Kiel, 06.07.2018

Dear Helge Niemann,

Thank you for considering our manuscript '*On the formation of hydrothermal vents and cold seeps in the Guaymas Basin, Gulf of California*' for publication in *Biogeosciences*.
We very much appreciate the insightful comments of the reviewers and have made substantial revisions in the manuscript accordingly. The most important changes include the revision of figures and tables, the rearrangement of section 4.1.1, discussing now first the hydrothermal anomalies, and the revision of section 4.3, in which we have clarified that we do not disagree with Lizarralde et al. (2010) in general, but only on the timing of thermogenic methane release. We shortened the manuscript where possible, clarified how our results differ from those of earlier studies, and emphasized the importance of the biological contribution to the geochemical and geophysical results.
We hope that you agree that our revision has substantially improved the manuscript and that you will find it fit for publication in *Biogeosciences*.

Yours Sincerely
Sonja Geilert

Response to Referee #1

General comments:

Reviewer comment: 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.
Reply: We proofread the manuscript and corrected errors, shortened sentences, and revised references. We hope that the manuscript is now well understandable and the content clearly stated.

Reviewer comment: The referee criticizes in his comment mostly our conclusion that hydrothermal activity has ceased in the Guaymas Basin deduced from the observation of dominantly seawater signatures in the pore fluids and biogenic methane emissions. The referee proposes that our data could also be interpreted in an opposite direction, namely that recent hydrothermal activity drives a shallow convection cell that draws seawater into the sediment.
Reply: At first, we do agree with Lizarralde et al. (2010) that hydrothermal activity in the Guaymas Basin was once driving seepage and an elevated thermogenic methane flux to the water column. We can also not exclude that there is still thermogenic methane released into the basin driven by off-axis sills. However, as all seep sites investigated in this study show predominantly seawater composition, a simple correlation of detected sills and active thermogenic methane release as done by Lizarralde et al. (2010) appears not to be feasible. Our data set shows that deep processes are extinct, at least at the investigated sites so that it is not unlikely that at other places deep processes are extinct as well. At least, it does not seem valid to assume that all other off-axis sills represent active hydrothermal systems. In order to calculate accurate thermogenic carbon fluxes, sill emplacement mechanisms like longevity and spatial distribution need further investigation. We emphasized these conclusions in lines 744-751 and 824-834 of the revised manuscript.

Reviewer comment: The referee claims that the heat provided by the Black Smoker field might '*decompose the organic matter and therefore explains the mostly biogenic methane source*'.
Reply: If organic matter is decomposed by an elevated heat source, than the isotopic signal would be indicative of this thermogenic source. The thermogenic $\delta^{13}C_{CH4}$ signal is relatively heavy (about -40 to -20‰) compared to the biogenic signal (< -55‰). All our (unaltered) $\delta^{13}C_{CH4}$ data falls in the biogenic field (see Fig. 8) and are thus not decomposed by thermogenic alteration. The lateral heat from the Smoker field might support and enhance biological processes but is not responsible for the isotopic signal as proposed by the referee.

Reviewer comment: The referee further criticizes that we just might not have detected the deep fluid phase as it is decoupled from the gas phase and might arrive later or at a different location. He proposes that seawater might have diluted the deep signal and that the young age of the authigenic carbonate would also support a recent seepage event.
Reply: We do not think that this is a likely alternative to the presented hypothesis. The known active hydrothermal systems from the southern (Von Damm et al., 1985) and northern (Berndt et al., 2016) rift axis in the Guaymas Basin emit hot fluids with clear

evidence for high temperature fluid-rock interactions and thermogenic gas production. Such a fluid is not found at any of the seeps. Instead, we found pore water containing predominantly biogenic methane, but which is otherwise only slightly diagenetic altered from seawater. Biogenic methane formation is expected to occur within the uppermost tens to a few hundreds of meters below the seafloor at low temperatures. Methane-enriched pore water sourced in those depths should be likewise enriched in other products of organic matter degradation (e.g. NH_4), like found at the Slope Site (lines 532-540 and Fig. 4, 7). The fact that only biogenic methane is significantly enriched at the seep locations lets us conclude that methane gas is percolating through shallow sediments (even forming gas hydrates as observed at North Site) rising along pre-existing low permeability pathways formed by previous hydrothermal activity. The detection of elevated gas flows at the investigated seep sites confirms our visible observation of active seep sites at the seafloor, like microbial mats or clams (lines 596-601).
The young age of the carbonate supports our hypothesis of a decoupled gas and fluid phase as only ascending gas is needed to drive AOM and the formation of authigenic carbonates. Biomarker, $\delta^{13}C_{CH4}$, $\delta^{18}O_{CaCO3}$ and $^{87}Sr/^{86}Sr$ signatures clearly point to a formation in seawater at ambient temperatures. We agree with the referee of a recent seepage event, however, mainly driven by shallow-sources, biogenic gas and not by deep-sourced, hydrothermal processes. From sediment thicknesses above extinct fluid conduits we estimated that the processes must have stopped more than 7 kyrs ago at least at the places investigated so far. We cannot exclude that there are still areas in the Guaymas Basin with active sill-induced methane release. At our investigated sites though, we have not found any evidence of thermogenic methane release. A simple extrapolation as done by Lizarralde et al. (2010) in which they compile all sills and estimate the potential methane release appears not applicable.
We have emphasized that we indeed detected active seepage sites in lines 596-601 of the revised manuscript.

Reviewer comment: The referee claims that the title of our manuscript might be misleading as it appears to argue for the process of active thermogenic methane release. The referee also thinks that we should present our opinion already in the final sentences in the introduction (e.g., Line 97-99). At present, the referee thinks that we would agree with the transition from hydrothermal vents to cold seeps until later in the discussion.
Reply: The title of the manuscript might indeed be misleading. We referred to the processes itself and not to the activity. We changed the title to a more general meaning: '*On the formation of hydrothermal vents and cold seeps in the Guaymas Basin, Gulf of California*'.
We also rephrased the last section of the introduction in order to clarify that we are comparing our findings to the hypothesis by Lizarralde et al. (2010) and added a sentence stating our findings (lines 116-123).

Specific comments:

Reviewer comment: Line 24: What does the 500m here mean?
Reply: 500 m is the distance to the Smoker field. Deleted in the abstract as it is more clearly defined in section 3.3 'Sediment characteristics and sedimentation rates'.

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

Reply: ‘Cold Seep’ is a general term for areas where fluids, gases, and/ or solid material are transported from depth to the seafloor. Seepage often provides bioactive reductants like sulfide, methane, and hydrogen which fuel biota. This biota consists of typical cold seep communities like tubeworms, clams, and mussels and often occur with authigenic carbonates precipitated on the seafloor. The term ‘cold’ does not refer to the temperature of the seepage but is meant in contrast to ‘hot’ hydrothermal fluids.
In the Guaymas Basin, we have observed the typical seepage biota like mussels and clams as well as authigenic carbonate manifestations through video-guided MUC observations. Thus, we refer to this areas as ‘cold seeps’ as an active seepage area was identified.
We changed the geochemical definition of cold seep fluids from seawater to ambient diagenetic fluids in the abstract (lines 29-32 and 34-36), in lines 571-573, and in the Conclusions (line 841-844).

Reviewer comment: Line 48: Kennett 2000 is not a good citation as this paper only dealt with the Quaternary
excursions not PETM
Reply: We replaced Kennett (2000) with Aarnes et al. (2010), who discuss how contact metamorphism can trigger global climate change (line 60).

Reviewer comment: Line 74: delete "that"
Reply: Deleted (line 87)

Reviewer comment: 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.
Reply: This sentence has been rephrased to indicate that fluids in contact with MORB were detected (lines 101-103).

Reviewer comment: Line 90: up to several hundred of meters.
Reply: The words ‘up to’ were added (line 104).

Reviewer comment: 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?
Reply: We agree that the word underlying is confusing here and replaced it with deep (line 106).

Reviewer comment: 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."
Reply: The sentence was rephrased (lines 94-112).

Reviewer comment: Line 105: were
Reply: Changed to plural (line 130).

Reviewer comment: Line 106: check the articles of this sentence, not always "a"
Reply: Changed (lines 129-132).

Reviewer comment: Line 109: locations of seeps
Reply: Changed to plural (line 133)

Reviewer comment: Line 115: why need "respectively" here? What is GI gun?
Reply: The definition of the streamer was corrected from ‘to’ to ‘and’ as ‘respectively’ refers to 150m correlating with 96 channels and 183.5m correlating with 112 channels. GI gun was specified in the text (lines 138-140).

Reviewer comment: Line 126: I assume you mean authigenic carbonate concretions
Reply: The word ‘carbonate’ was added (line 150).

Reviewer comment: Line 127, 128: "Hence, comparing results from different seeps might be biased in this regard." Unclear what you mean.
Reply: We added the explanation that seepage areas might not been hit at the most active area (lines 152-153).

Reviewer comment: 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.
Reply: We have rephrased the sentence (lines 156-160).

Reviewer comment: Line 133: Are you sure you gave definition of the reference site "above" not "below"?
Reply: We corrected the definition to ‘below’ (line 158).

Reviewer comment: Line 155: "at a sampling rate of 1s." sampling rate of what?
Reply: The definition of sampling rate was defined as one measurement per second (line 189).

Reviewer comment: Line 171: "were"
Reply: Present is the correct tense here, so we did not change the word ‘are’ (line 206).

Reviewer comment: 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".
Reply: We added a more detailed description of the methods. HS and NH_4 were analyzed right after core recovery and sampling. Before NH_4 analyses, the samples were treated with

argon to expel HS. The pore fluids were acidified on board to inhibit mineral precipitation prior to shore-based elemental analyzes (lines 223-231).

Reviewer comment: 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.
Reply: The potential impact of Rb interferences on Sr isotope ratios is avoided in multiple and independent steps as described below.
Based on prior Sr concentration measurements original sample aliquots typically equivalent to 1000 ng Sr were chemically separated for Sr after pre-treatment against potential organic content by single use highly selective Sr-Spec resin in a low blank one step chemistry. Usually, no significant amount of Rb is passing into the Sr eluate. However, a second physically purification is provided by measuring the isotope ratios on thermal ionisation mass spectrometry (TIMS). The lower ionisation temperature of Rb in comparison to Sr leads by slow heating and multiple focussing procedures on early Sr signals to preferential ionisation and depletion of potentially resin-passing traces of Rb.
The third and ultimate step to avoid any misleading data interpretation due to interfering 87Rb on 87Sr is the continuous monitoring of Rb abundances by measuring 85Rb in static mode simultaneously the Sr masses 84, 86, 87 and 88. This additional information was added in the manuscript in lines 243-247.

Reviewer comment: Line 209: VPDB needs to be explained
Reply: An explanation for VPDB was added (line 259).

Reviewer comment: Line 234: where in the supplement?
Reply: The text section in the supplement explaining the XRD measurements was indeed missing and was now added.

Reviewer comment: Line 231-241: This appears to be a ridiculously long sentence. Please revise the whole paragraph so that it's more readable.
Reply: We shortened and divided the sentence (lines 282-292).

Reviewer comment: Line 272: blankening? Blanking? and Line 272-273: Im 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?
Reply: Blanking is the correct term here. We added a more detailed explanation of the signal interpretation. Gas and/ or water can cause the signal blanking. In contrast, sediment mobilization can explain the observed deformed strata (lines 324-325).

Reviewer comment: Line 287-290: check the unit for 60, 15 mbsf. I think you mean ms. Also, explain what is mbsf.
Reply: The units were corrected and mbsf defined as meters below sea floor (lines 329-330).

Reviewer comment: Line 317: what do you "lower meter"? do you mean shallow in GCs?
Reply: Shell fragments occur in shallow depth in the GC. The sentence has been rephrased (lines 374-375).

Reviewer comment: Line 333: photometry method measures total hydrogen sulfide, S2-, HS-, and H2S.Please revise throughout the text. Why for some ions you specified their charge (like SO42-) for others you ignored the charge (NH4, Li, Mg)? Also, please revise alkalinity to total alkalinity (TA) for clarity throughout the text.
Reply: Alkalinity has been abbreviated with TA and all sulfide species with TH2S. The inconsistency in mentioning the charge was revised.

Reviewer comment: 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.
Reply: Fig. 4 was changed by adjusting the colors and symbols of the plot in order to improve readability. The scales of Mg and Li were increased to visualize concentration changes. There was indeed a mistake with the TA scale, which was corrected. Highest TA concentrations of GC7 are 65 meg/L.

Reviewer comment: Line 347: revise to TA and total HS.
Reply: Revised to TA and TH_2S (see comment to line 333).

Reviewer comment: Line 350: I do not agree Mg and Li concentrations are similar to seawater for all sites, you apparent have higher Mg and Li in GC07
Reply: We added a detailed description of the concentration variations for GC01, GC07, and GC09 (lines 408-415).

Reviewer comment: Line 370: the lowest and highest values I can see are -26.5 and -88.2
Reply: The values were corrected (lines 435-436).

Reviewer comment: Line 373: I don't see any dD-CH4 value reported for Smoker unless you mean VCTD data, which is not from porewater
Reply: dD-CH4 values for the Smoker area are from VCTD sampling and stem from the hydrothermal plume. We have specified this in the text (lines 431-440).

Reviewer comment: Line 385: There is no VCTD09 in your data from supplementary and figure 6.
Reply: We clarified in the text that the temperature values for the water column above the hydrothermal field (VCTD09) are from Berndt et al. (2016) and added the data in the figure (lines 452-454 and 461-462).

Reviewer comment: Line 398: I wonder what kind of calcite it is, high-Mg or low-Mg calcite.
Reply: By the uncertainty related maximum deviation of Δd104 (< 0.01) the XRD spectrum identifies calcite with a Mg fraction below 3 % according to Goldsmith et al. (1961). We added this information in lines 467-469.

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

Reply: The reproducibility was also mentioned in the method section (lines 242-243) and is now deleted here in lines 473-474.

Reviewer comment: 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.
Reply: We added the He-isotope value in line 471. Indeed it was shown in Berndt et al. (2016) that hydrocarbons are composed of hydrocarbons produced by thermogenic organic matter degradation (degradation driven by the released heat of the magmatic intrusion) and abiogenic hydrocarbon formation (see Figure DR9 in Berndt et al. (2016), supplement). However, the largest amount of methane stems from thermogenic organic matter degradation. We slightly adjusted the text to clarify that this discussion is presented in detail in Berndt et al., 2016 (supplement) (line 473).

Reviewer comment: Line 425: Check the format of citation
Reply: The sentence has been rephrased (lines 493-496).

Reviewer comment: 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 87Sr/86Sr 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.
Reply: We adjusted the scale in Fig. 4 and 5 in order to visualize the concentration ranges as suggested by the reviewer. There are six $^{87}Sr/^{86}Sr$ isotope signatures values for GC09 and two for GC10 (see Table S2). We forgot to plot GC10 in Fig. 5 which was now added.
We rearranged the discussion for section 4.1.1 in order to clarify where we have detected hydrothermal fluids and where seawater concentrations. Now, we are first discussing the hydrothermal signatures found in the deep core section of GC09 (>4m) and then the remaining sites which show seawater composition. Hydrothermal indicators are higher Li and lower Mg concentrations and $^{87}Sr/^{86}Sr$ isotope signatures clearly point to a hydrothermal endmember ($^{87}Sr/^{86}Sr = 0.7059$) for pore fluids from GC09 (>4m).
The seawater composition of the remaining pore fluids (shallow pore fluids (<4m) from GC09, GC10 and MUCs) is interpreted as shallow convection cell drawing seawater into the sediment. We hope the rearrangement of this section clarifies our interpretation of the data (lines 512-575).

