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## ***Interactive comment on “Processes determining the marine alkalinity and carbonate saturation distributions” by B. R. Carter et al.***

### **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 com-

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posite 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.

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 ( $\text{NH}_3$ ) should be replaced by ammonium ( $\text{NH}_4$ ) 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  $\text{N}_2$ . 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.

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  $\text{Alk}^*$  is calculated for rivers such as the Daugava which empties into the Baltic Sea, and the Yangtze which emp-

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ties into the Yellow Sea, both of which places are blacked out (because no carbonate system data) in figure 2c.

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). This is probably due to the problematic assumption in this study that surface seawater is in equilibrium with an atmosphere of 400 ppmv CO<sub>2</sub>, 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 pCO<sub>2</sub> (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 (CO<sub>2</sub> solubility) and hence CO<sub>2</sub> gas exchange (see in particular figure 6.5 and chapter 6 of Williams and Follows 2011). 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.

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

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what is seemingly quite a simple calculation. Example calculations should be shown to make the explanations more concrete.

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.

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

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

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.

137: is the physical process always upwelling?

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

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

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. . .”

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.

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.

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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.

268: better in what way?

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

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

339: the sentence should be reworded to explain that it is not the current (deep) temperature that ensures high  $\Omega$ , but rather the warm temperature when it last left the surface (which would have ensured CO<sub>2</sub> outgassing until the surface seawater was driven to a low [CO<sub>2</sub>(aq)] commensurate with a CO<sub>2</sub> partial pressure of ~400 ppm at low solubility; when low CO<sub>2</sub> concentration is achieved through gas exchange then it drives carbonate ion concentration to high values).

362-364: temperature has little direct effect on  $\Omega$  (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  $\Omega$ .

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

372-373: this sentence should be reworded – Alk\* is not a process. The meaning of the term “lower concentrations of recently-upwelled remineralized CT” is not clear.

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

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

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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. . ."

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

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