Response to Reviewer #4

I have embedded specific responses to Reviewer #4'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

Reviewer #4

*Comments on **Biogeosciences Discuss., 2014-354**: "Processes determining the marine alkalinity and carbonate saturation distributions" by **B. R. Carter** et al.*

I. General comments

In this manuscript, the authors introduce a composite tracer Alk to study the process determining the marine alkalinity and calcium carbonate saturation distributions. The authors present the global distributions of Alk* and estimate the riverine AT budget for different ocean basins. On regional scale, the authors highlight the high Alk* near river mouths due to riverine input and low Alk* in the Red Sea due to biological precipitation of CaCO3. For the variability of carbonate saturation state, the authors define a metric to evaluate the importance of various controlling factors. Overall, the subject of this manuscript meets the general interest of Biogeosciences and I support the publication of this work after a moderate modification. Please see below for my detailed comments.*

II. Specific comments

1. *p11141, line 18-21: "The marine AT distribution is affected by the cycling of carbonate, freshwater, and organic matter, so we develop the quasi-conservative tracer Alk* to isolate the influences carbonate cycling."*

Variations of alkalinity in the ocean are mainly controlled by the following processes: 1) mixing between different water masses, (2) precipitation and evaporation, (3) production and remineralization of organic matter, (4) precipitation and dissolution of CaCO3, (5) external sources such as riverine input, underground water, hydrothermal vent fluids, (6) redox reactions in anaerobic environment [Chen, 2002]. By integrating the concept of potential alkalinity, the tracer Alk is not affected by production and remineralization of organic matter (process 3). In addition, the influence of precipitation and evaporation (process 2) is removed by using the salinity-normalization method of Robbins (2001). On general, Alk* is primarily affected by mixing (process 1), precipitation and dissolution of CaCO3 (process 4), riverine input (process 5). However, it should be mentioned that, in some special marine environments, the contributions of hydrothermal vent fluids, and redox reactions may be significant. In these cases, Alk* is no longer a good "tracer to isolate the influences of carbonate cycling".*

We now explicitly mention other anaerobic redox processes throughout the paper, and include a reworded version of the caution suggested above. We feel confident implying *Alk** removes the majority of the influence of non-sedimentary redox reactions since potential alkalinity does adjust for denitrification, nitrate is the first of many electron acceptors to be utilized in anoxic environments, and nitrate is almost never fully depleted outside of sediments.

6. **It is however affected by anaerobic redox reactions (Chen, 2002).**

We are primarily interested calcium carbonate cycling, item 3 in our list. In section 2 of this paper we therefore define a tracer we call *Alk that removes the majority of the influences of organic matter cycling (item 4), freshwater cycling (item 2), and non-sedimentary anaerobic redox reactions (item 6) while still mixing conservatively, remaining insensitive to gas exchange, and responding to calcium carbonate cycling.**

…later…

The influence of organic matter cycling on A_T is due primarily to the biologically-driven marine nitrogen cycle. 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).

…later…

However, hydrothermal vent fluid and non-denitrification anaerobic redox chemistry may substantively affect alkalinity distributions in some marine environments. *Alk distributions could not be attributed purely to calcium carbonate cycling in these locations.**

7. *p11142, lines 7-19.*

Please revise these sentences for a more accurate description of nitrogen cycle and its influence on alkalinity.

The three reaction equations here are questionable (e.g., nitrification starts from NH3 or $NH4^+$ *in R1, R2 gives unrealistic product O2 in denitrification). These equations are not really useful for the following discussion and I suggest to remove them. If the authors want to keep these equations, please refer to the equations by Wolf-Gladrow et al. [2007]*

We have removed these equations and now refer to (Wolf-Gladrow et al., 2007) here. The revised text is provided as part of the response to the last point (beginning with "**The influence**…")

p11144, Eqs. 3-5

The global mean passive conservative potential alkalinity (AP^C*) is subtracted from potential alkalinity (AP) to calculate Alk* (Eqs. 3-5). Instead of using the global mean* AP^C*, is it better to use the mean surface* AP^C *in the low-latitude tropical open oceans? In these oligotrophic waters, influences of riverine input, convection and biogenic CaCO3 production are minor while most of alkalinity variability is controlled by precipitation and evaporation [Jiang et al., 2014; Millero et al., 1998]. Therefore, it provides a better reference for defining Alk*. In this way, positive Alk* indicates alkalinity inputs (riverine inputs, upwelled deep water et al.) while negative Alk* suggests alkalinity removal (CaCO3 precipitation et al.).*

These are indeed regions where evaporation and precipitation are more dominant of controls on alkalinity than elsewhere, but evaporation and precipitation play major roles in other regions as well. If we tailored our *Alk** definition to these regions, then our definition would be less well-suited for, for instance, the high latitudes where net precipitation dilutes waters enriched in alkalinity from upwelling and rivers. It seems to us that the most balanced definition is obtained by using the global volume-weighted surface mean value.

p11144, lines 14-24.