Reviewer comment: Line 445-446: again, if you look into the data clearly you would probably slightly change the conclusion here.
Reply: We do agree with the presence of hydrothermal fluids in some areas close to the hydrothermal smoker field and rearranged the discussion to clarify our statement (see also comment above). Indications of hydrothermal fluids are now discussed in lines 512-523.

Reviewer comment: Line 449-450: You only have one indicator, NH4, reported here. I don't think you can

justify for all. Not to mention NH4 concentration is affected not only by organic matter degradation but also cation exchange.
Reply: In the newly arranged manuscript, other indicators of deep fluids like Mg or Li are now mentioned in the section before (lines 512-523). The NH_4 serves as an example for catagenetic or diagenetic breakdown of organic matter and helps to clarify that none of these process occur at the seep sites. We rewrote this section in order to clarify this process (lines 524-546). Cation exchange might be responsible for the elevated NH_4 concentrations, but is of minor importance in this region with a high organic precipitation rate.

Reviewer comment: 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 NH4 levels.
Reply: Indeed, Fig.3 was a wrong reference here and was changed to Fig.4 (line 539). We rearranged the sentence and the whole section in order to clarify that the Slope Site serves only as an example of how a deep diagenetic altered fluid might look like. As the seep site fluids do not show similar elevated concentrations of NH_4 as well as seawater-like Mg and Li concentrations we concluded that no deep fluid is reaching the surface here anymore (lines 524-551).
Sulfate reduction and organic matter degradation are processes of AOM which serves as an umbrella term here.

Reviewer comment: Line 459-460: Of course the data could be explained this way, but alternatively, if there 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.
Reply: We deleted the sentence in lines 459-460. The rearrangement of this section deals now with the question of convection in lines 546-551. The sentence is phrased as a hypothesis and provides an explanation for the observed pore fluid composition. As the sentence is formulated as an assumption and not as fact, we see no need to change it here. We also added additional references to clarify that such a convection cell is a phenomenon observed before at sedimented hydrothermal areas (line 549).

Reviewer comment: Line 461: now you mentioned the Li anomaly. I think this observation should be mentioned earlier in the text.
Reply: The discussion of the Li anomaly is moved to the beginning of the discussion in section 4.1.1 (see also comment above to lines 434-435).

Reviewer comment: Line 464-466: both Sr and Ca concentrations are also slightly elevated and the one 87Sr/86Sr value from GC09 is also significantly lower than seawater value.
Reply: There are six $^{87}Sr/^{86}Sr$ isotope signatures for GC09 and two for GC10 (Table S2) which are discussed in lines 515 to 517 (see also comment to lines 434-435).

Reviewer comment: 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 a explanation of the process and how.

Reply: We think that mixing with hydrothermal fluids are causing the Li anomaly and that the hydrothermal deposits found in the deep section of the core solely facilitate fluid circulation in contrast to the diatomaceous clay (now discussed in lines 513 to 521).

Reviewer comment: 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.
Reply: We rearranged the discussion in section 4.1.1 as explained above in the comment to lines 434-435

Reviewer comment: 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.
Reply: Fig. 7 has been reduced to the upper plot (NH_4 vs Li) as the lower plot does not provide any new information. Further, the mixing line has been calculated following: $Li_{mix} = Li_{phase1} * f_1 + Li_{phase2} * f_2$, with $f_1 + f_2 = 1$. Phase 1 is the Li concentration of Guaymas Vent south (Von Damm, 1990) and phase 2 is the Li concentration of North Seep. The mixing proportions of NH_4 have been calculated accordingly. This formula has been added to the caption of Fig. 7. As the mixing line is not a linear regression, the look of it in the plot agrees with the used equation.

Reviewer comment: 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.
Reply: We revised the discussion as explained in the comment above to lines 434-435

Reviewer comment: Line 502 "(active?)" appears without context. Please clarify.
Reply: The blanking of the seismic profile indicates a fluid conduit, but the profile cannot differentiate between active fluid and/ or gas flow. As we only conclude later in this paragraph that the fluid and gas phases must have been decoupled we decided to put the 'active' in question. In order to eliminate misunderstandings, we deleted the question mark and put in question if it is fluid and/ or gas flow (lines 581).

Reviewer comment: 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.
Reply: The term 'thermogenic degradation of organic matter' also includes the process of degradation of organic matter and formation of hydrocarbons by additional heat provided by magmatic intrusions (see also comment to line 421). In the Gulf of California this process is indicated for deeply buried and shallow sediment where hydrocarbons are transported e.g. by hydrothermal circulation to the seafloor (e.g. Simoneit et al., 1988). Small gas contributions in hydrothermal fluids in the northern Guaymas Basin are derived from abiogenic methane formation which is indicated by $\delta^{13}C_{CH4}$ data and $^3He/^4He$ content (Berndt et al., 2016). This points to a deep magmatic (intrusion) source. However, hydrocarbon formation by abiogenic processes in hydrothermal circulation cells cannot be excluded here (e.g. McDermott et al., 2015; and discussions in Berndt et al., 2016, supplement). We added this information in lines 591-593.

Reviewer comment: 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 microM in the porewater.
Reply: Li is considered as a major indicator for high-temperature sediment-water interactions, as are Mg and Cl. We agree that it might be confusing in this context and rearranged the sentence (lines 599-603).

Reviewer comment: Line 531 as a tracer
Reply: Added

Reviewer comment: Line 565: what kind of oxidation of methane you are talking about? Aerobic or anaerobic?
Reply: The oxidation of methane is probably be affected by anaerobe microbial oxidation above the sulfate-methane transition zone utilizing sulfate and additional electron-acceptors like nitrate, manganese(IV) or iron(III) (e.g. Jørgensen, 2006). Edited in lines 658-661.

Reviewer comment: Line 566: AOM enriches DIC in 12C.
Reply: We replaced CO_2 with DIC in line 662.

Reviewer comment: Line 566-568: Im 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 d13C-CH4 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.
Reply: We changed the citing paper to Whiticar (1999), who is indeed describing the observed process more appropriate (line 664).

Reviewer comment: Line 570: for anaerobic methane oxidation. It's important to specify which oxidation.
Reply: The type of oxidation was specified (lines 658-661).

Reviewer comment: 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 capture 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?
Reply: We do not deny the activity of the hydrothermal system in general. We just state that at the investigated seep sites no deep signal is detected and there are no indications of actively released thermogenic methane. We cannot exclude that this process occurs in other areas of the basin, however Lizarralde et al. (2010) calculated methane flux might be excessive (see also reply to general comment). We clarified this in lines 744-750 and 823-833.

Reviewer comment: 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.
Reply: We have moved the AOM reaction to section 4.1.2 (*Cold seeps*) in which this process is explained in detailed for the first time.

Reviewer comment: 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. Isnt that the 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?
Reply: The $\delta^{13}C_{CH4}$ data of the bulk carbonate overlaps with the $\delta^{13}C_{CH4}$ values in the associated pore fluids. No indicators of a deep signal have been found in the carbonate. Indeed, carbonate formation requires a recent seepage event; therefore we concluded beneath others that the fluid and gas phase must have been decoupled and only gases are rising to the surface and precipitate together with Ca as authigenic carbonate. From our data, we observe that no deep fluids, in contrast to gases, are rising to the surface at the investigated sites. We cannot exclude that this process might still occur at other seepage areas not investigated in this study. However, from our data, which show predominantly seawater concentrations at the investigated seepage sites, we can conclude that deep processes are extinct. Furthermore, no thermogenic methane was detected at the seepage sites. Summarizing, we can say, that the thermogenic carbon flux calculated by Lizarralde et al. (2010) might be overrated. We conclude that carbon flux extrapolations need to take the longevity of sill-introduced thermogenic carbon emissions into account. We revised this section of our discussion to clarify our conclusions (lines 799-803 and 823-833).

Reviewer comment: Line 696: what is s.a.
Reply: s.a. refers to ‚see above', but is now deleted as the active CH4-emission period was just calculated in the section before

Supplement tables:

Reviewer comment: 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.
Reply: The units were revised accordingly and the '–' and blanks in the table replaced with not determined (n.d.), below detection limit (b.d.l.), and not applicable (n.a.). The measurements for δD were carried out first to check for variations at each site. If there were variations in δD, more analyses have been conducted. In the case of GC07 where high

methane concentrations are present, the δD values did not vary much (see Table S3). Therefore we decided not to perform any further measurements here.

Response to Referee #2

General comments:

Reviewer comment: Referee #2 has difficulties with three main aspects of our manuscript concerning the biological significance, the spatial coverage of sampling sites, and the new discoveries of our manuscript in contrast to earlier studies.
First, the referee claims that the biological aspects of our study are too small to get published in Biogeosciences.
Reply: The main findings and conclusions of our study are based on biological aspects, like the microbial signature of $\delta^{13}C$ data and the AOM-dominating biomarkers identified in the carbonate. The detected microbial signatures helped to identify that deep processes are extinct nowadays. The biological results support our geochemical and geophysical observations and form a key point of our discussion.
Additionally, we understand that the objective of this journal is to publish research which combines biological, chemical, and physical investigations and which highlights the interaction between them (*see homepage Biogeosciences*). Our manuscript combines all three aspects and emphasizes the importance of an interdisciplinary research approach to draw the best possible conclusions.
We emphasized the importance of the biological input to our study in the abstract (lines 36-42) and in the conclusions (lines 847-848). In general, the discussion of biological signals represents a considerable part of our manuscript, as shown in section 4.2 in lines 658-700, and section 4.3.2, lines 766-789.

Reviewer comment: Secondly, the referee expresses his concerns that the spatial coverage of our sampling sites is not sufficient to infer basin-wide phenomena.
Reply: Sample locations were chosen based on findings by Lizarralde et al. (2010) who describes sill intrusions associated with hydrocarbon gas emissions, biological communities, and authigenic carbonates. In this study, we investigated 3 seepage sites at various distances from the hydrothermal vent field based on locations identified by Lizarralde et al. (2010) as areas of active methane release. Additionally, a reference site, smoker sites as well as the water column have been sampled. With the exception of the active smoker site, there is no indication for a deep fluid advection and methane $\delta^{13}C$ data are predominantly of microbial origin (see Fig. 4 and section 4.4). Despite the fact that no deep fluids were detected at the seepage sites, an active methane flux was present, indicating that we hit the currently active sites described in Lizarralde et al. (2010). The detected methane was predominantly of microbial origin and no active thermogenic methane is released nowadays at the investigated sites as claimed by Lizarralde et al. (2010). We cannot exclude the possibility that thermogenic methane is still released in other areas of the basin, but the lack of evidence for high temperature geochemical processes at the investigated sites contradicts with Lizarralde's et al. (2010) conclusions. The seismic evidence of seep-induced hydrothermal systems alone is not sufficient for projecting methane emissions for the whole basin at present (see also comment to referee#1). Thermogenic methane release induced by off-axis sill intrusions is still a likely process to occur, but our study suggests that the lifetime

of these systems is limited and has to be taken into account for budget calculations. Hence, the study of Lizarralde remains valid and is highly valuable in terms of describing the general process and the potential magnitude, but care has to be taken concerning the longevity of the hydrothermal systems and associated thermogenic methane release after the occurrence of sill intrusions.
We clarified this section of our discussion and explained the applicability of our results to the whole basin (lines 744-750 and 823-833).

Reviewer comment: The last major point of criticism by the referee is that it is not clear how the findings of this study differ from those of Lizarralde et al. (2010) and Berndt et al. (2016).
Reply: While Berndt et al. (2016) focused on characterizing the geophysical and geochemical characteristics of the Smoker area, Lizarralde et al. (2010) investigated geophysical aspects of the wider basin and the water column. Our study is the first one to look at geochemical, biological, and geophysical characteristics of seepage sites and the water column above. Main findings are the decoupling of gas and fluid phases, the microbial origin of methane, and the detection of sediment layers above extinct fluid conduits. We used the sediment thickness to infer an age at which deep fluid and gas flow induced by magmatic intrusions must have ceased. Our results contrast with findings by Lizarralde et al. (2010) who claim that thermogenic methane is still actively released in all places presented in their study. As detailed above, we do not disagree with Lizarralde et al. (2010) about the general mechanism. However, we disagree that all of the off-axis sites are presently active in the sense of hydrothermal systems (we discovered none) and that their lifetime has to be taken into account. We claim that this process only occurs during and for a certain time (depending on the lifetime of a sill-driven hydrothermal system) after the magmatic intrusions intruded in the sediment. How long this process really occurs still needs further investigation.
We emphasized our study results in contrast to Berndt et al. (2016) and Lizarralde et al. (2010) throughout the whole manuscript, e.g. in the introduction (lines 109-123), in section 3.6 (lines 461-462), in section 4.1 (lines 488-495), in section 4.2 (lines 647-648 and 678-681), and in lines 744-750.

Specific comments:

Reviewer comment: L001: I think more specific wording describing what authors observed seems better.
Reply: We have changed the title according to the suggestion by Referee #1.

Reviewer comment: L021: This sentence seems inadequate as abstract of this study.
Reply: We have rearranged the sentence to a more introductory meaning and emphasize the motivation of our study (lines 23-26).

Reviewer comment: L024: In a research field for hydrothermal activity, horizontal distance of _500m is not "close". See Cruse&Seewald 2006; 2010; Reeves et al. 2011; Baumberger et al. 2016; or some other numerous papers.
Reply: In ‘close distance’ is meant here relatively to the other investigated sites.
Unfortunately, it was not possible to obtain samples closer to the hydrothermal vent field as

sediment composition did not allow core penetration. It is true that compared to other hydrothermal areas 500m is not close. We added relatively here to emphasize this (line 26).

Reviewer comment: L040: Introduction, carbon flux from seafloor to atmosphere, is not closely related to what authors observed in THIS study.
Reply: Indeed, our observations do not show a (thermogenic) carbon flux from the seafloor to the atmosphere. However, the aim of our study was to investigate the causes of global warming, e.g. during the PETM. One hypothesis is that magmatic intrusions into organic-rich sediments might release large amounts of thermogenic methane which might have triggered climate warming. Based on this theory, Lizarralde et al. (2010) studied water column anomalies above potential seepage areas in the Guaymas Basin and concluded that large amounts of thermogenic methane are still released today. Lizarralde et al. (2010) inferred therefore that magmatic intrusions might have triggered the climate warming during the PETM. In contrast, our detailed study of pore fluids and gases of the seepage areas mentioned in Lizarralde et al. (2010) did not show active thermogenic methane release or rising of deep fluids. We concluded therefore that the methane release calculated by Lizarralde et al. (2010) might be too high.
Our study investigates processes possibly responsible for climate warming and therefore we think that we can begin our introduction with introducing this hypothesis.

