

## ***Interactive comment on “Transition from hydrothermal vents to cold seeps records timing of carbon release in the Guaymas Basin, Gulf of California” by Sonja Geilert et al.***

### **Anonymous Referee #1**

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In this paper, the authors presented a rich set of geochemical data from pore fluid, water column, and authigenic carbonates to argue against the hypothesis by Lizarralde et al. (2010) that, hydrothermal intrusion in the Guaymas Basin recently induces methane seepages by producing methane from thermally decompose organic matter. The authors argue that the seepage, if it ever occurred, must have ceased several thousand years ago First of all, I would urge the authors to check the manuscript more carefully, there are numerous places with very obvious grammatical errors, unexplained abbreviations, and incorrect reference to the figures. Also, some of the long sentences and excessive use of comma make it difficult to read sometimes. I tried to point out some of these and hope the authors consider these comments as friendly critics from

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a reader's point-of-view. In terms of the interpretation and conclusion, I do not disagree with what the authors proposed but however do not think their interpretation is the sole explanation of their observations. Their primary observations are: 1) porewater geochemistry from the Smoker Sites is dominated by seawater signal with a minor contribution of hydrothermal fluid; 2) from the seep sites, porewater geochemistry show no sign of deep-sourced fluid, despite the high input of methane from a mixture source of biogenic and thermogenic methane; 3) the age of authigenic carbonate is dated to be very young with geochemical signatures all indicate a close-to-modern seafloor condition. The (1) observation was interpret by the authors as a seawater circulation in shallow sub-surface that has been observed in other hydrothermal systems. The (2) observation was interpret by the authors as due to the decoupling of gas from the water phase. With all these observations, the author concluded that the seepage has stopped now and therefore the mechanism proposed by Lizarralde et al. (2010) is over-rated. With the same set of observations, one can also interpret that the shallow circulation seen in the porewater profiles is driven by a recent hydrothermal activity that provides the heat source (as shown by all the temperature measurements presented in the paper) to decompose organic matter and therefore explains the mostly biogenic source of methane observed from the cold seep sites. The decoupling of gas and water phases is not uncommon and does not exclude the contribution of deep water; it might arrive later than the gas phase or at a different location. Also, the circulation of seawater must have diluted the signal from deep-sub surface. The young age dated from the authigenic carbonate also support such recent seepage event. The above interpretation turns the same set of observation to support the hypothesis proposed by Lizarralde et al. (2010). I want to emphasize it is difficult to interpret the observations of "no anomaly". The authors must be more careful about this.

I also think the title of the paper misleading. From the title alone, it appears that they are in favor of the transition from hydrothermal vents to cold seeps. I also think the authors should present their opinion already in the final sentences in the introduction (e.g., Line 97-99). When I read this, I thought they agree with the transition from

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hydrothermal vent to cold seep until later in the discussion.

Specific comments:

Line 24: What does the 500m here mean?

Line 31: If pore fluid is predominately seawater than you wouldn't call it "cold seep pore fluid".

Line 48: Kennett 2000 is not a good citation as this paper only dealt with the Quaternary excursions not PETM.

Line 74: delete "that"

Line 89: "a helium isotope signature indicative of mid-ocean ridge basalt." I guess you mean He isotopic signature tells them the fluid came from mid ocean ridge.

Line 90: up to several hundred of meters.

Line 91: "magmatic intrusions into underlying sediments" The orientation is weird in this sentence. Here the underlying should refer to the magmatic intrusion. Do you mean the intrusion penetrated strata deeper than it was?

Line: 94-97: Could you check the sentence again? If you intent to use two commas to form a clause, please remember to close the clause by adding the second comma. Also, consider using an active tone in this sentence, such as " during the SO241, we sampled at XXX and XXX locations."

Line 105: were

Line 106: check the articles of this sentence, not always "a"

Line 109: locations of seeps

Line 115: why need "respectively" here? What is GI gun?

Line 126: I assume you mean authigenic carbonate concretions

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Line 127, 128: "Hence, comparing results from different seeps might be biased in this regard." Unclear what you mean.

Line 131-134: The way you use comma is really confusing. For example, "at three seepage sites, North (GC01, MUC11), Central (GC03, GC13, GC15, MUC04), and Ring Seeps (MUC05)," Do you intent to say the three seepage sites include north, central and ring seeps sites? or the "three seepage site" is another site other than north, south, and Ring Seeps.

