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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.***

**S. Krause et al.**

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Krause and co-authors present an interesting study on the microbial activity and different isotope signatures in authigenic carbonates of the Pacific Costa Rican margin. Different types of analysis and numerical modeling are combined to illustrate the variable rates of activity, fluid flow velocities and sources of fluids for authigenic carbonate formation. The manuscript is mainly well written and carefully prepared.

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General comments: Rev.2: Chapter 2 should be arranged in a more logical way. Methods concerning porewater and carbonate could be combined. Sampling should be rather at the beginning (following 2.1) and a chapter describing the carbonates should be included.

Reply: We followed the advice of reviewer 2 and re-structured the M&M section according to suggestions made. The section describing the carbonate sampling was moved below section 2.2. In addition, The “Determination of methane concentrations” section was integrated into the “Porewater analysis” section. In addition, the sections X-ray diffraction of carbonates” and “Isotope analysis of carbonates” were combined.

Rev.2: Obviously two different data sets were combined in this study. Unfortunately, oxygen, carbon and strontium isotopes was not done on the same samples. However, this would have allowed a much more consistent interpretation.

Reply: We agree that oxygen, carbon and strontium data from the same carbonate samples are most desirable. The available strontium data from previous cruises result from pre-selected fragments of carbonate-dominated nodules and are intended to be used as an accessory data set in addition to the novel measurements of methane-dependent microbial rates. Light stable isotope signatures of these previously obtained carbonates match with those of carbonates sampled during SO206. This matching of stable isotope signatures was the reason why samples from previous cruises are included in the present study as supporting independent and unpublished data set. Therefore, we assume that also the strontium isotope signatures used are representative for carbonates of the two mounds. Using a strontium isotope data set from previously obtained carbonates provided an independent contribution for the discussion of fluid origin.

Rev.2: Chapter 4.2 needs careful reconsideration and rewriting. The first point that needs to be discussed is the mineralogy which is fundamental for the understanding and interpretation of especially oxygen isotopes. In this light, also the Han classification

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may be discussed. It is contradictory that first Mound 12 samples (from data set Table 5) are classified as group 2 high Mg-calcite. Later in the discussion Mound 12 samples (from data set Table 6) are mostly >98% aragonite. Maybe the Han classification is not suitable for the samples of this study?

Reply: We followed the advice of reviewer 2 and restructured chapter 4.2 starting with the discussion of the mineralogy, followed by the interpretation of carbonate stable carbon and oxygen isotope signatures. Reviewer 2 is absolutely right pointing out the different mineralogy between carbonates sampled during SO206 and previous cruises. For the Sr isotope signature analysis, samples with high carbonate contents were visually pre-selected. To avoid confusion, we included the information that high carbonate-content samples were pre-selected for Sr analysis, including also Table 6. The Han classification was exclusively applied to the carbonates sampled during the SO206 cruise (Table 5), which were not preselected by mineralogy, thus representing bulk samples.

Rev.2: In the discussion of oxygen isotopes the reader needs to know the equilibrium value (including bottom water d18O and bottom water temperature). Otherwise it is impossible to evaluate how 'heavy' or 'light' the values are. The point that is now at the very end of the discussion, that maybe the feeder systems of the mounds tap different depths should be incorporated in the oxygen discussion (origin of fluids).

Reply: For the discussion of carbonate d18O, in the revised manuscript the equilibrium values, based on measured d18O and temperature of the bottom water, were calculated and discussed for the present carbonate phases. In addition, the origin of the fluids was also discussed in this section.

Rev.2: Carbon isotopes are now discussed at two locations in the discussion this should be combined. Also carbon and strontium isotopes should be separated when discussing origin of fluids. Carbon isotopes are strongly process influenced and not a good tracer for (deep) fluid source. A deep signal might be completely changed by

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processes in the shallow part. This seems not to be the case for Sr isotopes at least in this setting. There should also be some discussion on the origin of the low Sr isotope values. Which processes at depth do these rather low ratios indicate?

