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Interactive comment on "Microbial activity and carbonate isotope signatures as a tool for identification of spatial differences in methane advection: a case study at the Pacific Costa Rican margin" *by* S. Krause et al.

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Krause and co-workers present measurements of microbial anaerobic oxidation of methane and sulfate reduction rates from sediments at the Pacific Costa Rican Margin. In addition, they discuss the analysis of carbonate 18O, 13C, and 87Sr/86Sr signatures. They combine these measurements with numerical modeling to constrain the advection velocities and the origin of methane fluxes at these mounds. Results indicate

pronounced differences between the two settings and thus reveal a strong temporal and spatial variability of methane charged fluid flow at the Pacific Costa Rican margin. The authors represent an interesting, multi-disciplinary analysis that integrates observations and numerical modeling techniques. The manuscript is generally well structured and well written. However, the authors need to emphasize the original aspects of their work. They should explain the differences between their study and previous studies. What is new? What distinguishes this study from the results presented in, for instance, Hensen et al., 2004; Mavromatis et al., 2012? How do their results fit into a regional/broader context? In addition, the description and rational for the chosen model approach could be improved. In particular, simplifying assumptions (e.g. CaCO3 treatment, FeS precipitation, pH dynamics, TA) should be better justified and critically discussed. The presented manuscript could be considered for publication if the authors address these points and emphasis the originality of the presented research.

General comments (extracted from text above):

Rev.1: However, the authors need to emphasize the original aspects of their work. They should explain the differences between their study and previous studies. What is new? What distinguishes this study from the results presented in, for instance, Hensen et al., 2004; Mavromatis et al., 2012?

Reply: The previous studies mentioned above focused on selected aspects such as fluid sources, the carbonate archive, or numerical modeling of environmental parameters. The present study provides, to our knowledge, for the first time a coherent data set, including novel results of the present microbial activity, the carbonate archive, and a modeling approach for seep locations of two mound structures. Due to the results of the present studies we were able to compare measured microbial turnover rates to modeled ones, supporting the validity of the model used. In doing so, we aim to constrain spatial and temporal dynamics of seep activity from the paleo- to recent times. Furthermore, this study provides a new tool for the identification of such dynamics through a combination of different analytical approaches. In order to emphasize the novel aspects, the last text block of the introduction chapter has now been re-written. We elaborated on the difference between previous studies to the presented one and also stressed that the study includes for the first time rates of anaerobic oxidation of methane (AOM) and sulfate reduction measurements in the study area. In addition, we highlighted that the present study aims to characterize past and present geochemical situation by combining measurements of microbial turnover, carbonate mineralogy and isotopy, as well as numerical modeling. We also added several text blocks to the discussion chapter, in which we emphasized the differences between previous investigations and the recent study.

Rev.1: How do their results (Hensen et al. 2004 and Mavromatis et al. 2012) fit into a regional/broader context?

Reply: Both studies showed that fluid dewatering and subsequent carbonate formation is an important and widespread process in the subduction zone off Costa Rica. Furthermore, the studies demonstrated that the resulting upward fluid flow and element flux have considerable local differences, which needs to be taken into account in order to constrain the dewatering budget for this highly active subduction zone. This regional information is provided in the text. The elaboration of a broader context would certainly be outside the scope of the present manuscript. Our study sites were selected on the basis of previous studies to present the most active and most inactive sites of this region.

Rev.1: In addition, the description and rationale for the chosen model approach could be improved. In particular, simplifying assumptions (e.g. CaCO3 treatment, FeS precipitation, pH dynamics, TA) should be better justified and critically discussed.

Reply: A simplified approach was used since the major goal was to constrain measured AOM rates by available pore water data. This can be regarded as relatively simple problem, and hence justifies using a model of low mechanistic complexity. Moreover, it is a reliable and correct method to derive CaCO3 precipitation rates from pore water

profiles. The aspects mentioned by the reviewer are only required, if more specific problems should be addressed such as following additional pathways of elements or and isotopes or specifying precipitation products. We have clarified this in the revised version of the manuscript.