Reviewer comment: L040: L051: This paragraph can move to M&M.
Reply: We do not agree that this paragraph should move to the *Materials & Method* section as it provides background information on the geological setting of the sampling area. The geological characteristics of the Guaymas Basin and the composition of the sediments are explained. As these are no new information gathered in this study, we concluded to describe them in the introductory paragraph. We will not move this section to the *Materials & Method* section as this section should only give information about samples investigated in this study and methods applied here.

Reviewer comment: L069: What is environmental conditions?
Reply: Environmental conditions refer to the enhancement of early-diagenetic reactions and with that the distinct changes in fluid and gas geochemistry. We specified environmental conditions with early-diagenetic processes in the main text (lines 80-83).

Reviewer comment: L071: Magmatic intrusion is geological process while fluid-rock and fluid-sediment interactions (associated with magmatic heat) influences fluid/sediment geochemistry. Because major part of this study is geochemical description, it seems better to make the wordings clear.
Reply: We agree that the sentence is imprecise and we defined now that the heat released by the magmatic intrusions is causing the fluid chemistry to change by accelerating early-diagenetic processes (lines 83-86).

Reviewer comment: L075: These sentences (L075-082) seem inadequate for this study.
Reply: We do not agree that these sentences are inadequate for this study as the process described by Lizarralde et al. (2010) was our motivation to conduct this study. Our reason to investigate these seepage sites was to study pore fluid and gas signatures influenced by magmatic-induced early-diagenetic reactions. Even though our results revealed that deep processes are extinct at the investigated sites, we think it is appropriate to introduce

Lizarralde et al. (2010) theory. Therefore we will leave the overview of Lizarralde et al.'s (2010) finding at the end of the introduction.

Reviewer comment: L097: Authors do not clearly state whether seismic data is acquired in this study or not. Clarify it.
Reply: Seismic data was acquired in this study and we clarified this in lines 115-116, 136-143, 319-344.

Reviewer comment: L125: Microbial mat is adequate
Reply: We have changed the definition of the mat to microbial (line 149).

Reviewer comment: L131: I feel the names of samples seem confusing. Rename of the samples based on geological or geochemical properties, such as North Seep site samples (NS01, NS02, NS03) and smoker site (SM01), seems better for readers.
Reply: The names of the samples refer to the type of core we retrieved as GC for gravity corer and MUC for multi-corer. We think that the names are appropriate as they indicate for the reader the core type and depth of the sample at once. We prefer to leave the naming of the samples as they are.

Reviewer comment: L137: immediately "subsampled"
Reply: We replaced sampled with subsampled (line 164).

Reviewer comment: L139: Please show a reference for pressure filtration.
Reply: A reference was added in line 165.

Reviewer comment: L141: What is difference from core retrieval in L137?
Reply: The difference of MUC core retrieval in contrast to GC core retrieval is described in the following lines (former manuscript lines 141-144). In contrast to GC samples, MUC samples were brought to a cooling lab and sampling was executed anoxic in an argon-flushed glove bag. Retrieved pore fluids were centrifugation and subsequent filtered. Explained in the revised manuscript in lines 167-171.

Reviewer comment: L144: Please show a reference for centrifugation
Reply: A reference was added in line 171.

Reviewer comment: L150: Purpose of temperature and conductivity measurements is unclear.
Reply: The heat flow measurements delivered fundamental knowledge about the heat distribution in the basin and helped to characterize the influence of the hydrothermal vent field and the sill-intrusions. As the heat flow significantly drops further away from the hydrothermal vent field, the heat flow analyses helped to support our hypothesis that deep processes are extinct. The intruded sills are no longer releasing heat which might accelerate early-diagenetic processes.

Reviewer comment: L167: Names seem confusing.
Reply: The names of the samples from the water column are following the same principle as the pore fluid samples. The name indicates the station name and in brackets we indicate the

type of instrument used. We think that this way of naming is reasonable and we see no need to change it.

Reviewer comment: L208: MAT 253?
Reply: Indeed, the 2 was missing in the name of the instrument (Thermo MAT 253) and it was added in line 257.

Reviewer comment: L217: What was the sample analyzed?
Reply: The sample was freeze dried sediment. We added this information in the text in lines 267-268.

Reviewer comment: L255: Purpose of biomarker measurements is unclear.
Reply: The analyses of biomarkers was providing (similar to the heat flow measurements, see above) fundamental knowledge about the origin and characteristics of the carbonate. The biomarkers showed a clear AOM origin, which supported our hypothesis that deep processes are extinct and that the methane needed to form the carbonate stems from shallow AOM processes.

Reviewer comment: L292: Please show (raw) vertical profiles of temperature in addition to (processed) heat flow values in figure 3 or figure 4.
Reply: 'Raw' vertical profiles are now shown in the supplement, Fig. S2.

Reviewer comment: L384: Is the water column chemistry already reported in Berndt et al. 2016? Is it first reported in this study? Please clarify it.
Reply: The water column chemistry was investigated and reported first in this study except for the one water column directly above the hydrothermal vent field (VCTD09), which was reported first in Berndt et al. (2016). We emphasized this in the result section now in lines 422-426.

Reviewer comment: L415: 4.2? 4.1?
Reply: We indeed confused the section numbering here and corrected it for 4.1

Reviewer comment: L418: Is it from Berndt et al. 2016?
Reply: The water column data directly above the hydrothermal vent field stems from Berndt et al. (2016). We clarified this in the text in lines 452-456 and 460-461.

Reviewer comment: L425: Because horizontal distribution of heat flows are highly heterogeneous at around high-temperature vents, such comparison may make no sense.
Reply: The sentence is formulated as an assumption and we see no reason to change it, as it simply provides a possible explanation for the observed high heat flow.

Reviewer comment: L446: Is this hypothesis supported by previous observations at sedimented hydrothermal vent sites?
Reply: Additional studies which observed convection cells in sedimentary basins are Gamo et al. (1991) and Kinoshiita and Yamano (1997). We added these references in the text in line 548.

Reviewer comment: L455: Fig4?

Reply: Fig. 3 is a wrong reference here and we changed it to Fig. 4 (line 538).

Reviewer comment: L491: I guess chemical reactions between sediment and intruded sill occur only at the time of eruption event. Fluid-sediment interaction associated with magmatic heat source occurs more likely. See Cruse&Seewald 2006 GCA, Ishibashi et al. 2014 Geochem.J, or some other papers reporting fluid geochemistry of sediment-covered vent sites.

Reply: We agree that after sill-emplacement, heat is the driving force to induce chemical reactions, as observed also in other regions (Cruse and Seewald, 2006; Ishibashi et al., 2014). We clarified this in the text in lines 567-569.

Reviewer comment: L599: The story of timing of methane release seems frail due to limited evidences for temporal scaling. Information about time is only derived from solid phase (carbonate geochronology and sedimentation rate), and no evidence about past methane release is presented. Although past intrusion into sediment suggested by seismic dataset may imply generation and and release of thermogenic methane at the time of intrusion, it is just interpretation.

Reply: Age data is in fact only available for the carbonate sample and can be deduced from the sedimentation rate. However, we approached the cessation of active thermogenic methane release by taking the sediment thickness above extinct conduits into account. Of course, the resulting time is only an approximation. As we stated in our manuscript and in the comments above, the lifetime of a magmatic system needs further investigation before conclusions of the timing of active methane release can be drawn (lines 743-749 and 822-832).

Reviewer comment: L703: This is not conclusion of this study.

Reply: We provided this information as an explanation for the motivation of our study. We think it is justified to provide this information here and see no need to change it.

Reviewer comment: L712: This interpretation has been clear before this study and is not proved in this Study

Reply: Seismic data acquired in this study clearly showed that fluid and gas conduits above sill-intrusions were active once. From pore fluid geochemical data we can deduce that no deep processes are acting anymore. We have proven in our study that the longevity of the magmatic system is a crucial factor which needs to be taken into consideration when interpolating active methane release. From sediment thicknesses above extinct conduits we deduced the time, when hydrothermal circulation must have stopped at the seep sites (lines 806-820). Therefore we think that this sentence is justified at the end of the conclusions.

Reviewer comment: Fig1: Not informative. Except DSDP site and zoom up for seep-vent sites are better.

Reply: We plotted the DSDP site in Fig. 1 as it is our geochemical reference site for the hydrothermal endmember described by Von Damm et al. (1985) and Von Damm (1990). Therefore we prefer to leave the DSDP site in our map. In order to improve the visibility of the seep and smoker stations, we added enlargements here.

Reviewer comment: Fig3: Y-axis scaling is not good. Using two panels for large and small heat flows is better.

Reply: We changed the appearance of Fig.3 and hope that the visibility of the heat flow distribution has now improved. We added an extra panel and scale for the high heat flow for the rift valley and Smoker Site.

References

Berndt C., Hensen C., Mortera-Gutierrez C., Sarkar S., Geilert S., Schmidt M., Liebetrau V., Kipfer R., Scholz F., Doll M., Muff S., Karstens J., Planke S., Petersen S., Böttner C., Chi W.-C., Moser M., Behrendt R., Fiskal A., Lever M. A., Su C.-C., Deng L., Brennwald M. S. and Lizarralde D. (2016) Rifting under steam – how rift magmatism triggers methane venting from sedimentary basins. *Geology* **44**, 767–770.

Cruse A. M. and Seewald J. S. (2006) Geochemistry of low-molecular weight hydrocarbons in hydrothermal fluids from Middle Valley, northern Juan de Fuca Ridge. *Geochim. Cosmochim. Acta* **70**, 2073–2092.

Von Damm K. L., Edmond J. M., Measures C. I. and Grant B. (1985) Chemistry of submarine hydrothermal solutions at Guaymas Basin, Gulf of California. *Geochim. Cosmochim. Acta* **49**, 2221–2237.

Von Damm K. (1990) Seafloor Hydrothermal Activity: Black Smoker Chemistry And Chimneys. *Annu. Rev. Earth Planet. Sci.* **18**, 173–204.

Gamo T., Sakai H., Kim E.-S., Shitashima K. and Ishibashi J. -i. (1991) High-alkalinity due to sulfate reduction in the CLAM hydrothermal field, Okinawa Trough. *Earth planet. Sci. Lett.* **107**, 328–338.

Goldsmith J. R., Graf D. L. and Heard H. C. (1961) Lattice constants of the calcium-magnesium carbonates. *Am. Miner.* **46**, 453–457.

Ishibashi J. I., Noguchi T., Toki T., Miyabe S., Yamagami S., Onishi Y., Yamanaka T., Yokoyama Y., Omori E., Takahashi Y., Hatada K., Nakaguchi Y., Yoshizaki M., Konno U., Shibuya T., Takai K., Inagaki F. and Kawagucci S. (2014) Diversity of fluid geochemistry affected by processes during fluid upwelling in active hydrothermal fields in the Izena Hole, the middle Okinawa Trough back-arc basin. *Geochem. J.* **48**, 357–369.

Jørgensen B. B. (2006) Bacteria and marine biogeochemistry. In *Marine Geochemistry* (eds. H. D. Schulz and M. Zabel). Springer, Berlin. pp. 169–206.

Kinoshita M. and Yamano M. (1997) Hydrothermal regime and constraints on reservoir depth of the Jade site in the Mid-Okinawa Trough inferred from heat flow measurements. *J. Geophys. Res.* **102**, 3183–3194.

Lizarralde D., Soule S. A., Seewald J. S. and Proskurowski G. (2010) Carbon release by off-axis magmatism in a young sedimented spreading centre. *Nat. Geosci.* **4**, 50–54. Available at: http://dx.doi.org/10.1038/ngeo1006.

McDermott J. M., Seewald J. S., German C. R. and Sylva S. P. (2015) Pathways for abiotic organic synthesis at submarine hydrothermal fields. *PNAS* **112**, 7668–7672.

Simoneit B. R. T., Kawka O. E. and Brault M. (1988) Origin of gases and condensates in the Guaymas Basin hydrothermal system (Gulf of California). *Chem. Geol.* **71**, 169–182.

On the formation of hydrothermal vents and cold seeps in the Guaymas Basin, Gulf of California

~~Transition from hydrothermal vents to cold seeps records timing of carbon release in the Guaymas Basin, Gulf of California~~

Sonja Geilert[1], Christian Hensen[1], Mark Schmidt[1], Volker Liebetrau[1], Florian Scholz[1], Mechthild Doll[2], Longhui Deng[3], Annika Fiskal[3], Mark A. Lever[3], Chih-Chieh Su[4], Stefan Schlömer[5], Sudipta Sarkar[6], Volker Thiel[7], Christian Berndt[1]

[1]GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstraße 1-3, 24148 Kiel, Germany
[2]Universität Bremen, Klagenfurter-Straße 4, 28359 Bremen, Germany
[3]Department of Environmental Systems Science, ETH Zurich, Universitätstrasse 16, 8092 Zurich, Switzerland
[4]Institute of Oceanography, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 106, Taiwan
[5]Federal Institute for Geosciences and Natural Resources, Stilleweg 2, 30655 Hannover, Germany
[6]Department of Earth and Climate Science, Indian Institute of Science Education and Research Pune, Dr. Homi Bhabha Road, Maharashtra-411008, India
[7]Geobiology, Geoscience Centre, Georg-August University Göttingen, Goldschmidtstr. 3, 37077 Göttingen, Germany

Abstract

The Guaymas Basin in the Gulf of California is an ideal ~~site~~location to investigate the hypothesis~~to test the hypothesis that~~ that magmatic intrusions into organic-rich sediments can cause the release ~~of large amounts~~ of thermogenic methane and CO_2 ~~that may lead~~which may contribute to climate warming. In this study pore fluids relatively close ~~(~500 m)~~ to a hydrothermal vent field and at cold seeps up to ~~20~~ 30 km away from the northern rift axis were studied to determine the influence of magmatic intrusions on pore fluid composition and gas migration. Pore fluids close to the hydrothermal vent ~~area~~ field show predominantly ~~seawater~~ ambient diagenetic fluid composition, indicating a shallow circulation system transporting seawater to the hydrothermal catchment area rather than being influenced by hydrothermal fluids themselves. Only in the deeper part of the sediment core, composed of hydrothermal vent debris, $^{87}Sr/^{86}Sr$ ratios and slightly elevated Li concentrations indicate the minor admixture of hydrothermal fluids (~3%). Pore fluids at cold seeps also show a mainly ambient diagenetic fluid composition without any imprint

from high temperature processes. Seep communities at the seafloor are mainly sustained by biogenic methane, which is rising along pre-formed pathways. Anaerobic oxidation of methane (AOM) is widespread at these sites as indicated by pore water profiles, isotope fractionation of hydrocarbons, as well as the occurrence of~~Only in the deeper part of the sediment core, composed of hydrothermal vent debris, Sr isotopes indicate a mixture with hydrothermal fluids of ~3%. Also cold seep pore fluids show mainly seawater composition.~~ authigenic carbonates and indicative biomarkers.

~~Most of the methane is of microbial origin and consumed by anaerobic oxidation in shallow sediments, whereas ethane has a clear thermogenic signature. Fluid~~ Deep fluid and thermogenic gas flow might have been active during sill emplacement ~~in the Guaymas Basin~~at the investigated sites, but ceased 28 to 7 ~~thousand~~ kyears ago, based on sediment thickness above extinct conduits. Our results indicate that carbon release depends on the longevity of sill-induced~~,~~ hydrothermal systems, which is a currently unconstrained factor.