Reply: We restructured the text and combined both sections, in which carbon isotopes are discussed. Further, we separately discussed carbon and strontium isotopes with regards to fluid origin. We completely agree with reviewer 2 that  $\delta^{13}\text{C}$  values are process influenced. Therefore,  $\delta^{13}\text{C}$  signatures were not used as a tracer for deep source fluids, but only for the potential methane source. In fact, we state that less depleted  $\delta^{13}\text{C}$  suggests thermogenic methane, while strongly depleted  $\delta^{13}\text{C}$  values indicate biogenic methane. We also added organic matter degradation as a potential alternative source for slightly negative ( $< -20$  permil)  $\delta^{13}\text{C}$  values in the discussion part. The encountered  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in carbonates from the two mounds was mainly lower than that of modern seawater. This indicates that deep source fluid was exposed to the weathering of ashes (e.g. Silver et al. 2000, Kastner et al. 2006). As the discussion on the origin of the low Sr isotope values has been neglected so far, we included this aspect into section 4.2

Rev.2: To me it has been confusing that Sr isotopy is being related to carbonate content. Maybe this is a matter of phrasing and the authors mean this a different way. But the Sr isotopy of aragonite will not be different whether the sample has 10% or 90% aragonite. It might rather be a question of mineralogy and environment/depth of formation. Aragonite is known to form in very shallow sediments where sulfate is still available (and calcite is inhibited). If there is seawater sulfate in the porewater, the Sr is likely mostly seawater derived as well.

Reply: This is a very good comment. To avoid confusion, large parts of this section were re-written. In deed, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the aragonite dominated samples from Mound 12 indicate that precipitation occurred under the main influence of bottom water with little contribution of deep-source fluid. The two samples from Mound 11 had different carbonate mineralogy, containing variable proportions of aragonite and calcite.

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Lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of Mound 11 carbonates were present in samples with 30 to 90wt% calcite, indicating that this carbonate phase precipitated under considerable influence of deep-source fluid. Consequently, it can be concluded that the less negative  $\delta^{13}\text{C}$  values of Mound 11 carbonates represent deep source fluids, charged with thermogenic methane, while a, presumably shallow, biogenic methane source dominated at Mound 12.

Rev.2: In many places of the manuscript, previous work is mentioned and this previous work is confirmed by this study. Please state clearly what are actually the new and innovative results of this study.

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.

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Specific comments Rev.2: 8160 15 a time component is only mentioned in the abstract but not discussed in the Manuscript.

Reply: We agree to reviewer 2 and deleted the time component from the abstract as this aspect is rather accessory. However, at the end of section 4.2 we discussed the results of the present study and previous findings by Kutterolf et al. (2008). While the sediment petrographic interpretation of the previous study indicate that Mound 12 has been inactive for the last 5 ka. In contrast, the novel rate measurement data of out study clearly showed current fluid advection at Mound 12.

Rev.2: 8161 13-14 'geological formation' includes subseafloor and suprasedfloor. In my understanding you mean only the suprasedfloor expressions. Subseafloor there is a lot more happening geologically. You should specify that you mean above seafloor.

Reply: As the term 'geological formations' might have been used inappropriately, we changed it to 'geological structures'.

Rev.2: 25'microbial sulfate'? The sulfate is seawater sulfate. Reply: In order to avoid confusion the sentence was re-phrased to "...by microbial, sulfate-dependent (SO42-), AOM ...

Rev.2: 8162 2 dissociate 16 setting

Reply: According to the reviewer's suggestion the word "dissociates" was changed to "dissociate". In the title of section 2.1 "settings" was changed to "setting".

Rev.2: 8163 4 water depth of: :.Klaucke et al., 16 Sampling (there are no methods described in the chapter)

Reply: 4: The sentence ending in line 4 was changed according to the reviewer's suggestion. 16 : From the section 2.2 title "and analytical methods" was deleted. In addition, the two sections describing sediment and carbonate sampling were combined.

Rev.2: 8164 2 what is the length of the GC?

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Reply: The core length (300 cm) was be added to the sentence.

Rev.2: 8165 Please include the accuracy of AOM and SR rate determination.

Reply: The absolute accuracy of AOM and SR rate determination is difficult to determine and cannot be provided, since these methods investigate processes mediated by living organisms in natural sediments. The threshold for microbial activity detection is given by the control samples. A sample is considered microbial active if its value is higher than the control mean plus three times the standard deviation of the controls.

Rev.2: 8167 4ff Please include scan rate and voltage 12ff It is common practice to give reproducibility of carbonate standards for oxygen and carbon isotopes. 25ff Give value for IAPSO measurements

Reply: 4ff .The used voltage (40 kV9, ampere (35 mA), and scan rate (0.01° s-1) was added to the sentence.

12ff In order to comply to the common practice, the reproducibility of the carbonate laboratory standard for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  was added.

25ff The  $^{87}\text{Sr}/^{86}\text{Sr}$  value for IAPSO was added

Rev.2: 8169 Stay consistent with year abbreviation, either 'yr' or 'a'. Reply: For consistency we decided to use 'yr' as the year abbreviation and made according changes throughout the manuscript.

