

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.

Anonymous Referee #2

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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 modelling 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.

General comments:

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

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(following 2.1) and a chapter describing the carbonates should be included.

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.

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 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?

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).

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 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?

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.

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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.

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.

Specific comments

8160 15 a time component is only mentioned in the abstract but not discussed in the manuscript.

8161 13-14 'geological formation' includes subseafloor and suprasediment. In my understanding you mean only the suprasediment expressions. Subseafloor there is a lot more happening geologically. You should specify that you mean above seafloor. 25 'microbial sulfate'? The sulfate is seawater sulfate.

8162 2 dissociate 16 setting

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

8164 2 what is the length of the GC?

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

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

8169 Stay consistent with year abbreviation, either 'yr' or 'a'.

8172 Stay consistent with usage of abbreviation cmbsf (I believe this is the more common form) or cmb.s.f. 24ff if you are talking about methane concentration there is no

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need to write again mmol CH4L-1.

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% 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.

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.

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?

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% MgCO₃ is. This can easily be derived from XRD measurements if a standard was used or quartz is present.

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 HNO₃ is a very strong reagent. To obtain more

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reliable results a weak acetic acid is usually used. With 2.25N HNO₃ 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.

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.

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 arguments 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

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).

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 >15ka and Mound 12 currently inactive and for the last 5ka. In this sense Mound 12 is actually the more active one. 27 Mound

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

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