REVISED MODEL LIMITATIONS SECTION -- DRAFT

Areal resolution

The present model approach adopts a very coarse representation of the global coastal ocean, dividing the total coastal seafloor area of $2 \cdot 10^7$ km^2 into merely four characteristic environments as described by Milliman and Droxler (1996), which are characterized by an average depth or further subdivided into three depth intervals. By averaging over such large areas, many local diagenetic features cannot be captured. The main reasons behind the approach chosen here are the scarcity and resolution of the observational data and, in particular, our current inability to obtain estimates of boundary conditions and model parameters at a finer areal resolution. In this context, the lack of higher resolution estimates of organic matter deposition fluxes and reactivity in the heterogeneous and dynamic global coastal ocean is by far the most important limitation towards a finer-scale regionalization of benthic C fluxes (Arndt et al., submitted).

Within a sufficiently narrow range, major model outputs such as A_T* vary roughly linearly with the driving input, POC flux (**eq. 19**). To the extent that the relationship remains linear, an average value multiplied by area should give the same result as a finer resolution model. The main complication occurs when the nature of the underlying processes changes. For example, very large local POC fluxes could eventually result in local depletion of some or all CaCO$_3$ phases, which would limit the sediment's buffering capacity. Further POC addition could ultimately result in methanogenesis– a process which we did not include because it is not predicted to occur in the upper sediment layers under average POC flux conditions (Regnier et al., 2011).

Modeling approach for different environments

An essential assumption to the model is that the sediments are accumulating due to POC and PIC deposition from above. However, in shallow environments and particularly in reefs, benthic productivity may be the dominant means of carbon delivery to the sediment. It is not clear how this difference might affect the modeling results. The approach presented here also may not be appropriate for modeling non-accumulating permeable sands. There is very little information on carbon fluxes from such sediments (Reimers et al. 2004; Jahnke, 2005; Rusch, 2006). Nevertheless, the few studies reveal a significant potential for organic oxidation and DIC release from these environments and further attention should thus be given to these settings in the future.

Temporal variability

One of the principal concerns in applying a steady state model is its ability to capture temporal changes. Primary productivity, temperature and river inputs vary seasonally, and seawater chemistry may vary diurnally. The extent to which these changes in boundary condition will be transmitted into the sediment is unknown. The primary driver of all processes in the model is POC degradation, which has a rate constant of 1 y^{-1} (for the more reactive fraction). Conditions that vary significantly more rapidly than that could presumably be represented by their average without much loss in fidelity. However, similar to averaging over area, temporal averaging will be applicable only so long as the response is roughly linear and the underlying processes do not change. For example, while on average seawater remains saturated with respect to the modeled CaCO$_3$ phases, it is possible that there are certain points

in the diurnal cycle when the water is undersaturated. This would lead to PIC dissolution that would go unaccounted for using only averages.

On the other hand, we would expect that the steady state approach should be able to accurately reflect changes to boundary condition changes that occur much slower than 1 y^{-1}. Thus, the global environmental change scenarios, where POC deposition increases by ~ 50% in a century (Andersson et al. 2005) and seawater DIC increases by up to 5% over that time period should be accurately captured.

POC fluxes

Previously published estimates of the global POC deposition flux vary by more than an order of magnitude (**Table 1**). The average value of these estimates is ca. 90 Tmol y^{-1}. Therefore, our baseline simulation with a reactive POC deposition flux of 117 Tmol y^{-1} and a total flux of 140 Tmol y^{-1} should be viewed as an upper bound estimate for DIC and A_T* fluxes. The results of the sensitivity study indicate that, for the bulk range of 60-120 Tmol y^{-1} (± 30 % of the average value), the predicted global coastal ocean flux of A_T* is most likely constrained within a factor of 2 (**Figure 4B**). Over this POC flux range, degradation driven dissolution of shallow water carbonates generates ~ 4-7 Tmol y^{-1} of A_T*, while the total irreversible buffering source of alkalinity from shallow marine sediments (PIC dissolution, denitrification and sulfur burial) is on the order of 11-19 Tmol y^{-1}. Taking the contribution of net ammonification and net iron reduction, A_T* fluxes increase to 16-29 Tmol y^{-1} (**Figure 4B**). In contrast, the uncertainty in key internal model parameter values has little influence on the uncertainty in estimated A_T* fluxes for a given POC flux (**Figure 5B**).