Rev.2: 8172 Stay consistent with usage of abbreviation cmb.s.f. (I believe this is the more common form) or cmb.s.f. 24ff if you are talking about methane concentration there is no need to write again mmol CH<sub>4</sub>L-1. Reply: For consistency, we use the abbreviation cmb.s.f. and made according changes throughout the manuscript.

Rev.2: 8176 15ff A more thorough description of the carbonate mineralogy is needed. Especially in the light of stable isotope interpretation. Only the dominant mineralogy is given in Table 5. In the text it is stated that this dominant mineralogy is only about 50%

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of the present carbonate minerals in some samples. What are the other carbonate minerals? For Mound 11 dolomite was found in the samples. This has a strong effect on oxygen isotopic composition due to mineral dependent fractionation. This needs to be considered. Currently the heavy oxygen isotopic composition of these samples is interpreted as deep fluid source. This can possibly be attributed to the relatively heavy oxygen isotopic composition of dolomite. The authors should calculate with the different percentages of carbonate mineralogies in the sample and the equivalent equilibrium values for the different mineralogies if this alternative interpretation is possible.

Reply: The description of the carbonate mineralogy was re-structured. We now describe the main carbonate minerals and calculated the different weight percentages of carbonate mass of each sample. We also constrained the Mg content of magnesian carbonate by calculating the mol% of  $\text{MgCO}_3$  by the  $d_{104}$  calcite peak shift. The refined analysis of the XRD spectra has shown no evidence of dolomite, despite in one sample from Mound 11. In addition, we calculated the equilibrium values for the different carbonates and included this aspect into the discussion. The comparison of the equilibrium values with the measured  $d_{18\text{O}}$  values of Mound 11 samples revealed that the authigenic carbonates could not have been precipitated solely under bottom water conditions. Therefore it seems plausible to assume that, during carbonate precipitation, the liquid phase was influenced by varying admixtures of advecting fluids. In contrast, the two shell fragments from Mound 11 showed  $d_{18\text{O}}$  values in the range of the equilibrium values, indicating that the shell were indeed precipitated under bottom water conditions. The one sample from Mound 11 containing dolomite also showed a  $d_{18\text{O}}$  value, which was rather close to the equilibrium values from bottom water.

Rev.2: 16 Unfortunately, there is no description of the samples (see comment in method section). However I doubt that all the samples are ‘concretions’. These are by definition concentric carbonate accumulations around a seed. You rather might want to talk about nodules which is a more neutral term.

Reply: We agree with reviewer 2 and prefer the more neutral term “nodules”. In addi-

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tion, we shortly described the sampled carbonates.

Rev.2: 17ff I wonder how calcium carbonate content was determined by XRD? This is not mentioned in the method part but needs to be explained. In addition, XRD is rather a qualitative method. Did you use standards? What is the precision of calcium carbonate content determinations?

Reply: The quantitative analysis of the SO206 carbonate spectra was carried out with Boolean searches of Xpowder's mineral databank using the reference intensity (RIR) method. For the calculation of aragonite/calcite ratios of carbonates from previous cruises laboratory standards were used. In addition, the precision of the calcium carbonate content determination was added. This information was added to the Material and Method section.

Rev.2: 19 mineral names are not capitalized Please define 'Mg-calcite'. Mg-rich calcium carbonates are typical for cold seeps. Therefore it is of great interest what the mol% MgCO<sub>3</sub> is. This can easily be derived from XRD measurements if a standard was used or quartz is present.

Reply: The mol% of MgCO<sub>3</sub> was derived from the d104 peak shift of the XRD spectra. The results showed that the mol% of MgCO<sub>3</sub> in magnesian calcite ranged between 12 and 15.5 mol%, defined Mg-rich calcite. For clarity, Mg-calcite was changed to Mg-rich calcite. The MgCO<sub>3</sub> contribution was not determined for carbonates from previous cruises.

Rev.2: 8177 11ff results from Mound 11 and 12 alternate. Please combine. 3 leachates are mentioned here for the first time. Please explain in the method section which samples were treated this way and why. A 2.25N HNO<sub>3</sub> is a very strong reagent. To obtain more reliable results a weak acetic acid is usually used. With 2.25N HNO<sub>3</sub> surely clay minerals and maybe other minerals were partly dissolved. The non-seawater like values should be discussed in this light not so surprising. This needs to be mentioned and discussed. 12ff This belongs to the methods part.