1 Introduction

Climate change events in Earth's history have been partly related to the injection of large amounts of greenhouse gases into the atmosphere (e.g. Svensen et al., 2004; Gutjahr et al., 2017). ~~One of~~Among the most prominent of these events was the Paleocene-Eocene Thermal Maximum (PETM) during which the Earth's atmosphere warmed by about 8°C in less than 10,000 years (Zachos et al., 2003). The PETM was possibly triggered by the emission of about 2000 Gt of carbon (Dickens, 2003; Zachos et al., 2003). Processes discussed to release these large amounts of carbon in a relatively short time are gas hydrate dissociation and igneous intrusions into organic-rich sediments, triggering the release of carbon during contact metamorphism (Aarnes et al., 2010; Svensen et al., 2004). The Guaymas Basin in the Gulf of California is considered one of the few key sites to study carbon release in a rift basin exposed to high sedimentation rates.

The Gulf of California is located between the Mexican mainland and the Baja California Peninsula, north of the East Pacific Rise (EPR; Fig. 1). The spreading regime at EPR continues into the Gulf of California and changes from a mature, open ocean-type to an early-opening continental rifting environment with spreading rates of about 6 cm yr^{-1} (Curray & Moore, 1982). The Guaymas Basin, which is about 240 km long, 60 km wide, and reaching water

depths of up to 2000 m, is known as a region of vigorous hydrothermal activity (e.g. Curray and Moore, 1982; Gieskes et al., 1982; Von Damm et al., 1985). Its spreading axis consists of two graben systems (northern and southern troughs) offset by a transform fault (Fig. 1). In contrast to open ocean spreading ~~centres~~centers like the EPR, the rifting environment in the Guaymas Basin shows a high sediment accumulation rate of up to 0.8-2.5 m kyr^{-1} resulting in organic-rich sedimentary deposits of several hundreds of meters in thickness (e.g. Calvert, 1966; DeMaster, 1981; Berndt et al., 2016). The high sedimentation rate is caused by high biological productivity in the water column and influx of terrigenous matter from the Mexican mainland (Calvert, 1966).

Hydrothermal activity in the Guaymas Basin was first reported in the southern trough (e.g. Lupton, 1979; Gieskes et al., 1982; Campbell and Gieskes, 1984; Von Damm et al., 1985). Here, fluids emanate~~,~~ partly from Black Smoker type vents at temperatures of up to 315°C (Von Damm et al., 1985). Sills and dikes intruding into the sediment cover significantly affect temperature distribution~~,~~ and hence environmental conditions like early-diagenetic processes (Biddle et al., 2012; Einsele et al., 1980; Kastner, 1982; Kastner and Siever, 1983; Simoneit et al., 1992; Lizarralde et al., 2010; Teske et al., 2014). The heat released by magmatic intrusions accelerate early-diagenetic processes ~~and~~ which strongly influence the chemistry of the interstitial waters (e.g. Gieskes et al., 1982; Brumsack and Gieskes, 1983; Kastner and Siever, 1983; Von Damm et al., 1985). ~~Lizarralde et al. (2010) reported that s~~Sills intruded into the sediment cover and~~ that~~ cold seeps at the seafloor ~~are visible~~were observed up to 50 km away from the rift axis~~. They proposed~~ and a recently active magmatic process ~~that released much higher amounts of carbon into the water column than previously thought. It was assumed that magmatic intrusions~~ triggering the alteration of organic-rich sediments and ~~release~~ releasing thermogenic methane and CO_2 was proposed (Lizarralde et al., 2010). Varying methane concentrations and temperature anomalies in the water column ~~were interpreted as~~may result from active thermogenic methane production generated by contact metamorphism (Lizarralde et al., 2010). This process might cause a maximum carbon flux of 240 kt C yr^{-1} and might induce profound climatic changes.

During the SO241 expedition in June/ July 2015 a new hydrothermal vent field was discovered at the flank of the northern trough (Fig. 1; Berndt et al., 2016). The discovered mound rises up to 100 m above the seafloor and predominantly Black Smoker~~-~~-type vents suggest similar endmember temperatures and geochemical composition as found at the

southern trough (~~Berndt et al., 2016;~~ Von Damm et al., 1985; Von Damm, 1990; Berndt et al., 2016). ~~Berndt et al. (2016) discovered an active~~The hydrothermal vent system ~~comprised of black smoker type chimneys that release~~emits methane-rich fluids with a helium isotope signature indicative of fluids in contact with mid-ocean ridge basalt. The vigorous release of large amounts of methane and CO_2 up to several hundred of meters into the water column ~~combined with magmatic intrusions into underlying sediments~~ led Berndt et al. (2016) to support the hypothesis that magmatic intrusions into deep sediments ~~this process~~ might have triggered the PETM during opening of the North Atlantic as proposed by Svensen et al. (2004).

During RV SONNE cruise SO241, ~~both,~~we sampled the recently discovered hydrothermal vent in the northern trough (Berndt et al., 2016) and some of the off-axis seeps described by ~~(~~Lizarralde et al. (2010), which are located above potential sill intrusions. ~~were investigated by~~We collected sediment, carbonate, and water column samples~~ing~~. Here, we present fluid and/ or gas geochemical data from ~~both~~ the cold seeps, the hydrothermal ~~system~~vent field, the water column~~s~~, and gas hydrates. ~~as well as~~ In addition, an authigenic carbonate, exposed at the surface of one seep site, was examined~~–~~. ~~data~~Furthermore, we performed seismic scans and temperature measurements. ~~and~~ All data will be discussed ~~these data in the context of seismic data~~ in order to ~~constrain~~ identify subsurface processes and fluid origin and will be compared to results by ~~(~~Lizarralde et al. ~~,~~(-2010). ~~-~~ Our data reveal that pore fluids and hydrocarbon gases at the seep locations essentially reflect shallow diagenetic processes. Hence, at the investigated sites (except close to the hydrothermal vent field), deep-seated, hydrothermal processes appear to be extinct nowadays suggesting that any sill-induced release of thermogenic methane highly depends on the longevity of the magmatic systems underneath.

2 Materials and methods

2.1 Sampling devices and strategy

During the RV SONNE expedition SO241 seven sites across the central graben of the Guaymas basin were investigated (Fig. 1). Site-specific sampling and data recording ~~was~~ were performed using ~~a~~ (1) a video-guided multicorer (MUC), (2) a gravity corer (GC), (3) temperature loggers attached to ~~the~~ a GC or sediment probe, (5) a video-guided VCTD /

Rosette water sampler, and (6) a video-guided hydraulic grab (VgHG). Sites were selected according to published data on the locations of seeps (Lizarralde et al., 2010) and seismic data acquired during the cruise (see below).

2.1.1 Seismic data recording

Seismic data were collected using a Geometrics GeoEel Streamer of 150 ~~to~~ and 183.5 m length and 96 and 112 channels, respectively. Two ~~GI guns~~generator-injector guns in harmonic mode (105/105 cubic inch) served as the seismic source. Processing included navigation processing (1.5625 m crooked line binning), 20, 45, 250, 400 Hz frequency filtering, and poststack Stolt migration with water velocity yielding approximately 2 m horizontal and 5 m vertical resolution close to the seafloor.

2.1.2 Sediment and pore fluid sampling

At seepage and vent sites, the video-guided ~~multicorer~~ MUC was used to discover recent fluid release, which is indicated by typical chemosynthetic biological communities at the seafloor (~~bacterial~~ microbial mats, bivalves, etc.). However, small-scale, patchy distributions of active seepage spots and visibility of authigenic carbonate concretions made it difficult to select the "best possible" sampling locations for ~~getting~~ fine-grained sediment ~~samples~~. Hence, comparing results from different seeps might be biased in this regard as seepage areas might not have been hit at the most active place. GC deployments were typically performed at pre-inspected MUC sites or at the center of suspected seeps (based on bathymetry and seismic data).

In total, we present pore fluid and gas data collected at th~~re~~e seepage sites~~,~~ North (GC01, MUC11), Central (GC03, GC13, GC15, MUC04), and Ring Seep~~s~~ (MUC05), one ~~Reference~~ reference ~~Site~~ site (~~no active seep site,~~ see ~~definition above~~below; Reference Site; GC04, MUC02), and ~~one~~ the ~~active~~ hydrothermal ~~site,~~vent field ~~–~~ (Smoker Site; ~~(~~GC09, GC10, MUC15, MUC16). ~~A~~ The Reference Site, that did not show active seepage or faults indicated by seismic data, was chosen to obtain geochemical background values. In addition, the slope towards the Mexican mainland was sampled as well (Slope Site; GC07) (Fig. 1, Table 1). ~~After~~ Immediately after core retrieval, ~~gravity cores~~GCs were cut, ~~and~~ split, ~~on deck~~ and

~~immediately~~ subsampled. Samples were transferred into a cooling lab at 4°C and processed within 1 or 2 hours. Pore fluids were obtained by pressure filtration (e.g. Jahnke et al., 1982). Sediment samples for hydrocarbon gases were taken on deck with syringes and transferred to vials containing concentrated NaCl solution (after Sommer et al., 2009). After ~~multicorer~~ MUC retrieval, bottom water was sampled and immediately filtered for further analyses. The sediment was transferred into a cooling lab and sampling was executed in an argon-flushed glove bag. Pore fluids were retrieved by centrifugation and subsequent filtration using 0.2 µm cellulose acetate membrane filters (e.g. Jahnke et al., 1982).

Figure 1:~~–~~ Sample locations in the Guaymas Basin, Gulf of California~~,~~ ~~–~~ studied during RV SONNE expedition SO241. (a) Overview of stations (Seep Sites, Smoker Site, and Slope Site). Black square indicates enlargement area in (b). Site DSDP 477 in the southern trough is shown for comparison. (b) Enlargement of the sampling locations. Red circles refer to GC employments and yellow triangles to MUCs. Brown square at Graben Site refers to water column sampling and temperature measurements. Black lines refer to seismic profiles, displayed in Fig. 2. ~~Graben Site refers to water column sampling only.~~ (c) Enlargement of Smoker Site sampling locations. Note the different scale compared to (a) and (b). Black arrow refers to the location of the hydrothermal mound described in ~~(~~Berndt et al.~~,~~ (2016).

2.1.3 Subseafloor temperature measurements

Temperature gradients and thermal conductivity were measured at North Seep, Central Seep, Reference Site, and Smoker Site as well as along a transect across the newly discovered hydrothermal vent field and the rift valley (Graben Site). Miniaturized temperature loggers (MTL) were attached to ~~gravity cores~~GCs or to a 5 m long sediment lance at a sampling rate of 1 measurement per second. The absolute accuracy of these temperature measurements is about 0.1 K and the temperature resolution is 0.001 K (Pfender and Villinger, 2002).

Thermal conductivity was measured on recovered core material in close vicinity to the MTLs using the KD2 Pro Needle Probe instrument. For temperature measurements obtained by a lance, a constant thermal conductivity of 0.7 W ~~/~~m^{-1} K was assumed. Data processing was done according to Hartmann and Villinger (2002).

196

197 2.1.4 Water column sampling

198

199 Water samples were taken by using a video-guided Niskin Water sampler Rosette System
200 (Schmidt et al., 2015) in order to study water column chemistry (i.e. dissolved CH_4) and
201 oceanographic parameters (i.e. temperature, salinity, turbidity). Eight water sampling
202 locations were chosen in the vicinity of MUC and GC stations and are termed North Seep
203 (VCTD03), Central Seep (VCTD02), Ring Seep (VCTD01), Graben Site (CTD01; no video-guided
204 sampling), Smoker Site (VCTD06 and 10), and Slope Site (VCTD07). Additionally, hydrocarbon
205 data published in Berndt et al. (2016) from the ~~Smoker Site~~hydrothermal plume (VCTD09)
206 are shown. The (V)CTDs were either used in a towed mode (VCTD03, 06, 09, 10) or in station
207 (CTD01; VCTD01, 02, 07) keeping hydrocast mode. The water depth was controlled based on
208 pressure readings, altitude sensors (<50 m distance to bottom), and online video
209 observation (1 - 2 m above the seafloor).

210

211 2.1.5 Authigenic carbonate sampling

212

213 At Central Seep a block (approx. 1 x 0.5 x 0.3 m~~)) mainly consisting of solidified carbonate~~
214 ~~matrix covered by a whitish carbonate rim and characterized by coarse open pore space in~~
215 ~~mm to cm scale (see supplementary Fig. 1S)~~ was recovered in 1843 m water depth from the
216 surface of a typical cold seep environment (close to high abundance of tube worms) by the
217 deployment of a video-guided hydraulic grab (VgHG, GEOMAR). The block consisted mainly
218 of solidified carbonate matrix covered by a whitish carbonate rim and was characterized by
219 coarse open pore space in mm to cm scale (see supplementary Fig. S1).

220

221 2.2 Sample treatment and analytical procedures

222

223 Pore fluids were analyzed onboard for total dissolved sulfide (TH_2S) and NH_4 directly after
224 recovery by photometer using standard methods described in Grasshoff et al. (2002). Prior
225 to NH_4 measurements, pore fluids containing dissolved sulfide were treated with argon to
226 prevent biased NH_4 measurements. Total alkalinity (TA) was determined by titration
227 immediately after pore water separation using 0.02 M HCl (Ivanenkov and Lyakhin, 1978).

Shore-based analyses of the remaining acidified pore water included dissolved anions (SO_4, Cl) and cations (Li, Mg) using ion chromatography (IC, METROHM 761 Compact, conductivity mode) and inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN 720-ES), respectively. ~~Pore fluids were analyzed onboard by photometry (hydrogen sulfide and NH_4) and titration (total alkalinity = TA). Subsamples were analyzed in shore-based laboratories for major anions and cations using ion chromatography (IC, METROHM 761 Compact, conductivity mode) and inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN 720-ES), respectively. Detailed descriptions can be found elsewhere (e.g. Scholz et al., 2013).~~ All chemical analyses were tested for accuracy and reproducibility using the IAPSO salinity standard (Gieskes et al., 1991).

Strontium isotope ratios were analyzed by Thermal Ionization Mass Spectrometry (TIMS, Triton, ThermoFisher Scientific). The samples were chemically separated via cation exchange chromatography using the SrSpec resin (Eichrom). The isotope ratios were normalized to the NIST SRM 987 value of 0.710248 (Howarth and McArthur, 2004) which reached a precision of ± 0.000015 (2 sd, n = 12). Potential influences of ^{87}Rb interferences on $^{87}Sr/^{86}Sr$ isotope ratios are eliminated by combining the highly selective Sr-Spec resin and Rb/Sr-discriminating TIMS pre-heating procedures with the static mode measurement of ^{85}Rb simultaneously to the Sr masses 84, 86, 87 and 88 for optional Rb/Sr corrections (not required in this study).

Water samples taken from Niskin bottles were transferred into 100 ml glass vials with helium headspace of 5 ml and poisoned with 50 µl of saturated mercury chloride solution.

Hydrocarbon composition of headspace gases was determined using a CE 8000 TOP gas chromatograph equipped with a 30 m capillary column (Restek Q-PLOT, 0.32 mm) and a flame ionization detector (FID). Replicate measurements yielded a precision of <3 % (2 sd).