Specific Comments: Rev.1: p.2, l.24: a-1

Reply: The notation of the minus-symbol was corrected as suggested by Rev.1

Rev.1: p.3, l.67: dissociate

Reply: The word “dissociates” has been corrected to “dissociate” according to the reviewer’s suggestion.

Rev.1: p.9, l.228: remove brackets around Berner, 1980

Reply: The brackets around the citation have been corrected according to the reviewer’s suggestion.

Rev.1: p.9, l.228: The equation is only formulated for dissolved species. What about solid species?

Reply: Only pore water species are modeled. Solid phases are only defined as sink terms.

Rev.1: p. 10, l. 250: What about bioturbation?

Reply: Bioturbation is not considered as only dissolved chemical species are simulated. The effect of bioturbation has been shown to be usually negligible for pore water constituents. However, pore water irrigation / mixing seems to occur in the upper portion of the sediment. Hence, a non-local mixing term was introduced.

Rev.1: p. 10, l. 258: add with

Reply: For clarity, the sentence was rephrased to “Methane is oxidized with sulfate, resulting in the production of hydrogen sulfide and bicarbonate.”

Rev.1: p. 10, l. 261: mixed

Reply:”mixing” was changed to “mixed” according to the reviewer’s suggestion.

Rev.1: p. 11, l. 271: justify the use of this equation for iron sulphide precipitation. Why don’t you consider precipitation as a two step reversible process? What about the oxidation of FeS by O2 and the oxidation of H2S by Fe(OH)3?

Reply: Iron sulphide precipitation was introduced to define a sink term for pore water hydrogen sulfide in order to fit the model to the data. Re-oxidation processes are beyond the scope of the paper.

Rev.1: p. 11, l. 279: explain/justify why you use this simplified approach. Why is pH and the carbonate system not explicitly resolved? What are the errors associated with the chosen approach?

Reply: Based on measurements, pore water profiles of Ca were simply modeled to derive precipitation rates of calcium carbonate in order to provide a quantitative link to the solid phase archive. This is, with reasonable precision, also possible by calculation of concentration gradients. A more complex approach is only required if specific questions are addressed such as regarding the precipitating phase (e.g. aragonite or calcite) or deciphering sinks and sources of specific elements/tracers (e.g. 13C). In addition, pH was not measured and hence, model data could not have been constrained.

Rev.1: p.11, l. 289: how do you quantify HCO3- HS- and CO32- concentrations without resolving pH dynamics? For instance, the speciation of DIC and TH2S released during AOM will depend on ambient pH and will also influence ambient pH.

Reply: It is not necessary to quantify single alkalinity species in this approach. The effect on total alkalinity is sufficiently described.

Rev.1: p.11, l.290: B(OH)4- is an important component of TA in the marine environment.

Reply: We are aware that B(OH)4- belongs to the components considered for seawater alkalinity. At seawater pH and below B(OH)4- contributes < 4% to the alkalinity. In order to avoid over-parameterization, the calculations of TA were simplified, including the main components HCO3-, and HS-.

Rev.1: p. 12, l. 293: What are the boundary conditions for Fe2O3 and CaCO3?

Reply: As mentioned above, solid phases are only defined as sink terms. They are not modeled and hence, there is no need to define boundary conditions.

Rev.1: p. 13, Result section: reference the figures more often

Reply: Following the suggestion of reviewer 1 we added letters (A-H) to the individual plots of figure 3 and 4. We also added references to the individual plots of both figures at various locations in the result section. In addition, we added references to Table 4 into the sections describing the model results.

Rev.1: p.19-20, l. 495 onwards and l. 507: what is new?

Reply: Lines 495 to 507 are indeed descriptive and primarily confirm results of previous studies. New carbonate material was analyzed for the present study and we compare our results with those of previous studies. However, in the new manuscript version we added information to this section, specifically highlighting the differences between the presented studies and previous investigations. This includes primarily the comparison of the first microbial rate measurements with recent and previous model results.

Interactive comment on Biogeosciences Discuss., 10, 8159, 2013.