The authors discuss the difference between Alk and the typical salinity-normalized result (sAP). The reasons why "sAP does not mix conservatively, has a variable response to carbonate production, and yields an undefined value for a riverine end-member with zero salinity and non-zero AP" and "the non-linearity of sAP" are discussed in detailed by Jiang et al. [2014].*

This recent paper was unfamiliar to me. We now cite this paper, which does indeed discuss this topic at length, and use it to justify pushing more of our analysis of the *Alk** salinity normalization approach (and one figure) into supplementary material.

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).**

3. *p11145- 11146, section 3.1*

This section is not well-organized and Figs. 2-5 need more explanations. Consider to discuss the surface distribution (Fig. 2&3) in one paragraph and discuss the vertical gradient (Fig. 4&5) in the second paragraph.

We reorganized this section in keeping with this suggestion and R3's comments. We hope the new presentation is easier to read. We shortened the discussion in lieu of dividing discussion of the surface and vertical gradient figures into two paragraphs.

The phosphate (Fig. 2d) and *Alk (Fig. 2c) distributions are similar at the surface. They are also similar at depth. Figures 3 and 4 show zonally-averaged gridded depth sections of *Alk** and phosphate. *Alk** and phosphate concentrations are low in the deep Arctic Ocean (Figs. 3d, and 4d), intermediate in the deep Atlantic Ocean (Figs. 3a and 4a), and high in the deep North Pacific (Figs. 3b and 4b) and deep North Indian (Figs. 3c and 4c) Oceans. *Alk** and phosphate distributions are similar because similar processes shape them: the hard and soft tissue pumps transport A_T and phosphate, respectively, from the surface to depth. The "oldest" water therefore has the highest net phosphate and *Alk** accumulation. High surface phosphate and *Alk** in the Southern Ocean and North Pacific in Figs. 2, 3, and 4 are due to upwelled old deep waters.**

4. *"The similarity between phosphate and Alk* distributions suggests that Alk* captures the portion of AT that varies in response to biological cycling as the hard parts of marine organisms." p11145, lines 23-24*

This statement is not really true and need more explanations. Although the surface ocean Alk and phosphate have the same sources (upwelled deep water enriched in Alk* and nutrient, riverine inputs), they are removed by different biological activities. Production of particle organic carbon (POC) decreases phosphate but has no effect on changing Alk*. In contrast, precipitation of CaCO3 decreases Alk* without changing phosphate. As a result, the low surface concentrations of phosphate and Alk* in the low-latitude open ocean are due to the weak convention and low biological productions of POC and CaCO3. The high concentrations of phosphate and Alk* are generally in the high-nutrient low-chlorophyll (HNLC) regions, which is mainly due to the strong convention and low productions of POC and CaCO3. On the other hand, the surface concentrations of phosphate and Alk* are related to the ratio of CaCO3/POC production (the rain ratio). Given the same initial condition, high rain ratio would result in relatively low Alk* and high phosphate, and vice versa.*

We reworded this sentence, and clarified our meaning:

Alk* **and phosphate distributions are similar because similar processes shape them: the hard and soft tissue pumps transport A_T and phosphate, respectively, from the surface to depth.**

5. *Section 3.3:*

Although the Amazon is the largest AT source, its Alk is relatively low. Therefore, the Amazon is not the best example to show the riverine Alk*. I don't find Fig. 7 and the discussion on winter-summer difference (p11148, line 19 - p11149, line 2) are closed related to the main objectives of this study.*

In keeping with this and other reviewer comments, we shortened this discussion.

The third paragraph (p11149, lines 15-30) only presents the estimates of the rivrine Alk. It should be moved to section 3.2 (constructing the riverine AT budget for ocean basins) or moved to supplement.*

We removed this paragraph.