Stable carbon isotopes of methane were measured using a continuous flow isotope ratio mass spectrometer (cf-IRMS). A Thermo TRACE gas chromatograph was used to separate the light hydrocarbon gases by injecting up to 1 ml headspace gas on a ShinCarbon ST100/120 packed gas chromatography column. The separated gases were combusted and corresponding $\delta^{13}C$ values were determined using a Thermo MAT 253 mass spectrometer. The reproducibility of $\delta^{13}C$ measurements was ±0.3 ‰ (2 sd) based on repeated measurements of the reference standard Vienna Pee Dee Belemnite (VPDB) ~~(2 sd)~~.

Stable hydrogen isotope compositions of methane were analyzed by separating methane from other gases by online gas chromatography (Thermo Trace GC; isotherm at 30°C; 30 m RT-Q-Bond column, 0.25 mm ID, film thickness 8 µm). Prior to stable isotope analysis using a coupled MAT 253 mass spectrometer (Thermo) methane-H was reduced to dihydrogen at 1420°C. Data are reported in per mil relative to Standard Mean Ocean Water (SMOW). The precision of δD-CH_4 measurements was ±3 ‰ (2 sd).

^{210}Pb (46.52 keV) and ^{214}Pb (351.99 keV) were simultaneously measured on freeze dried sediments by two HPGe gamma spectrometry systems (ORTEC GMX-120265 and GWL-100230), each interfaced to a digital gamma-ray spectrometer (DSPecPlus™). Efficiency calibration of the gamma detectors were calibrated using IAEA reference materials, coupled with an in-house secondary standard for various masses (Lee et al., 2004; Huh et al., 2006~~; Lee et al., 2004~~). ^{214}Pb was used as an index of ^{226}Ra (supported ^{210}Pb) whose activity concentration was subtracted from the total ^{210}Pb to obtain excess ^{210}Pb ($^{210}Pb_{ex}$). The activities of radionuclides were decay-corrected to the date of sample collection. All radionuclide data are calculated on salt-free dry weight basis.

A representative sample of the authigenic carbonate (cm-scale) was broken from the upper surface of the block, gently cleaned from loosely bound sediment and organic remains and dried at 20°C for 12 h~~rs~~. Two different subsamples were prepared by drilling material with a handheld mm-sized mini-drill from the outer rim (whitish coating, lab code: 470-15) and the related inner core (dark matrix, lab code: 472-15).

Prior to aliquot procedures both subsamples were finely ground in an agate mortar providing homogeneous aliquots of suitable grain size for ~~the combined approach of~~ mineral identification by X-ray diffractometry (XRD) (Philips X-ray diffractometer PW 1710 in monochromatic CuKα mode between 2 and 70 2θ (incident angle), for details see supplement)~~.~~. Subsamples were analyzed for δ^{18}O and δ^{13}C ~~analyses~~ by stable isotope ratio mass spectrometry (SIRMS) and U-Th geochronology by multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) on a parallel leachate / sequential dissolution approach for single and isochron ages (method see supplement). ~~as well as~~Furthermore, $^{87}Sr/^{86}Sr$ isotope signatures for aliquots of the individual U-Th solutions by thermal ionization mass spectrometry (TIMS, for method details please refer to pore water Sr isotope analyses)

were determined. Lipids extracts for biomarker determination were analyzed as well (see below).

From each homogenized carbonate powder sample (see above), an aliquot of 10 mg was separated for carbon $\delta^{13}C$ and oxygen $\delta^{18}O$ stable isotope analysis. A fraction from this (approximately 1 mg) was dissolved by water-free phosphoric acid at 73°C in a "Carbo-Kiel" (Thermo Fischer Scientific Inc.) online carbonate preparation line and measured for carbon and oxygen stable isotope ratios with a MAT 253 mass spectrometer (Thermo-Fischer Inc.). The $\delta^{13}C$ and $\delta^{18}O$ values are calculated as deviations from laboratory standard referred to the PDB scale and reported in ‰ relative to V-PDB. The external reproducibility was checked by replicate analyses of laboratory standards as being better than ±0.04 ‰ for $\delta^{13}C$ and ±0.1 ‰ for $\delta^{18}O$ (1 ~~SD~~sd, n=7) for this sample set. However, the single measurement uncertainties were significantly better and the resulting ~~2SD~~ 2 sd (n=3) for both main samples are given in the supplement ~~table~~ Table ~~S5~~S6.

Biomarkers were ~~determined by grounding~~extracted from 4 g of powderized ~~the~~ sample and were then sequentially extracted with dichloromethane (DCM)/methanol (3/1, v/v), DCM, and *n*-hexane (ultrasonication, 20 min). The combined extracts were dried, derivatized using a BSTFA/trimethylchlorosilane mixture (95/5, v/v; 1h; 40°C) and analysed by coupled gas chromatography-mass spectrometry (GC-MS). GC-MS analyses were carried out with a Thermo Fisher Trace 1310 -GC coupled to a Quantum XLS Ultra MS. The ~~GC~~ instrument was equipped with a Phenomenex Zebron ZB 5MS capillary column (30 m, 0.1 µm film thickness, inner diameter 0.25 mm). Fractions were injected splitless at 270°C. The carrier gas was He (1.5 mL/min). The GC oven temperature was ramped from 80°C (1 min) to 310°C at 5°C min^{-1} and held for 20 min. Electron ionization mass spectra were recorded at 70 eV.

3 Results

3.1 Subsurface structure and evidence for sill-related fluid mobilization

Seismic profiles show a wide range of sediment deformation (Fig. 2). Seismic amplitude blanking along vertical zones below the seafloor indicates ~~apparent fluid~~the flow of gaseous pore fluids at North, Central, and Ring Seep (Fig. 2). Underneath these locations~~,~~ sediments

are deformed~~. Blankening of the seismic signal is attributed to~~, probably due to sediment mobilization associated with hydrothermal activity in response to sill intrusion.~~ sediment mobilization due to the hydrothermal activity in response to sill intrusion.~~ In contrast~~, at~~ the Reference Site sediments show a more or less continuous succession without vertical disturbance. At North Seep, a shallow high-amplitude reversed polarity reflector occurs at 50-60 m~~b~~s~~f~~. Sill depths are inferred from the seismic profiles at ~500 to 600 meter below seafloor (mbsf) for North Seep and with ~350 to 400 mbsf at the other sites, assuming seismic interval velocities of 1600 to 2000 m s^{-1}. Seismic images suggest that massive disturbance of sediments and vertical pipe structures are related to channeled fluid and/or gas advection caused by sill intrusions (Fig. 2). Faults are indicated which may serve as fluid pathways above potential sill intrusions. Closer inspection of the seismic reflectors at the Central Seep (Fig. 2c) shows onlap onto a doming structure. On the NW flank of the dome the deepest onlap occurs at 60 ms or 48 mbsf ~~m below the sea floor~~ (assuming 1600 m s^{-1} sediment interval velocity) whereas on the SE flank the shallowest onlap occurs at 15 ms or 12 mbsf~~m below the sea floor~~.

Figure ~~.~~2: Seismic profiles of North Seep (a), Smoker Site (b) as well as of Central Seep and Reference Site (c). Seismic section showing doming above the Central Seep. There are different phases of onlap starting about 60 ms~~mbsf~~ (maximum deposition) until about 15 ~~mbsf~~ ms (minimum deposition) or 48 and 12 mbsf respectively assuming a sediment interval velocity of 1600 m s^{-1}.

3.2 Temperature measurements

Heat flow and temperature gradients were measured at North and Central Seep, Reference Site, and Smoker Site (attached to GCs) as well as in transects along the hydrothermal ridge and rift axis (attached to a temperature lance; Fig. 3 and S2, Table 1). Temperature gradients are shown in Figure S2. Highest heat flows ~~values~~ occurred close to the Smoker Site and ranged between 599 and 10835 mW m^{-2}. Temperature gradients were also highest at the Smoker Site (~15 K m^{-1}). In contrast, heat flows ~~values~~ and temperature gradients in the rift valley close to the rift axis ranged between 262 and 338 mW m^{-2} and 0.4 to 0.5 K m^{-1},

355 respectively. Generally heat flow values decreased with increasing distance to the rift axis
356 with 140 mW m^{-2} at the Reference Site, 113 mW m^{-2} at Central Seep, and 28 mW m^{-2} at North
357 Seep. Temperature gradients are 0.22 K m^{-1} at the Reference Site, 0.16 K m^{-1} at Central Site
358 and 0.14 K m^{-1} at North Site.
359
360 Figure 3: (a) Heat flow ~~in the Guaymas Basin~~ in ~~relative distance to the rift axis~~the vicinity of
361 the northern trough. Note the different heat flow scale in the enlarged area of the Smoker
362 Site (b).
363
364 3.3 Sediment characteristics and sedimentation rates
365
366 The sediments are mainly composed of organic-rich diatomaceous clay, consistent with
367 earlier analyses (e.g. Kastner, 1982). At North Seep, the sediments are composed of
368 homogeneous diatomaceous clay~~.~~ containing r~~R~~are shell fragments and carbonate
369 concretions ~~are present~~. Gas hydrates were discovered at 2.5 ~~meters below seafloor (~~mbsf~~)~~.
370 Authigenic carbonates were ~~present~~ exposed at the seafloor. At Ring Seep, SW of North
371 Seep, sediments are predominantly composed of diatomaceous clay. At Central Seep,
372 located between North Seep and Smoker Site, sediments are composed of homogeneous
373 diatomaceous clay intercalated with whitish layers and shell fragments occurring shallow in
374 the sediment (≤ 70cm)~~and banding of whitish layers in the lower meter of the GC~~. ~~At the~~
375 ~~seafloor~~Again, authigenic carbonates were ~~present as well~~observed on the seafloor. At
376 Smoker Site, ca. 500 m SE of the hydrothermal vent field, surface sediments are likewise
377 composed of diatomaceous clay with light and dark greyish banding. Traces of bioturbation
378 are visible in the upper 4 m. ~~Below about 4 m depth~~At this depth, a sharp contact defines
379 the transition to the underlying hydrothermal deposits, which are composed of mm-to-cm
380 sized black to grey Fe-rich sulfides (for a detailed description see Berndt et al. (2016)). Within
381 the hydrothermal deposits brownish to grey clay lenses appear. At the Slope Site, sediments
382 are laminated in the mm- to cm-range. The sediment is dominated by diatomaceous clay ~~and~~
383 ~~only~~that contains a few ash lenses ~~exist~~.

384 The sedimentation rates ranged between 0.4 m kyr^{-1} at Smoker Site and 3.5 m kyr^{-1} at North
385 ~~seep~~ Seep based on radionuclide~~s~~ measurements (Table 1). Sedimentation rates at all other
386 sites are about 2 m kyr^{-1}.

3.4 Pore water geochemistry

All pore water data and isotope measurements of $^{87}Sr/^{86}Sr$ are listed in supplementary ~~table~~ Tables S1~~2~~ and S2. Pore water profiles of ~~alkalinity~~TA, TH_2S, SO_4^{2-}, CH_4, NH_4, Cl^-, Mg, and Li are shown in Fig. 4a (GCs) and 4b (MUCs).

Figure 4: Pore water profiles of GCs (a) and MUCs (b). For Central Seep, GC13 is shown exemplary here, geochemical data of the remaining cores (GC03, 15) can be found in Table S1. Endmember composition of hydrothermal solutions from Von Damm et al. (1985) and hydrothermal plume geochemical composition from Berndt et al. (2016) are shown ~~as well~~ in (a) for comparison.

Pore water constituents plotted in Figure 4 were selected to characterize variations in organic matter diagenesis, anaerobic oxidation of methane (AOM), as well as potential water-rock interactions related to subsurface hydrothermal activity. In general, methane concentrations are elevated at the seep locations and at the slope, thus enhancing AOM. ~~Alkalinity~~ TA and TH_2S increase with depth for North Seep, Central Seep (only MUC04), and Slope Site, while SO_4^{2-} is decreasing. AOM depths can only be inferred for North Seep with ~160 cm and Slope Site with ~300 cm. NH_4 is only slightly increasing with depth; higher NH_4-levels are only found at the Slope Site (Fig. 4). Concentrations of Cl^-, Mg, and Li do not show significant variations from seawater in shallow sediment depths (MUCs). At greater depths (GCs) some deviations from seawater concentration occur at North Seep, Smoker Site, and Slope Site. At North Seep, Mg shows a minor offset at ~150 cm depth, while at Smoker Site Mg concentrations increase continuously. In GC09 at Smoker Site, Li concentrations increase and Mg concentrations decrease abruptly in a depth of ~400 cm. At the Slope Site, Mg increases slightly below 400 cm sediment depth while Li shows a small decrease above 400 cm.

Sr concentrations and isotopes are plotted in Fig. 5. Sr concentrations show predominantly modern seawater values, except at North Seep where they strongly decrease. The $^{87}Sr/^{86}Sr$ isotope ratios also show predominantly seawater values (0.709176; Howarth and McArthur,

2004)~~.~~, except ~~North and Ring Seeps show slight decreases in $^{87}Sr/^{86}Sr$, whereas values at~~for the Smoker Site where the isotope ratios decrease strongly below the transition between hemipelagic sediments and hydrothermal deposits (Fig. 5). North and Ring Seeps as well as Smoker Site (GC10) show slight decreases in $^{87}Sr/^{86}Sr$. The ratios show a similar depletion as those from the hydrothermal plume (Berndt et al., 2016).

Figure~~.~~ 5. Sr concentrations and $^{87}Sr/^{86}Sr$ ratios for GCs (~~upper panels~~a) and MUCs (~~lower panels~~b). For comparison, data from the hydrothermal ~~smoker~~ plume (Berndt et al., 2016), the hydrothermal endmember (Von Damm et al., 1985), and modern seawater (Howarth and McArthur, 2004) are shown ~~in the upper panel~~. Note the different x-axis scales for MUC Sr concentration and $^{87}Sr/^{86}Sr$ ratios.

3.5 ~~Pore water h~~Hydrocarbon gases, carbon and hydrogen isotope data

Concentrations of dissolved hydrocarbons and $\delta^{13}C_{CH4}$, $\delta^{13}C_{C2H6}$, and δD_{CH4} data are reported in supplementary ~~table~~ Table S3. Overall, our pore fluid data show a large variability in $CH_4/(C_2H_6+C_3H_8)$ with ratios between 100 and 10,000 and $\delta^{13}C_{CH4}$ between ~~-25~~ -26.5 and ~~-90~~ -88.2 ‰. Gas hydrate $\delta^{13}C_{CH4}$ ranges between -57.9 and -58.9 ‰. The $\delta^{13}C_{C2H6}$ values range between -26.1 and -38.3 ‰ for North Seep and -29.6 and -37.7 ‰ for Central Seep. The δD_{CH4} values at both seeps range between -97 and -196 ‰, for the gas hydrates between -196 and -198 ‰, for Slope Site between -192 and -196 ‰, and for the ~~Smoker~~ hydrothermal plume between -98 and -113 ‰ (VCTD09).

