Review of Krumins et al.

This paper uses a diagenetic model to estimate the global fluxes of DIC and alkalinity from oceanic shelf. It presents an impressive amount of work and is generally well organized and enjoyable to read. A particularly useful aspect is the elucidation of the individual process contributions to the DIC and alkalinity fluxes. Obtaining global fluxes, for which this work offers a first-order approximation, is a challenging task. An inherent challenge in this kind of modeling work is making sure that the model approximations and parameters represent the “typical”, or “average”, values for the modeled global environment, despite its variability. A related challenge is including all the important processes and testing the model’s sensitivity to them. I feel that this paper, which is ultimately worthy of publication, still has room for improvement in these areas. Several questions about the model implementation and validation also remain (especially number 4 below), which can be addressed on a major revision.

Criticisms and suggestions

1. All the results in the model are presented for a steady state situation, which the text states is achieved on a time scale 200-400 years. Yet, these results are used to predict the response of sediment effluxes to ocean acidification over the next century. Quantification is needed for how well such a transient situation may be described by steady state results.
2. Results for the baseline scenario are not shown. I feel that seeing these results is important for evaluating the quality of the model. I wish the authors included a corresponding figure with the depth profiles of the most important model variables: DIC, Alkalinity, pH, saturation with respect to carbonate phases, DOC, POC, etc. Showing the depth of oxygen penetration would help evaluate the correctness of the simulated redox balance.
3. The model neglects several potentially important processes. Doing this in the absence of model calibration to a specific dataset requires justification. For example, anammox is not considered and methanogenesis is neglected, as well as Mn reduction.
    a. Mn reduction may contribute insignificantly to the total C mineralization (which is not obvious by itself), but the oxidation of Fe(II) by Mn oxides may contribute substantially to the recycling of Fe, thus affecting the rate of Fe turnover and the contribution of the Fe cycle to C mineralization and pH regulation.
    b. Reduction of Fe(III) phases by hydrogen sulfide is not considered.

c. Anammox has been shown to contribute more than 30% to total N removal in shelves (e.g., Trimmer and Nichols 2009) and may affect alkalinity.

d. What may be the role of anaerobic methane oxidation? The fraction of organic carbon that is non-reactive on the time scale of the model (upper 50 cm) is neglected, yet this fraction is reactive on longer time scales and may contribute to methanogenesis deeper in the sediment and thus to the upward fluxes of methane that becomes oxidized closer to the sediment surface. The absence of methane in the upper decimeters of sediment by itself does not mean that methanogenesis is insignificant, there could be a “stealth” methanogenesis+oxidation cycle. One needs to cite, for example, the typical sulfate values for which methanogenesis is inhibited.

4. The inhibition factors in the Michaelis-Menten kinetics (Table 4) are implemented in a rather non-orthodox way. The reactions of Fe reduction and sulfate reduction are considered inhibited by oxygen only. Thus, the model allows for Fe reduction in presence of any concentrations of nitrate, and sulfate reduction and Fe reduction can co-occur. In addition, the reactions are scaled by “yield” factors (listed in Table 5). These are taken from Thullner et al. 2005 and need to be explained here; otherwise their meaning is obscure. The values of these yield factors (0.75, 0.25, 0.2) suggest, in particular, that the maximum possible combined rate of the three anaerobic pathways (R4+R5+R6) is 1.2 times higher than the maximum rate of oxic respiration (R3). This is incorrect, as under oxic conditions organic carbon is mineralized at least as fast as under anoxic conditions, if not much faster. Incidentally, the rate equations of Thullner et al. 2005 contain explicit biomass terms, as well as additional inhibition factors, so this problem does not arise there.

Minor criticisms

- Table 5 needs more references to show that the listed parameter values are indeed representative. For example, the value of kO2 of 20 uM seems high to me, whereas the half-saturation constant kNO3=5uM is rather low.
- P.8482 “existing data reveals a bi-modal distribution of carbonate contents” - a reference is needed, as well as the values at the two peaks.
- Eqs. 3 and 4: Units for the burial rate and bioturbation coefficient need to be specified. If the burial rate is in cm/yr (as

in the cited Middelburg et al 1997) then it needs to be specified whether it is at the sediment surface or in the deep sediment, as this changes due to compaction.

- P.8486 – a reference is needed to support the partitioning of POC input between highly reactive and weakly reactive C pools.
- P.8487 : “the overall DOC oxidation rate constant k3 is common to all anaerobic respiration pathways” – the same constant appears in R3 (Table 4) for the aerobic respiration. Is it meant to be different? The value of this constant is missing from Table 5.
- P.8489: “soluble ferrous iron, ammonium, and phosphate are assumed to adsorb non-specifically to solids” – this is at odds with a typically high sorption capacity of Fe oxyhydroxides, which leads to high rates of recycling of Fe and phosphate near the zone of Fe reduction.
- P.8494: “because sulfide oxidation exactly cancels the alkalinity generated by sulfate reduction” – the rates of the respective reactions are not the same due to FeS precipitation – rephrase.
- P.8502: In the discussion of model estimates for the fractions of POC mineralized by each pathway, it is important to distinguish between the reactive POC in the model and the total POC as typically measured in sediment cores or sediment traps. A sizable fraction of the deposited organic carbon may decompose on longer time scales that are not considered by the current model.