8. *The authors define surface ocean as the top 50m of water column. It seems that 50m is a little bit deep. Normally, it is 20m depth in the (sub)tropics and 30m depth at high latitudes [Lee et al., 2006]. Meanwhile, the boundary between the Atlantic and the Arctic defined by the authors (40°N) seems a little bit south?*

We changed our *Alk** definition to rely upon to the top 20 m since evaporation and precipitation happen at the surface… however, we didn't update our section 4 calculations to a shallower depth because the mean mixed layer depth in the Holte et al. (http://mixedlayer.ucsd.edu/) climatology is ~60 m. The 40°N parallel is indeed fairly far south as far as most conventions for the Arctic/Atlantic. However, the biogeochemical fronts separating the high latitude Atlantic and the North Atlantic Gyre appear to fall closer to this cutoff.

9. *Section 4.2, p11153, lines 13-25:*

S2=[Ca^{2+}] [CO3^{--}] / K'sp, any factor affecting [Ca^{2+}], [CO3^{--}] , or $_{K'sp}$ can modulate S2.

Why only CT is mentioned in the discussions here?

The discussion in this section is limited to how the well-equilibrated case differs from the atmospherically-isolated case. The other factors controlling calcite saturation besides C_T behave in essential the same ways in these two cases. We had originally included a discussion of the various factors that control calcite saturation, but cut it for brevity.

10. Conclusions:

This section is too long. Please provide more concise conclusions.

We have truncated this section considerably (except where Reviewer #1 requested more detail on future plans).

III. Technical corrections

"carbonate saturation" => calcium carbonate saturation throughout the manuscript.

Changed

p11140, line 20:

"to isolate the influences carbonate" => to isolate the influences of carbonate

Changed

p11142, line 5:

"while still mixing" => while still mixing conservatively

Added

p11145, lines 21-22:

"The similarity of the AT and salinity distributions demonstrates the strong influence of freshwater cycling on the surface marine AT distribution [Jiang et al., 2014; Millero et al., 1998]". Please add references here.

Added

p11146, line 1-2

"The Alk distribution has a broadly similar explanation to the phosphate distribution."*

is a repetitive sentence. Delete it.

Deleted

p11149, line 27:

"into the Yellow Sea" => into the East China Sea

This paragraph was removed.

p11152, line 21:

“alongside the ... values”. Please correct the symbols in this sentence.

Fixed

p11154, lines 17-18:

“A plot of Alk against salinity reveals the large AT input from the Amazon River”.*

This sentence come from nowhere (which plot?).

We removed this sentence.

Fig. 6:

The color (the numbers of measurements) in this figure is not really useful.

As we argued in our response to R3, we feel the color plays the important role of showing which regions of the plot represent common water masses vs. which simply have at least one measurement representing them. We’ve added verbiage (in red) to highlight this distinction:

The *Alk elevation associated with upwelled water is most visible in Fig. 5e where Upper Circumpolar Deep Water upwelling near the Polar Front results in high-frequency (i.e. warm colored) bins at high-*Alk**. Similarly, the high-frequency *Alk** bins in Fig. 5b with salinity between 32.5 and 33.5 are from the North Pacific Subpolar Gyre, and are also due to upwelled old high-*Alk** water (cf. the Si* tracer in Sarmiento et al. (2004)). River water contributions can be most easily seen in a scattering of low-frequency (cool colored) very high-*Alk** and very low-salinity bins in the Arctic Ocean.**

References:

Chen, C.-T. A. (2002), Shelf-vs. dissolution-generated alkalinity above the chemical lysocline, Deep Sea Research Part II: Topical Studies in Oceanography, 49(24–25), 5365-5375, doi: 10.1016/S0967-0645(02)00196-0.

Jiang, Z.-P., T. Tyrrell, D. J. Hydes, M. Dai, and S. Hartman (2014), Variability of alkalinity and alkalinity-salinity relationship in the tropical and subtropical surface ocean, Global Biogeochemical Cycles, 28, 729-742.

Lee, K., L. T. Tong, F. J. Millero, C. L. Sabine, A. G. Dickson, C. Goyet, G. H. Park, R. Wanninkhof, R. A. Feely, and R. M. Key (2006), Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, Geophysical Research Letters, 33(19), L19605, doi: 10.1029/2006gl027207.

Millero, F. J., K. Lee, and M. Roche (1998), Distribution of alkalinity in the surface waters of the major oceans, Marine Chemistry, 60(1-2), 111-130.

Wolf-Gladrow, D. A., R. E. Zeebe, C. Klaas, A. Kortzinger, and A. G. Dickson (2007), Total alkalinity: The explicit conservative expression and its application to biogeochemical processes, Marine Chemistry, 106(1-2), 287-300, doi: 10.1016/j.marchem.2007.01.006