3.6 Water column data

Water column characteristics like temperature, salinity, turbidity, and ~~as well as~~ methane concentrations are shown in Fig. 6 and Table S4.~~are shown in figure 6 and supplementary table S4.~~ Surface waters in the Guaymas Basin show warm temperatures up to 29.5°C (salinity: 34.5 ‰) close to the Mexican mainland (Slope Site, VCTD07) and up to 24.6°C (salinity: 34.6 ‰) in the central basin (Central Seep, VCTD02). With depth, temperatures decrease continuously ~~to~~ and range between 2.8 ~~to~~ and 3.0°C (salinity: 34.6 ‰) close to the sea floor (1600 ~~-~~– 1800 m). Turbidity values are high in the deep water layer (~1400-1800 m)

and indicate a well-mixed deep basin, also shown by relatively homogeneous temperature and salinity data. Only the water column directly above the hydrothermal ~~smoker~~ vent field ~~(VCTD09)~~ shows strongly elevated temperature (28.4°C) and salinity (35.1 ‰) (Berndt et al., 2016). Methane concentrations are highest close to the hydrothermal ~~smoker~~ vent field (up to 400 µM, (VCTD09, ~~;~~ Berndt et al., 2016)~~)~~, but still vary in the deep water column of the basin between 2 and 28.1 nM (Central Seep (VCTD02) and Ring Seep (VCTD01), respectively).

Figure ~~.~~6: Water column temperature, salinity, turbidity, and methane concentrations. Note that the upper ~300 m below sea level (bsl)~~sl~~ in the turbidity data are not shown for scale matters. VCDT09 and temperature data from VCDT10 ~~temperature data~~ are from Berndt et al. (2016), all other parameters were acquired in this study.

3.7 Authigenic carbonate data

The authigenic carbonate sample (Fig. S1) consists of 88 to 90 % aragonite and 6 to 12 % calcite (supplementary Table S5). By the uncertainty related maximum deviation of Δd104 (< 0.01) the XRD spectrum identifies calcite with a Mg fraction below 3 % according to ~~(~~Goldsmith et al.~~,~~ (1961). The bulk outer rim carbonate has an average carbon isotope signature ($\delta^{13}C_{V\text{-}PDB}$) of -46.6±0.2 ‰ and an oxygen isotope signature ($\delta^{18}O_{V\text{-}PDB}$) of 3.7±0.3 ‰. Inner core carbonate isotope signatures yield similar values with $\delta^{13}C_{V\text{-}PDB}$ of -44.7±0.~~2~~ 4 ‰ and $\delta^{18}O_{V\text{-}PDB}$ of 3.6 ±0.1 ‰ (Table S5). The average outer rim $^{87}Sr/^{86}Sr$ ratio is 0.709184±0.000027 and the inner core ratio is 0.709176±0.000003. ~~External reproducibility of NIST-SRM987 is 0.000015 (2 SEM).~~ The U-Th carbonate dating approach on these authigenic carbonates implies formation ages younger than 240 yrs BP.

Lipids extracts obtained from seep carbonate 56-VgHG-4 (Central SiteSeep) revealed a strong signal of specific prokaryote-derived biomarkers (Fig. S1). These compounds encompassed archaeal isoprenoid lipids derived from archaea, namely crocetane, 2,6,10,15,19-pentamethylicosane(-icosenes (PMI, PMIΔ) archaeol, and *sn*2-hydroxyarchaeol (see Fig. S1 for structures). In addition, the sample contained a suite of non-isoprenoid 1,2-dialkylglycerolethers (DAGE) of bacterial origin. Typical compounds of planktonic origin, such as sterols, were also present, but low in abundance.

4 Discussion

4.2 1 Origin of seeping fluids

4.21.1 Black Smoker Site

The water column above the newly discovered hydrothermal vent field exhibits elevated CH_4 concentrations (up to 400 µM) and pCO_2 data (>6000 µatm) (Berndt et al., 2016)., and t The range of the measured stable isotope signature of methane ($\delta^{13}C_{CH4}$ between -39‰ and -14.9‰) and a the Helium helium (³He) isotope anomaly ($^3He/^4He$ ratio of 10.8 x 10^{-6}) clearly indicates gas exhalations from thermogenic organic matter degradation with contributions from a mantle source (see Berndt et al., 2016). These northern trough hydrothermal fluids are comparable in their gas geochemistry to the southern trough (Lupton, 1979; Von Damm et al., 1985; Berndt et al., 2016) as was demonstrated by endmember calculations in Berndt et al., 2016. However, the highest heat flow values of up to 10835 mW /m^{-2} measured in this study are found close to the Smoker Site and are much higher than those observed in earlier studies in which maximal 2000 mW/m² were measured in the center of the trough (maximal 2000 mW m^{-2}, Fisher and Becker, 1991). The high heat flow at Smoker Site even exceeds the hydrothermally more active southern trough where heat flow values of 2000 to 9000 mW m^{-2} mW/m² were measured (Fisher and Becker, 1991; Lonsdale and Becker, 1985; Fisher and Becker, 1991). This might indicate that hydrothermal activity at the northern trough is younger and possibly a more recent process compared to the southern trough.

Hydrothermal fluids are typically depleted in Mg and highly enriched in fluid-mobile elements like Li caused by high-temperature reactions with mafic rocks (here sills) and/ or

sediments through which they percolate (e.g. Einsele et al., 1980; Gieskes et al., 1982; Kastner, 1982; Von Damm et al., 1985; Lizarralde et al., 2010; Teske et al., 2016). Such compositions ~~are~~ were reported from DSDP site 477 (Gieskes et al., 1982) and fluids obtained by Alvin dives (Von Damm et al., 1985) (see Fig. 1 for location of Site DSDP 477). Although strongly diluted, CTD samples from the hydrothermal ~~Black Smoker~~ plume in the ~~Northern~~ northern trough show this trend (Berndt et al., 2016).

An indication for the presence of hydrothermal fluids in pore waters in the vicinity of the hydrothermal vent field is found at about 4 m depth in core GC09. Here, positive Li and negative Mg concentrations (Fig. 4a) are probably caused by weak admixing of hydrothermal solutions (Gieskes et al., 1982; Hensen et al., 2007). Likewise, $^{87}Sr/^{86}Sr$ isotope ratios decrease to a value of 0.708949 (Fig. 5) and thus tend towards the $^{87}Sr/^{86}Sr$ ratio of the local hydrothermal endmember ($^{87}Sr/^{86}Sr$ = 0.7052; Von Damm, 1990). Hydrothermal endmember Li concentrations in the Guaymas Basin have been reported in a range between 630 and 1076 µM (Von Damm et al., 1985) and are 20 to 30 times higher than those measured at Smoker Site (~34 µM; Fig. 4a, Table S1). Here, hydrothermal fluids account for about 3 % in the mix with seawater (Fig. 7). The sediments in this core section also change from diatomaceous clay to unconsolidated, coarse-grained hydrothermal deposits (Fe-rich sulfides; see also Sect. 3.3) which may facilitate the circulation of hydrothermal fluids.

Despite the proximity of the remaining ~~gravity cores (GC09, GC10) and multicorer cores (MUC15, MUC16)~~GCs and MUCs to the hydrothermal vent field (~500 m distance; temperatures ~~measured~~ immediately after retrieval are up to 60°C) typical pore fluid ~~geochemical signatures within nearby sediments are not much different from those in seawater (Fig. 4). Specifically~~ indicators such as Mg, Li, ~~Cl,~~ and $^{87}Sr/^{86}Sr$ ~~which are considered as good indicators for hydrothermal alterations and/or deep-seated diagenetic processes~~ do not show ~~any prominent~~major excursions from seawater values (Fig. 4). ~~Geochemical~~ Similarly, NH_4, an indicator~~s~~ for a diagenetic or catagenetic breakdown of organic matter, is ~~like NH_4 are~~ only poorly enriched in sediments surrounding the hydrothermal ~~black smoker~~ vents ($NH_4 \leq 0.3$ mM). ~~. Expected end-member values should be similar to those~~NH_4 remains well below the value reported from the southern trough (20 mM; Von Damm et al. (1985))~~,~~ ~~but they remain well below (≤ 0.3mM). For comparison, intense organic matter breakdown occurs in areas with high sediment accumulation rates like the continental slope (Simoneit et al., 1986). Here~~ and the Slope Site (GC07) where~~, maximum NH_4 levels of 1~~ 10 mM

~~(accompanied by high levels of alkalinity and AOM; Fig. 3)~~ are reached ~~in the pore water~~ already at subsurface depths of only a few meters (Fig. 4)~~, confirming that a fluid mobilized from greater subsurface depth must be enriched in NH_4 and other products of organic matter degradation. Overall, this~~ The pore fluid geochemistry around the hydrothermal vent field therefore confirms that early-diagenetic processes are not intense (Fig. 7) and that the ~~around the Smoker Mound and further indicates a shallow convection mixing seawater into the sediments in ≤4m depth. Our data therefore suggest that the~~ shallow sediments ~~surrounding the Black Smoker area are not~~ are not significantly affected ~~percolated~~ by hydrothermal fluids. We hypothesize that hydrothermal venting causes a shallow convection cell~~ (e.g. Henry et al., 1996)~~ drawing seawater through the sediments towards the hydrothermal vent field, while the sediments become heated by lateral heat conduction (cf. Gamo et al., 1991; Henry et al., 1996; Kinoshita and Yamano, 1997)~~drawing seawater through the sediments towards the smoker, while the sediments become heated by lateral heat conduction~~.

Fig. 7: NH_4 (µM) ~~(a) and $^{87}Sr/^{86}Sr$ ratios (b)~~ versus Li concentrations (µM) of Guaymas Basin cold seeps (North, Central) and the ~~hydrothermal Smoker vent field~~Smoker Site. D~~Guaymas d~~eep ~~Smoker~~ fluids from Smoker Site (GC09) mix with hydrothermal fluids with a share of ~3%. The mixing line has been calculated following: $x_{mix} = x_{phase1} * f_1 + x_{phase2} * f_2$ (1), with $f_1 + f_2 = 1$. Endmember 1 is the Guaymas Vent South (Von Damm, 1985, 1990) and endmember 2 is Guaymas North Seep. For comparison, Guaymas hydrothermal endmember fluid composition (Von Damm, 1985, 1990), hydrothermal plume fluid composition (Berndt et al., 2016), Guaymas slope sediments (GC07), and deep-sourced cold seeps (Aloisi et al., 2004; Hensen et al., 2007) are shown.

~~The hydrothermal activity in the northern trough of the Guaymas Basin can be summarized to occur only in a relatively confined area affecting the surrounding sediments in a minor way by lateral heat transfer.~~ The diatomaceous clay might act as a seal to upwards migrating fluids, which are channeled to the catchment area of the rising hydrothermal fluids of the hydrothermal vent field ~~Black Smoker vent field~~ (~~Fig. 4 in~~see also Berndt et al., 2016, their Fig. 4). The geochemical composition of these ~~upwards migrating hydrothermal~~ fluids is

likely influenced by high temperature chemical alteration ~~reactions between~~ of the sediment caused by~~and~~ the intruded sills (Fig. 2b). However, shallower pore fluids of surface sediments at the ~~smoker~~ Smoker ~~site~~ Site (i.e. 0-4 m) are not much affected by contributions from these fluids and show predominantly ambient diagenetic~~seawater~~ fluid signatures. ~~Despite the elevated heat flow in the vicinity of the hydrothermal vent field, early diagenetic reactions are also not enhanced as seen e.g. by only slightly elevated NH_4 concentrations and sulfate concentrations that remain at seawater values throughout the cores (Fig. 4).~~

4.~~2~~1.2 Cold seeps

The selection of sampling sites at presumed seep locations was based on existing published data (Lizarralde et al., 2010) and information from seismic records (~~see~~ Fig. 2). Seismic amplitude blanking along vertical zones below the seafloor indicates ~~(~~active~~?)~~ fluid and/ or gas conduits at North and Central Seep. ~~Following the hypothesis~~Given that sill intrusions and related high-temperature alteration of sediments are driving the seepage, the expectation was to find deeply-sourced (average sill depth ~400 m) fluids~~, characterized by~~ with a typical geochemical signature analogous to findings at hydrothermal ~~Black Smoker~~ vents in the Guaymas Basin (~~Berndt et al., 2016;~~ Von Damm et al., 1985; Von Damm, 1990; Berndt et al., 2016). Such characteristics are e.g. a high concentration of thermogenic hydrocarbon gases formed by organic-matter degradation, ~~which is accompanied by~~ enrichments in ~~other organic tracers such as ammonium~~ NH_4, ~~as well as~~ depletion in Mg, and a strong enrichment in fluid-mobile tracers like Li and B (e.g. Aloisi et al., 2004; Scholz et al., 2009). Hydrocarbon formation caused by abiogenic processes plays only a minor role in the hydrothermal vent field (~~Berndt et al., 2016;~~ McDermott et al., 2015; and discussion in Berndt et al. (2016)).

~~The results from s~~Samples obtained using a video-guided MUC ~~show~~ revealed ~~that~~ the highest methane concentrations ~~compared to all other sites were measured~~ at North, Central, and Ring Seeps (Fig. 4b). In conjunction with ~~This and the fact that methane concentrations are exceeding those at the high-accumulation slope station underlines the~~ visual evidence (abundant chemosynthetic biological communities) ~~of active methane seepage~~this confirms that we have hit active seepage areas during our sampling campaign.

At the two most active sites, North and Central, high methane levels are accompanied by a significant drop in sulfate and increase in ~~alkalinity~~ TA and TH_2S, providing evidence for AOM, ~~.~~according to the net reaction:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \quad (2)$$

(e.g. Nauhaus et al., 2005; see Wegener et al., 2016 for a recent update).

These pore water trends are even more pronounced in GC01 (North) where the AOM zone was completely penetrated and gas hydrate was found at about 2.5 mbsf. Unfortunately, GCs from similarly active sites could not be obtained from Central and Ring ~~seeps~~Seeps, mainly because of patchiness of seepage spots and widespread ~~occurrence of~~ authigenic mineralizations at the seafloor preventing sufficient penetration. Nevertheless, ~~the occurrence of~~ active methane seepage at all three investigated sites is evident. ~~A closer look at the lower panel of Fig. 4 a,b (and Table S2) illustrates that t~~The methane flux is, however, not accompanied by any significant excursion of ~~major~~ pore water constituents ~~that would be~~ typical for deeply-sourced, high-temperature sediment-water interactions (e.g. Mg, Cl, Li). Also Sr concentrations show seawater values ~~throughout~~ at all seep sites (Fig. 5), ~~with the exception of~~except for North Seep where ~~Sr concentrations in conjunction~~values drop together with Ca ~~(not shown) decrease and point~~due to co-precipitation ~~with Ca~~ during carbonate formation. The $^{87}Sr/^{86}Sr$ ratios show predominantly seawater signatures as well (Fig. 5, Table S2). Similarly, low NH_4 concentrations of <1 mM indicate a low ~~, as tracer for the~~ intensity of organic matter decomposition (as discussed in Sect. 4.1.1).~~, in both MUCs and GCs, remain at levels <1mM. This is much lower than the end-member reported from vent fluids in the Southern Trough (Von Damm, 1985) and also lower compared to high-accumulation areas like the Slope and the Graben Site (Fig. 4a,b). Essentially, all data presented in Figure 4~~Taken together, our data show that, with exception of methane and sulfate, the pore water corresponds to ambient diagenetic conditions~~,~~ that are typically met in this shallow subsurface depth.~~–~~ An explanation for the decoupling ~~between high~~of methane levels~~, sulfate depletion at shallow depths, and otherwise more or less unchanged~~ and pore water composition is that only methane ~~in form of free gas~~ is rising to the seafloor as a free gas. This assumption requires a closer look at the composition of dissolved hydrocarbons in general, which is given below.