Line 133: Are you sure you gave definition of the reference site "above" not "below"?

Line 155: "at a sampling rate of 1s." sampling rate of what?

Line 171: "were" Line 187-193: I understand one can sure find details in the paper cited. However, I think it's important to mention things that are absolutely crucial. For example, it is important to mention how soon were the HS and ammonium analyzed after recovery of the porewater as both species are easily degraded due to oxidation and microbial consumption. It's also known that ammonium measurements by photometry method are heavily impacted by the presence of HS. What treatment did you do to prevent that. Titration of alkalinity is also a time-sensitive analyses as carbonate precipitation is still happening in the water samples. For the cation and anion samples brought back to shore lab, what preservation measure was performed. All of such information are crucial and I would like to see more description in the main text but not just "please refer to XXX".

Line 194-198: As volcanic material might be present in the study area, it is important to check the abundance of Rb and see if that affect the strontium isotopic ratios. This is supposed to be a routine for analyses like this. I would like to see some more information on this.

Line 209: VPDB needs to be explained

Line 234: where in the supplement?

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Line 231-241: This appears to be a ridiculously long sentence. Please revise the whole paragraph so that it's more readable.

Line 272: blankening? Blanking?

Line 272-273: I'm not a geophysicist but I thought the blanking zone in seismic profile is due to gas/water (stuff with low density) instead of sediment mobilization?

Line 287-290: check the unit for 60, 15 mbsf. I think you mean ms. Also, explain what is mbsf.

Line 317: what do you "lower meter"? do you mean shallow in GCs?

Line 333: photometry method measures total hydrogen sulfide, S<sup>2-</sup>, HS<sup>-</sup>, and H<sub>2</sub>S. Please revise throughout the text. Why for some ions you specified their charge (like SO<sub>4</sub><sup>2-</sup>) for others you ignored the charge (NH<sub>4</sub>, Li, Mg)? Also, please revise alkalinity to total alkalinity (TA) for clarity throughout the text.

Figure 4: From the figure, the TA from GC07 could be as high as over 70 meg/L however the highest value listed in supplementary is only 65 meg/L. Could you check this again? Also, I suggest modify the scale of the plot. For example, it is really hard to see the changes in Mg and Li concentrations from the plot despite the 10% increase and decrease in concentrations of these two ions. The figure should be able to reflect these variations better.

Line 347: revise to TA and total HS.

Line 350: I do not agree Mg and Li concentrations are similar to seawater for all sites, you apparently have higher Mg and Li in GC07

Line 370: the lowest and highest values I can see are -26.5 and -88.2.

Line 373: I don't see any dD-CH<sub>4</sub> value reported for Smoker unless you mean VCTD data, which is not from porewater.

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Line 385: There is no VCTD09 in your data from supplementary and figure 6.

Line 398: I wonder what kind of calcite it is, high-Mg or low-Mg calcite.

Line 403, 403: isn't the reproducibility should be reported in the method section.

Line 421: I wouldn't be so sure about this conclusion. Besides of methane from thermogenic degradation of organic matter, it is possible you have methane from hydrothermal activity, which is not much related to the organic matter. This would make sense with the mantle source helium reported in Berndt et al. (2016). I also suggest you report the exact value of helium isotopic anomaly reported by Berndt et al here, so readers could have a better sense of the information.

Line 425: Check the format of citation.

Line 434-435: If you look closely to the raw data, both Sr and Ca concentrations are 10% elevated compared to the seawater value. Also one of the only two <sup>87</sup>Sr/<sup>86</sup>Sr values reported from GC09 shows significantly lower value from seawater values. This again emphasize the authors should really adjust the scale of the plot (Figure 4) to reflect these small but significant changes.

Line 445-446: again, if you look into the data clearly you would probably slightly change the conclusion here.

Line 449-450: You only have one indicator, NH<sub>4</sub>, reported here. I don't think you can justify for all. Not to mention NH<sub>4</sub> concentration is affected not only by organic matter degradation but also cation exchange.