Organic matter reactivity and quality

The overall reactivity of POC is probably one of the weakest constrained parameters. Coastal sediments receive highly variable organic matter loads from very different sources (fossil, terrestrial, in-situ produced or laterally transported, pre-aged marine organic matter) and are subject of erosion/deposition cycles, as well as a strong temporal variability and a marked seasonality. The dynamic and heterogeneous nature of these organic matter inputs is reflected in extremely variable organic radio-carbon ages (^{14}C contents of total organic carbon as fraction of modern F=1-0.1; Griffith et al., 2010) and model-derived organic matter degradation rate constants ($k=10^2$-10^{-2} yr^{-1}; Arndt et al., submitted). Understanding the observed high degree of variability in coastal organic matter reactivity and developing a general framework that allows constraining organic matter reactivity in data-poor areas is currently not achievable with the existing set of model-derived values. In addition, previously published global relationships between organic matter reactivity and easily observable quantities, such as sedimentation rate or organic matter deposition flux are, because of the limited number, as well as the predominantly open ocean provenance of observations that form the basis for these correlations and the strong heterogeneity of the coastal environment not representative of coastal sediments. Hence, there is no generic theoretical framework that would allow one to constrain the reactivity and fractions of different organic matter pools on the basis of globally available information (e.g. water depth, sedimentation rate, OM flux). Most 2G models assign 51-92% of the deposited organic matter to the most reactive fraction while 8-49% are assigned to the least reactive fraction (e.g. Hammond et al., 1996; Rabouille et al., 1998; Haeckel et al., 2001; Luff et al., 2004). However, organic matter depositing in coastal sediments represents a complex and dynamic mixture of terrestrial organic matter, in-situ produced organic matter and pre-aged (i.e. eroded and re-deposited) organic matter (e.g. Mollenhauer

et al., 2005). Our partitioning of 67% "fast" POC (k = 1 y^{-1}), 17% "slow" POC (k = 0.1 y^{-1}) and 16% non-degradable POC represents a compromise that in our judgment reflects the complex and dynamic mixture of various organic carbon sources. Increasing POC reactivity in our model would allow the primary redox reactions would occur closer to the SWI. This would increase the rate of POC oxidation by oxygen relative to other TEAs and increase the diffusive and bioirrigation effluxes of all reduced products from the sediment. Both effects would decrease the secondary redox reactions occurring within the sediment, resulting in decreased PIC dissolution.

In this model, all degradable organic matter is assumed to have Redfield stoichiometry. Terrestrial organic matter is relatively poorly characterized with respect to composition or reactivity compared with algae, though it presumably has a higher C content (higher C:N) than algal biomass. Variations in C:N ratio of degrading organic matter affect the reaction stoichiometries. For instance, higher C:N ratios would release less ammonium and consume fewer protons (see **R1**). As discussed in section 3.1.3, nitrification consumes more alkalinity than is generated during protonation of ammonia. However, in all modeled cases, "net ammonification" (the alkalinity effect of ammonification minus that of nitrification) is positive. We therefore expect that a decrease in the N content of the degrading organic matter will decrease net alkalinity generation by combined ammonification and nitrification. The effect on denitrification will be muted, because redox process rates are to a large extent determined by the POC hydrolysis rate and the rates of competing redox processes. Therefore, the overall effect of decreased C:N during organic matter degradation should be a small decrease in alkalinity generation within the sediment.

Terrestrial POC is also expected to be more refractory than that produced in the water column (Andersson et al. 2005). We limit our study to more labile phases, which is likely to exclude a large fraction (though not all) of the terrestrial organic matter. Implementing a model that distinguishes between terrestrial and pelagic POC would require detailed knowledge of regional sources of POC, which is beyond the scope of this initial modeling effort.

Other boundary conditions

After POC flux, the other boundary conditions such as bottom water oxygen, nitrate, DIC or temperature exert a second-order influence on A_T* estimates. In particular, temperature effects are small in our model because the only temperature-dependent aspects of the model are diffusion coefficients, equilibrium constants, and the solubility of the carbonate phases, while organic matter decomposition, which is the main driver of PIC dissolution and A_T* generation, is modeled as independent of temperature. Explicitly accounting for the effect of temperature on primary redox reactions is not straightforward. These processes proceed via multiple enzymatic reactions resulting from the combined effort of billions of individual microorganisms and involving a number of different oxidants and intermediate compounds. Therefore, factors such as physiological adaption, selective pressure and the exact reaction path also play an important role in determining the effect of temperature. Observations show that the dominant microbial populations in each environment are optimally adapted to the prevailing environmental conditions and mineralization rates in permanently cold Arctic sediments are similar to that of temperate nearshore environments (Arnosti et al. 1998, Kostka et al. 1999, Jørgensen, 2006; Arndt et al, submitted).

Secondary redox processes

The secondary redox processes we model are limited to the reactions of major reduced species (NH_4^+, Fe^{2+}, HS^-, and FeS) with oxygen. In order to minimize model complexity and uncertainty, we did not model several other possible reactions, including oxidation of sulfides by Fe^{3+}, NO_3^-, or Mn^{4+}. These reactions also consume alkalinity and would be expected to increase $CaCO_3$ dissolution somewhat. By reacting other potential terminal electron acceptors, these secondary redox reactions would increase the fraction of organic carbon oxidized by oxygen and sulfate at the expense of the other processes. Future research will include an evaluation of the significance of these processes to overall sediment alkalinity generation.

Any attempt to infer the global coastal benthic dynamics from the currently limited observational data set should be viewed as a work in progress that requires constant reevaluation and testing in the context of our evolving mechanistic understanding of this environment. Nevertheless, our modeling study provides a first-order global estimate of the coupled carbon dynamics in coastal sediments and of the associated benthic DIC and alkalinity fluxes. It also reveals knowledge and data gaps in our understanding of DIC and alkalinity fluxes in the global ocean, unravels the sensitivity of coastal carbon cycling to ongoing global change and highlights the need for comparative, spatially resolved approaches in understanding and quantifying global, coastal ocean biogeochemical dynamics.