4.~~3~~ 2 Origin of hydrocarbon gases

4.~~3~~2.1 Alteration effects

The origin of hydrocarbon gases can be deciphered by plotting ~~hydrocarbon~~ $CH_4/(C_2H_6+C_3H_8)$ ratios versus $\delta^{13}C_{CH4}$ data in a modified Bernard diagram (Schmidt et al., 2005 and literature therein) (Fig. 8a) and $\delta^{13}C_{CH4}$ versus δD_{CH4} after Whiticar (1999) and Welhan (1988) (Fig. ~~9~~8b). Most of the measured stable isotope data of pore water methane indicate a microbial origin or a mixed microbial and thermogenic origin (Fig. 8~~, 9~~). By contrast, ~~the isotopic and geochemical signature of~~ hydrocarbons venting at the ~~Smoker~~ hydrothermal vent field ~~Site~~ reflect~~s~~ a mixture of thermogenic methane ~~of thermogenic~~ and abiogenic ~~(~~methane derived from water-rock interactions~~) origin~~ (Berndt et al., 2016).

Figure 8: Hydrocarbon, $\delta^{13}C_{CH4}$ and δD isotope data for Guaymas Basin seep sites, Smoker and Slope Site. Hydrothermal plume data are shown for comparison. Note that hydrocarbon and $\delta^{13}C_{CH4}$ data are from Berndt et al. (2016). (a) ~~Hydrocarbon~~ $CH_4/(C_2H_6+C_3H_8)$ ratios versus $\delta^{13}C_{CH4}$ data are shown after a modified Bernard diagram (Schmidt et al., 2005). Pale symbols indicate samples above the AOM zone. Rayleigh fractionation lines show the effect of (microbial) methane oxidation, labels indicate the residual methane in %. (b) Carbon ($\delta^{13}C_{CH4}$) and hydrogen (δD_{CH4}) isotope data after Whiticar (1999) and (Welhan, 1988). Pale symbols (Central Seep (MUC04)) indicate samples above AOM zone.

~~Figure 9: Carbon ($\delta^{13}C_{CH4}$) and hydrogen δD isotope data after Whiticar (1999) and (Welhan, 1988). Pale symbols (Central Seep (MUC04)) indicate samples above AOM.~~

Interestingly, all but ~~two~~ three ~~samples~~North Seep sediments, analyzed for $\delta^{13}C_{CH4}$ ~~from North Seep sediments~~ are located above the AOM zone (see Fig. 4) and could therefore be affected by ~~-~~microbial metabolisms utilizing electron-acceptors other than sulfate, namely nitrate, manganese(IV) or iron(III) (e.g. Jørgensen, 2006)~~(Fig. 8)~~. ~~Anaerobic methane oxidation enriches~~AOM enriches ~~CO_2~~ DIC in ^{12}C ~~which results in a~~and results in progressively ~~^{13}C-enriched methane residue shifting the~~increasing $\delta^{13}C_{CH4}$ values ~~towards heavier values~~in

the residual methane (Whiticar, 1999) ~~(e.g. Borowski et al., 1997; Dowell et al., 2016)~~. Considering the $\delta^{13}C_{CH4}$ at Slope Site ~~methane signatures~~ as a microbial endmember composition for the Guaymas Basin (Fig. 8a), most of the data fall on calculated fractionation lines for AOM~~methane oxidation~~ following a Rayleigh trend (Whiticar, 1999). Methane sampled close to the Smoker Site (MUC15) is obviously also affected by ~~anaerobic methane oxidation~~AOM (Fig. 8a). This is in line with recent studies on hydrothermal sediments of the southern trough of the Guaymas Basin, where bacterial and archaeal communities catalyze the oxidation of methane and higher hydrocarbons and shift $\delta^{13}C_{CH4}$ values to heavier signatures (Dowell et al., 2016). ~~This process has recently been described by Dowell et al. (2016), who detected bacterial and archaeal communities in hydrothermal sediments of the southern trough of the Guaymas Basin, which were found to catalyze the oxidation of methane and higher hydrocarbons and shift $\delta^{13}C_{CH4}$ values to heavier signatures.~~

~~Origin~~

The origin of methane and oxidation effects can further be identified in the $\delta^{13}C_{CH4}$ versus δD_{CH4} plot after Whiticar (1999) and Welhan (1988) (Fig. ~~9~~8b). Slope Site samples plot in the field of microbial CO_2 reduction while ~~Smoker~~ hydrothermal plume samples plot in the thermogenic field~~,~~. O~~o~~ne sample ~~of the Smoker Site~~ even points to a mantle signature, and thus shows ~~clear~~ potential endmember isotope signatures (Berndt et al., 2016). North Seep samples (pore fluids and gas hydrates) plot in the mixing region while samples from Central Seep clearly shift away from the microbial field and are considered to be affected by bacterial oxidation (Whiticar, 1999).

Considering ~~only~~ the methane below the AOM as being unaltered, ~~two~~ three North Seep samples and the majority of the Slope Site samples show a clear microbial source of methane (Fig. 8a). All other samples appear to be affected by ~~high degrees of~~major oxidation following a Rayleigh fractionation process and show that only a fraction between 2 % (MUC 04, Central Seep) and 0.05 % (GC15, Central Seep) remains as unoxidized methane (Fig. 8a).

4.~~3~~2.2 Origin of unaltered samples

The $\delta^{13}C_{CH4}$ versus δD_{CH4} plot of u~~U~~naltered North Seep samples ~~show~~ suggests a mixing ~~origin in the $\delta^{13}C_{CH4}$ versus δD_{CH4} plot (Fig. 9), possibly stemming from~~of microbial and

694 thermogenic ~~sources~~methane (Fig. 8b). Similar ~~mixing~~ signals ~~of thermogenic and microbial~~
695 ~~methane~~ have also been observed at Hydrate Ridge (Milkov et al., 2005) and seem to be a
696 common phenomenon in hydrothermal and cold seep affected sediments. In a few samples
697 from North and Central Seep ethane concentrations have been high enough to measure
698 stable carbon isotopes and the $\delta^{13}C_{C2H6}$ values point to a thermogenic origin ~~of ethane~~ (Table
699 S3).
700
701 4.~~4~~ 3 Timing of active (thermogenic) methane release
702 4.3.1 Seep site geochemistry
703
704 Based on ~~the presented~~our data set~~, even when considering some uncertainties with respect~~
705 ~~to the fraction of thermogenic methane, the lack of any other geochemical evidence~~
706 ~~underlines that probably~~ no deep-sourced fluid is currently migrating upwards ~~at present~~ at
707 the cold seeps investigated ~~seepage sites~~ (compare deep-sourced seepage sites from the
708 Gulf of Cadiz in Fig. 7). Hence, in terms of the original hypothesis that fluid emanation is
709 directly linked to recent sill intrusions, these ~~investigated "~~cold seep~~"~~ sites cannot be
710 considered as being active as claimed by Lizarralde et al. (2010~~),~~). These authors ~~who~~ argued
711 that thermogenic carbon is currently released up to 50 km away from the rift axis causing a
712 maximum carbon flux of 240 kt C yr^{-1}. ~~First results~~Further, ~~by~~ Lizarralde et al. (2010) showed
713 temperature anomalies, high methane concentrations, and helium isotopic anomalies in the
714 water column potentially indicative of a magmatic source. These anomalies were detected
715 ~~above~~ in close vicinity to ~~bright features identified as~~ bacterial mats, tubeworms, and
716 authigenic carbonates, ~~. These features are~~ situated above areas of ~~shallow gas above~~ sill
717 intrusions. ~~comparable~~ Comparable~~to~~ structures have been identified in this study by video-
718 guided MUCs and seismic data (Fig. 2). ~~The more~~Our detailed results ~~of this study~~
719 ~~regarding~~on pore fluid, water column, and gas geochemistry now show that most methane
720 was of microbial origin (Fig. 8) and only traces of thermogenic methane were found up to
721 ~20 km off axis (North Seep) ~~and most methane was of microbial origin (Fig. 8, 9)~~. Even pore
722 fluids taken close to the hydrothermal vent ~~area~~ field are dominated by shallow microbial
723 degradation processes, indicating that hydrothermal fluid flow in the Guaymas Basin is
724 rather localized and bound to focused fluid pathways. The temperature and chemical
725 anomalies detected by Lizarralde et al. (2010) ~~could~~ might also arise~~stem~~ from the deep

water layer in the Guaymas Basin itself which is influenced by hydrothermal fluids (Campbell and Gieskes, 1984). Hydrothermal activity in the Guaymas Basin produces hydrothermal plumes which are ~~which rise to~~rising 100-300 m above seafloor and ~~then~~ spreading out along density gradients throughout the basin (Campbell and Gieskes, 1984). ~~Results~~ Our results nevertheless~~of this study~~ show that the Guaymas Basin has a well-mixed bottom seawater layer ~~consisting of patchy and elevated CH_4, as well as~~with temperatures ranging between 2.8 and ~~4.5~~3.9°C in >1000 m depth ~~(Fig. 6 and 10, Table).~~and o~~O~~ff-axis methane concentrations that vary quite considerably ~~and show~~(e.g. ~~a range from~~ 6 to 28 nM ~~for~~ at Ring Seep, Fig. 9) ~~and a temperature range from 2.8 to 3.9 for Central Seep~~. These bottom seawater variabilities are bigger than the reported anomalies by Lizarralde et al. (2010) and might indicate ~~that their findings might have been overrated~~that thermogenic methane release might not be as widespread as suspected before.

Figure~~.~~ 9~~10~~. Water column CH_4 (~~colored symbols~~a) and temperature (~~black crosses~~b) at cold seeps ~~and~~ as well as Smoker and~~/~~ Graben S~~s~~ite~~s~~ relative to the rift axis.

Pore fluids taken in a transect ~~from the rift axis~~ up to ~~20~~ 30 km away from the rift axis show no evidence for ~~seepage of fluids that are affected by~~ high-T reactions (Fig. 4, 7). We can still not exclude the possibility that thermogenic methane is released in other areas of the basin, but the lack of evidence for high temperature geochemical processes at our sites is evident and clearly contradicts with the conclusions drawn by Lizarralde et al. (2010). Our findings suggest that a projection of the thermogenic methane release based on the number of detected sills (Lizarralde et al., 2010) represents a maximum estimate as it does neither consider the time of the emplacement of a sill nor the lifetime of such magmatic systems. ~~Shallow~~ Today, shallow microbial degradation processes determine pore fluid signatures ~~and control the majority of the released methane~~ (Fig. 4, 8). ~~It is likely the case that~~Whereas high temperature thermogenic reactions have certainly been active~~acted~~ during sill emplacement and once released large amounts of carbon, ~~but~~ these processes have ~~appear~~ apparently ~~to have~~ ceased ~~since then~~. However, pipe structures ~~still~~ may still act as high-permeability pathways and facilitate the advection of gas. As a result, s~~S~~mall amounts of thermogenic carbon might ~~still~~ be released as ~~seen in microbial and thermogenic mixing~~reflected by the signatures of $\delta^{13}C_{CH4}$ and thermogenic $\delta^{13}C_{C2H6}$ isotope data at North and Central Seep~~Site~~.

However, present methane advection rates are slow (probably <1 cm yr^{-1}) as observed by low methane gradients in the pore fluid profiles (Fig. 4). These conditions favor an effective turnover of CH_4 to bicarbonate and authigenic carbonates by AOM (Wallmann et al., 2006; Karaca et al., 2010~~; Wallmann et al., 2006~~).

4.3.2 Origin of the authigenic carbonate

The porous authigenic carbonate block recovered from the seafloor at Central Seep can ~~provide~~ preserve long-term information about seepage in this area. The predominant biomarkers found in the seep carbonate from the Central Site (56-VgHG-4) are consistent with ~~an origin from dual species~~ microbial consortia performing ~~the anaerobic oxidation of methane (~~AOM~~)~~. In particular, h~~H~~igh ~~relative~~ abundances of crocetane and *sn*2-hydroxyarchaeol~~, along with DAGE,~~ indicate major contributions from methanotrophic archaea of the ANME-2 cluster, whereas DAGE originate from~~and~~ syntrophic sulfate-reducing bacteria, probably of the *Desulfosarcina–Desulfococcus* group (Blumenberg et al., 2004; Niemann and Elvert, 2008). These consortia ~~appear to~~ gain energy from AOM~~,~~ with sulfate as the final electron acceptor (see Eq. (2))~~,~~. ~~according to the net reaction~~

~~$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$~~

~~.~~

~~The~~ At Central Seep, the increase in ~~alkalinity~~ TA due to the AOM reaction plausibly explains the precipitation of isotopically depleted authigenic carbonates. Particularly, ANME-2 biomarkers have been reported in association with abundant fibrous, often botryoidal aragonite cements (Leefmann et al., 2008), which is ~~fully~~ in line with the observations made at the Central ~~Site~~ Seep (see ~~ch.~~Sect. 3.3). Moreover, the ~~inferred major~~high abundance of ANME-2 indicates that seep carbonate formation ~~once~~ took place under high sulfate concentrations, strong advective methane flow, but no elevated water temperatures (c.f. Nauhaus et al., 2005; Peckmann et al., 2009; Timmers et al., 2015). ~~The observation of m~~Minor amounts of typical ~~water column~~marine sterols also show~~s~~ that the~~se~~ seep carbonates ~~do not only carry their inherent AOM signature, but~~ also captured detritus from the surrounding sediment and ~~background~~ water column ~~sources~~ during their ongoing cementation.