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Reply: In the result section we aim to compare the porewater profiles, rates and fluxes of the two Mounds, therefore alternating between Mound 11 and 12 is sometimes necessary. However, we combined as many results for one Mound as possible. Originally, the solutions for Sr isotope measurements were generated as complete decarbonatization leachate required for U/Th isochrone approaches. For the present study, the intention was to use the solutions not for the definition of fluid composition, but as a supporting indicator for potentially different fluid sources and their contribution during precipitation. Consequently, the strontium data represent an accessory data set to the novel microbial rate measurements. However, due to the high authigenic carbonate/terrigenous material ratio the partial dissolution of minor amounts of terrigenous material was considered to be of minor impact regarding the strontium isotope signal. In addition, the non-seawater Sr ratios were discussed. The Sr Analysis uncertainties were moved to the method section.

Rev.2: 8179 21ff An essential information is the expected equilibrium value for oxygen isotopes. To be able to evaluate what a 'higher value' for the carbonates is, the equilibrium value needs to be known. Please, also explain how you derive the equilibrium value by giving bottom water temperature and the oxygen isotopic composition of the involved fluids and local seawater. 26ff Fluid flux and methane supply are not necessarily coupled. Especially not if fluids are derived from the deeper sedimentary section due to e.g. clay mineral dehydration and methane is generated in the shallower part due to biogenic methane formation.

Reply: 21ff: The equilibrium values of d18O for all analyzed carbonates and bottom water were calculated. The used equations were added to the method section. 26ff: reviewer 2 is right. Fluid flux and methane supply are not necessarily coupled. Therefore, the word 'corresponding' was deleted.

Rev.2: 8180 15 Please also discuss other possible sources of less depleted d13C values like organic matter. A values of -21permil can be derived solely from organic matter as carbon source. Methane carbon is not needed at all. What are the argu-

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ments to assume a methane source? 6-9 First, kinetic isotope fractionation is stated to be responsible for the measured signatures. Then, the fluids are responsible for the signatures. This seems contradictory. 1ff+25ff Repetitive

Reply: Organic matter degradation was added to the discussion as another potential source for carbonates showing a  $\delta^{13}\text{C} < 20$ . However, according to Karaca et al., 2010 and Wallmann et al. 2006) organic matter degradation is inconsiderable. For clarification, we clearly state that the fluids are responsible for the carbonate isotopic signatures. Repetitive parts of the section were removed.

Rev.2: 8181 5 please correct -39 to -49, same in line 7 18 carbonate 26 do you really mean 'carbonate content'? The argumentation is based on mineralogy (aragonite).

Reply: The corrections were made according to the reviewer's suggestions. The paragraph reviewer 2 is referring to was re-written. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the carbonates did not correlate with carbonate content, but with carbonate composition.

Rev.2: 8182 17ff the relationship to the carbonate study is unclear in this section. Please make the relationship between activity of mounds and carbonate isotope systematics clear or delete. Also there seems to be a mistake. Mound 11 is said to be recently active since  $>15\text{ka}$  and Mound 12 currently inactive and for the last 5ka. In this sense Mound 12 is actually the more active one.

Reply: The study by Kutterolf et al. (2008) was discussed as the authors concluded that Mound 12 is a currently inactive seep structure, regarding mud extrusion and carbonate recovery. In contrast, in the present study measured methane-dependent microbial activity and modeled porewater profiles demonstrate current fluid advection in a low mode. Therefore, we would like to keep this section in the manuscript. The authors intended to express that, according to the study by Kutterolf et al. (2008), Mound 12 has been inactive for at least 5ka by the external manifestations used for classification.

Rev.2: Table1 Please stay consistent with Lat/Long notation. Other figures use different

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notation. The correct abbreviation is Long. Table 2 : : stable isotope analysis. Correct:  $^{87}\text{Sr}/^{86}\text{Sr}$  Table 4 Defined in the header is SR. In the table, SRR is used. Please correct. Table 6 standard deviation see previous comments on mineralogy. If there is 10% aragonite in a sample, what is the mineralogy of 90% of the carbonate fraction? Fig. 1 Pacific Fig. 2 How do you define 'depth' on the left scale? Water depth? Useful for the reader would be sediment depth. Fig. 5 Please indicate used standard on axes labels ( $\%$  V-PDB) Fig. 6 See comment on Fig. 5 Correct writing should be: standard errors, second standard error

Reply: The tables and figures were changed according to the reviewer's suggestions. In addition, the carbonate mineralogy of the Sr samples was clarified in the table 6.

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