions section.

375: the direct temperature effect is minimal. It is the other two factors that matter.

We also got rid of that sentence entirely.

382-383: this should be explained more clearly or removed, given that the direct temperature effect is minimal.

We got rid of this sentence as well.

Figure 6: the colorbar needs a label with units. The meaning is unclear for the sentence in the caption beginning "Due to the log scale..."

We remade the figure without cutting off the label, and removed that sentence from the caption (we removed the 2nd set of panels for A_T and S because we didn't discuss them):

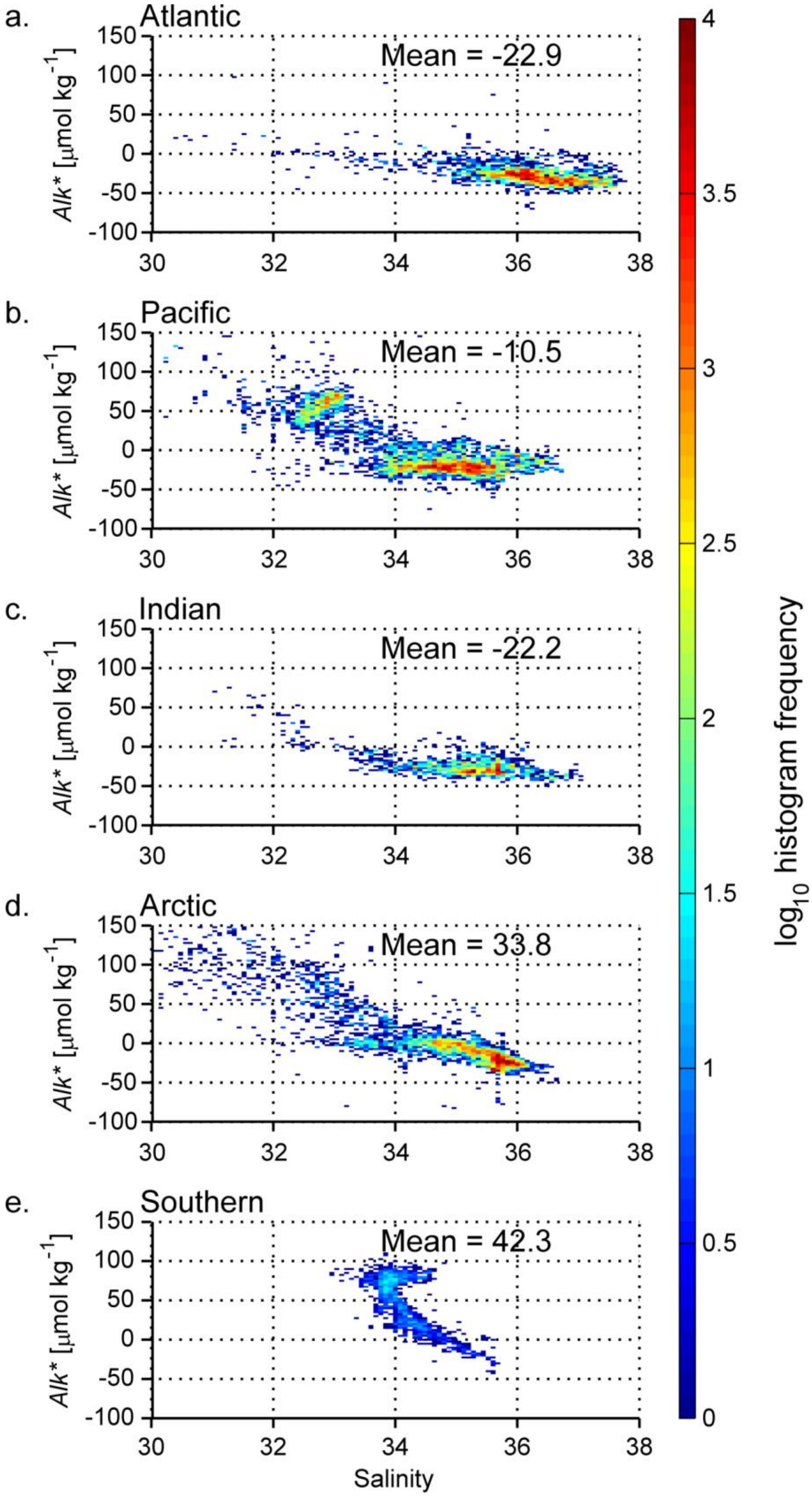

Figure 7: The red circles showing discharge volumes should be positioned closer to the point of entry of the rivers into the ocean.

I am hesitant to move these circles because I only have the locations as given in the Dai and Tenberth paper. It would be guesswork if I moved them closer to the ocean. Also, I believe the dots correspond to where the flow was estimated.

References:

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