Line 455. I don't see why is relevant to refer fig 3 here. I thought you mean fig4. Also, this sentence is so odd. I don't quite sure I get your point. How do you know it's high level of AOM but not just sulfate reduction+organic matter degradation, which is in line with your high TA and NH<sub>4</sub> levels.

Line 459-460: Of course the data could be explained this way, but alternatively, if there

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is just no input of methane from the Smoker site (GC09, GC10), then one would expect exactly the same porewater profiles as reported here. The present data provide no justification of whether seawater convection exists or not at these coring sites.

Line 461: now you mentioned the Li anomaly. I think this observation should be mentioned earlier in the text.

Line 464-466: both Sr and Ca concentrations are also slightly elevated and the one  $^{87}\text{Sr}/^{86}\text{Sr}$  value from GC09 is also significantly lower than seawater value.

Line 464: What is the cause of high Li? Hydrothermal solution (Line 465) or mineral composition (Line 462). If the authors think it's the latter, you should provide an explanation of the process and how.

Line 473-474: I in general agree this conclusion but think this paragraph could be better integrated with the paragraph discussing the porewater data of Smoker site. Especially the statement here is in contradiction to the statement in Line 434-435.

Fig. 7: what is the x-axis of (A)? Also, how the mixing lines were determined in (a) and (b), especially in the log-log plot and log-linear plot. I think for the mixing lines should look differently the ones from the current plots.

Line 491-494: The authors really need to work on this statement to get a self-consistent conclusion on this. See my earlier comments on this.

Line 502 "(active?)" appears without context. Please clarify.

Line 505-509: Since methane can also be generated through hydrothermal activity and even abiogenic processes, I don't see why organic matter degradation signal is necessarily expected.

Line 526: In my view, it's weird to see one calls Li as a major porewater constituent, as it's only less than 30  $\mu\text{M}$  in the porewater.

Line 531 as a tracer

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Line 565: what kind of oxidation of methane you are talking about? Aerobic or anaerobic?

Line 566: AOM enriches DIC in  $^{12}\text{C}$ .

Line 566-568: I'm not sure how you this process you described can help explain your data. Besides, if you look into the Borowski et al (1997) paper, the paper is intent to explain why  $\delta^{13}\text{C}-\text{CH}_4$  is actually counter-intuitively light in the AOM zone. It's true that AOM supposes to make the residual methane heavier in isotopic signature but this is not what usually observed and definitely not what Borowski et al intent to explain in their paper.

Line 570: for anaerobic methane oxidation. It's important to specify which oxidation.

Line 601-629: In the argument against the conclusion by Lizarralde et al., how does the observation the authors had, a convection of seawater into the shallow sub-surface in the Smoker Sites, affect such argument. It is likely that seawater convection in the hydrothermal is a short-term and contemporary process, the geochemical signal happened to be captured by the current study. In this case, how do you actually use the observation of no geochemical signal to argue against the conclusion by Lizarralde et al. Besides, the convection of seawater in hydrothermal regions must be driven by seeping of fluid in the hydrothermal vents. If as the authors claimed, the porewater profiles are indicative to seawater convection, isn't that just confirmed the hydrothermal activity?

Line 656: It's unexpected to see the authors show AOM reaction such late in the paper as they have talked about a lot earlier in the text. I suggest move part of this discussion when they use porewater profiles to infer intensive AOM activity.

Line 677-680: I agree that the various lines of evidence from the carbonate suggest the recent formation but I don't see how do these support the conclusion "cessation of deep fluid and gas mobilization" the authors derived from porewater data. Isn't that the

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young ages from authigenic carbonate suggest a very recent seepage event? Since porewater profiles are probably contemporary signatures, can really conclude that the seepage has died just because they see nothing from the porewater profiles? Similar to my earlier comment, the "boring" and seawater-like porewater profiles were interpreted by the authors as due to seawater convection in the shallow subsurface. If this is true, how can the authors use this to say that the deep fluid migration has stopped?

Line 696: what is s.a.

Supplement tables:

Please revise the units of mmol or micromol to mM and microM throughout the table. There is no such unit.

The meaning of "-" in all the tables are unclear. Does it mean samples/analyses are not available or it is below detection limit. Especially for the table of d13C and dD of methane, not clear why sometimes there is not measurements of dD despite the high concentration. Also, it's not clear how "-" different from just a blank in the table.

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