The bulk carbonate carbon isotope signature ($\delta^{13}C_{V\text{-}PDB}$ = -46.6‰) overlaps with the shallow heavy $\delta^{13}C_{CH4}$ values (-27.5 and -48.6 ‰) in the pore fluids at Central Seep~~. Biomarkers found in the bulk carbonate~~ and confirms a dominant AOM signature with a ~~significant~~ minor planktonic and potentially $\delta^{13}C$ diluting background signal ~~(Fig. S2)~~. The oxygen isotopes ~~signature of the bulk carbonate~~ point~~s~~ to a low formation temperature of about 3°C~~. This is~~, consistent with a ~~formation at~~precipitation in ~~ambient seawater which has~~ bottom waters ~~temperatures between~~ (~~-~~2.8 ~~and~~ to 3.0°C (Fig. 6, ~~10~~9; Table S4). The $^{87}Sr/^{86}Sr$ analyses support this assumption by values within uncertainty identical to modern seawater. ~~Also~~ U-Th carbonate dating ~~performed at these authigenic carbonates~~ provide ~~formation~~ ages younger than 240 yrs BP. ~~In conclusion, authigenic carbonate shows a recent to~~Summarizing, authigenic carbonates originate from shallow methane and were sub-recently formed in ambient seawater.~~ formation age with methane from shallow sources at ambient seawater and thus confirms the results from pore fluid and gas geochemistry of cessation of deep fluid and gas mobilization.~~

4.3.3 Timing of off-axis hydrothermal activity

~~Taking a closer look at the~~The seismic ~~lines~~ data taken across the seep locations~~, it becomes obvious~~ indicate that the disrupted sediment layers are not reaching to the sediment surface (Fig. 2a, c). This implies that fluid mobilization ceased at some time before the uppermost sediment layers were deposited. The doming above the Central Seep provides some clues on the timing of fluid migration (Fig. 2c). Assuming that the doming is the result of buoyancy-related uplift (Koch et al., 2015) it represents the time when intrusion-related gas reached the sea floor. Assuming further a sedimentation rate of 1.7 m per 1000 years (Central Seep; Table 1) and maxima and minima deposition depths of 48 and 12 m ~~respectively~~ below seafloor, respectively (see Fig. 2c) this would imply that most of the gas reached the seafloor between 28 and 7 kyrs ago. Even ~~assuming~~ at maxima and minima ~~and maxima~~ sedimentation rates of 3.5 m (North Seep) and 0.5 m (Ring Seep) per 1000 years, gas flow would have ceased ~~at the earliest~~ between 14 and 3 kyrs ago at the earliest and~~or~~ ~~at the latest~~ between 96 and 24 kyrs ago at the latest. Accordingly, t~~T~~his finding further supports the results of the pore fluid and gas geochemistry which show no sign of active fluid flow from depth at the cold seep sites in the northern Guaymas Basin.

We agree with Lizarralde et al. (2010) that hydrothermal activity in the Guaymas Basin is an important driver for CH_4 (and CO_2) emissions into bottom waters. However, our data set shows that there is no deep fluid advection at the investigated sites. Our interpretation is that hydrothermal activity at these off-axis locations has ceased and previously formed pathways seem to mediate the advection of biogenic gas at present. It is not unlikely that seep-induced, hydrothermal activity is still ongoing in other places than those investigated in this study, but in order to provide more accurate predictions for (thermogenic) carbon fluxes and the potential impact on climate, sill emplacement mechanisms need to be better constrained. Apart from their spatial distribution, the most important and currently unknown factors are the determination of the time of their emplacement and the longevity of the sill-systems that require further investigation.

5 Conclusions

Magmatic intrusions into organic-rich sediments can potentially release large amounts of carbon into the water column and atmosphere and are therefore discussed as potential trigger mechanisms for rapid climate change, e.g. during the PETM. In the Guaymas Basin, off-axis cold seeps do not show indications for present-day hydrothermal activity. Pore fluids sampled from cold seeps ~~structures~~ and in the vicinity of hydrothermal vents in the northern Guaymas Basin~~,~~ are dominated by ~~seawater concentrations~~ambient diagenetic composition and show no sign of deep fluids or temperature-related diagenesis. Methane ~~measured~~ at the investigated sites ~~stems~~ shows ~~from~~ a mixed origin (biogenic~~microbial~~ and thermogenic ~~sources~~), ~~though mainly~~with a main contribution from microbial processes. ~~This may~~We suggest that hydrothermal circulation has largely stopped at depth and, based on seismic data, ceased more than 7 kyrs ago. Likewise, authigenic carbonates formed at cold seeps originate from shallow methane and were sub-recently formed in ambient seawater. Sill-induced hydrothermal systems appear to be an effective way to release carbon, but ~~the period of time depends on~~ the longevity of this type of ~~the~~ magmatic systems is still an unconstrained factor.

Acknowledgments

This work was undertaken within the MAKS project ~~which was~~ funded by the German Ministry of Science and Education (BMBF). We ~~would like to~~ thank the master and crew of the R/V Sonne for their ~~help and~~ support during the SO241 cruise. Further thanks goes to Regina Surberg, Bettina Domeyer, and Anke Bleyer for analytical support during the cruise and on shore. We greatly appreciate the support from Ana Kolevica, Tyler Goepfert, Sebastian Fessler, Andrea Bodenbinder, Yan Shen, and Jutta Heinze for onshore analyses. Additional support of this work was provided by EU-COST Action ES1301 "FLOWS" (www.flows-cost.eu).

References

Aarnes, I., Svensen, H., Connolly, J. A. D. and Podladchikov, Y. Y.: How contact metamorphism can trigger global climate changes: Modeling gas generation around igneous sills in sedimentary basins, Geochim. Cosmochim. Acta, 74(24), 7179–7195, doi:10.1016/j.gca.2010.09.011, 2010.

Aloisi, G., Drews, M., Wallmann, K. and Bohrmann, G.: Fluid expulsion from the Dvurechenskii mud volcano (Black Sea). Part I. Fluid sources and relevance to Li, B, Sr, I and dissolved inorganic nitrogen cycles, Earth Planet. Sci. Lett., 225(3–4), 347–363, doi:10.1016/j.epsl.2004.07.006, 2004.

Berndt, C., Hensen, C., Mortera-Gutierrez, C., Sarkar, S., Geilert, S., Schmidt, M., Liebetrau, V., Kipfer, R., Scholz, F., Doll, M., Muff, S., Karstens, J., Planke, S., Petersen, S., Böttner, C., Chi, W.-C., Moser, M., Behrendt, R., Fiskal, A., Lever, M. A., Su, C.-C., Deng, L., Brennwald, M. S. and Lizarralde, D.: Rifting under steam – how rift magmatism triggers methane venting from sedimentary basins, Geology, 44(9), 767–770, 2016.

Biddle, J. F., Cardman, Z., Mendlovitz, H., Albert, D. B., Lloyd, K. G., Boetius, A. and Teske, A.: Anaerobic oxidation of methane at different temperature regimes in Guaymas Basin hydrothermal sediments, ISME J., 6(5), 1018–1031, doi:10.1038/ismej.2011.164, 2012.

Blumenberg, M., Seifert, R., Reitner, J., Pape, T. and Michaelis, W.: Membrane lipid patterns typify distinct anaerobic methanotrophic consortia, Proc. Natl. Acad. Sci. USA, 101, 11111–11116, 2004.

Brumsack, H. J. and Gieskes, J. M.: INTERSTITIAL WATER TRACE-METAL CHEMISTRY OF LAMINATED SEDIMENTS FROM THE GULF OF CALIFORNIA, MEXICO, Mar. Chem., 14, 89–106, 1983.

Calvert, S. E.: Accumulation of Diatomaceous Silica in the Sediments of the Gulf of California, Geol. Soc. Am. Bull., 77(June), 569–596, 1966.

Campbell, A. C. and Gieskes, J. M.: Water column anomalies associated with hydrothermal activity in the Guaymas Basin, Gulf of California Andrew C. Campbell and Joris M. Gieskes, Earth Planet. Sci. Lett., 68, 57–72, 1984.

Chan, L. H., Gieskes, J. M., You, C. F. and Edmond, J. M.: Lithium Isotope Geochemistry of Sediments and Hydrothermal Fluids of the Guaymas Basin, Gulf of California, Geochim. Cosmochim. Acta, 58(20), 4443–4454, 1994.

Curray, J. R. and Moore, D. G. et al.: Initial Reports of the Deep Sea Drillrng Project. vol. 64., U.S. Govt. Printing Office, Washington., 1982.

892 Von Damm, K. L., Edmond, J. M., Measures, C. I. and Grant, B.: Chemistry of submarine hydrothermal
893 solutions at Guaymas Basin, Gulf of California, Geochim. Cosmochim. Acta, 49(11), 2221–2237, 1985.

894 Von Damm, K.: Seafloor Hydrothermal Activity: Black Smoker Chemistry And Chimneys, Annu. Rev.
895 Earth Planet. Sci., 18(1), 173–204, doi:10.1146/annurev.earth.18.1.173, 1990.

896 DeMaster, D.: The supply and accumalation of silica in the marine environment, Geochim.
897 Cosmoclumica Acta, 5, 1715–1732, 1981.

898 Dickens, G. R.: Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas
899 hydrate capacitor, Earth Planet. Sci. Lett., 213(3–4), 169–183, doi:10.1016/S0012-821X(03)00325-X,
900 2003.

901 Dowell, F., Cardman, Z., Dasarathy, S., Kellermann, M. Y., Lipp, J. S., Ruff, S. E., Biddle, J. F., McKay, L.
902 J., MacGregor, B. J., Lloyd, K. G., Albert, D. B., Mendlovitz, H., Hinrichs, K. U. and Teske, A.: Microbial
903 communities in methane- and short chain alkane-rich hydrothermal sediments of Guaymas Basin,
904 Front. Microbiol., 7(JAN), doi:10.3389/fmicb.2016.00017, 2016.

905 Einsele, G., Gieskes, J. M., Curray, J., Moore, D. M., Aguayo, E., Aubry, M.-P., Fornari, D., Guerrero, J.,
906 Kastner, M., Kelts, K., Lyle, M., Matoba, Y., Molina-Cruz, A., Niemitz, J., Rueda, J., Saunders, A.,
907 Schrader, H., Simoneit, B. and Vacquier, V.: Intrusion of basaltic sills into highly porous sediments,
908 and resulting hydrothermal activity, Nature, 283, 441–445, doi:10.1017/CBO9781107415324.004,
909 1980.

910 Fisher, A. T. and Becker, K.: Heat flow, hydrothermal circulation and basalt intrusions in the Guaymas
911 Basin, Gulf of California, Earth Planet. Sci. Lett., 103(1–4), 84–99, doi:10.1016/0012-821X(91)90152-
912 8, 1991.

913 Gamo, T., Sakai, H., Kim, E.-S., Shitashima, K. and Ishibashi, J. -i.: High-alkalinity due to sulfate
914 reduction in the CLAM hydrothermal field, Okinawa Trough, Earth planet. Sci. Lett., 107, 328–338,
915 1991.

916 Gieskes, J. M., Kastner, M., Einsele, G., Kelts, K. and Niemitz, J.: Hydrothermal Activity in the Guaymas
917 Basin, Gulf of California: A synthesis, in In Initial Reports of the Deep Sea Drilling Project. vol. 64, Pt.
918 2, edited by D. G. et al. Curray, J.R., Moore, pp. 1159–1167., 1982.

919 Gieskes, J. M., Gamo, T. and Brumsack, H.: Chemical methods for interstitial water analysis aboard
920 Joides Resolution, Ocean Drill. Prog. Tech. Note 15. Texas A&M Univ. Coll. Stn., 1991.

921 Goldsmith, J. R., Graf, D. L. and Heard, H. C.: Lattice constants of the calcium-magnesium carbonates,
922 Am. Miner., 46, 453–457, 1961.

923 Grasshoff, K., Erhardt, M. and Kremling, K.: Methods of Seawater Analysis, Wiley-VCH, Weinheim.,
924 2002.

925 Gutjahr, M., Ridgwell, A., Sexton, P. F., Anagnostou, E., Pearson, P. N., Pälike, H., Norris, R. D.,
926 Thomas, E. and Foster, G. L.: Very large release of mostly volcanic carbon during the Palaeocene–
927 Eocene Thermal Maximum, Nature, 548(7669), 573–577, doi:10.1038/nature23646, 2017.

928 Hartmann, A. and Villinger, H.: Inversion of marine heat flow measurements by expansion of the
929 temperature decay function, Geophys. J. Int., 148(3), 628–636, doi:10.1046/j.1365-
930 246X.2002.01600.x, 2002.

931 Henry, P., Le Pichon, X., Lallement, S., Lance, S., Martin, J. B., Foucher, J. P., Fiala-Médioni, A., Rostek,
932 F., Guilhaumou, N., Pranal, V. and Castrec, M.: Fluid flow in and around a mud volcano seaward of
933 the Barbados accretionary wedge: Results from Manon cruise, J. Geophys. Res., 101(9), 20297–

20323, 1996.

Hensen, C., Nuzzo, M., Hornibrook, E., Pinheiro, L. M., Bock, B., Magalhães, V. H. and Brückmann, W.: Sources of mud volcano fluids in the Gulf of Cadiz-indications for hydrothermal imprint, Geochim. Cosmochim. Acta, 71(5), 1232–1248, doi:10.1016/j.gca.2006.11.022, 2007.

Howarth, R. J. and McArthur, J. M.: Strontium isotope stratigraphy, in A Geological Time Scale, with Look-up Table Version 4, edited by F. M. Gradstein and J. G. Ogg, pp. 96–105, Cambridge University Press, Cambridge, U.K pp. ., 2004.

Huh, C.-A., Su, C.-C., Wang, C.-H., Lee, S.-Y. and Lin, I.-T.: Sedimentation in the Southern Okinawa Trough – Rates, turbidites and a sediment budget, Mar. Geol., 231, 129–139, 2006.

Ivanenkov, V. N. and Lyakhin, Y. I.: Determination of total alkalinity in seawater, in In Methods of Hydrochemical Investigations in the Ocean, edited by O. K. Bordovsky and V. N. Ivanenkov, p. 110–114 (in Russian), Nauka Publishing House, Moscow., 1978.

Jahnke, R. A., Emerson, S. R. and Murray, J. W.: A model of oxygen reduction, denitrification, and organic matter mineralization in marine sediments, Limnol. Oceanogr., 27(4), 610–623, doi:10.4319/lo.1982.27.4.0610, 1982.

Jørgensen, B. B.: Bacteria and marine biogeochemistry, in Marine Geochemistry, edited by H. D. Schulz and M. Zabel, pp. 169–206, Springer, Berlin., 2006.

Karaca, D., Hensen, C. and Wallmann, K.: Controls on authigenic carbonate precipitation at cold seeps along the convergent margin off Costa Rica, Geochemistry, Geophys. Geosystems, 11(8), 1–19, doi:10.1029/2010GC003062, 2010.

Kastner, M.: Evidence for Two Distinct Hydrothermal Systems in the Guaymas Basin, in In Initial Reports of the Deep Sea Drilling Project. vol. 64, Pt. 2, edited by D. G. et al. Curray, J.R., Moore, pp. 1143–1157, U.S. Govt. Printing Office, Washington., 1982.

Kastner, M. and Siever, R.: Siliceous Sediments of the Guaymas Basin: The Effect of High Thermal Gradients on Diagenesis, J. Geol., 91(6), 629–641, doi:10.1086/628816, 1983.

Kinoshita, M. and Yamano, M.: Hydrothermal regime and constraints on reservoir depth of the Jade site in the Mid-Okinawa Trough inferred from heat flow measurements, J. Geophys. Res., 102(B2), 3183–3194, 1997.

Koch, S., Berndt, C., Bialas, J., Haeckel, M., Crutchley, G., Papenberg, C., Klaeschen, D. and Greinert, J.: Gas-controlled seafloor doming, Geology, 43(7), 571–574, doi:doi: 10.1130/G36596.1, 2015.

Lee, S.-Y., Huh, C.-A., Su, C.-C. and You, C.-F.: Sedimentation in the Southern Okinawa Trough: enhanced particle scavenging and teleconnection between the Equatorial Pacific and western Pacific margins, Deep. Res., 51, 1769–1780, 2004.

Leefmann, T., Bauermeister, J., Kronz, A., Liebetrau, V., Reitner, J. and Thiel, V.: Miniaturized biosignature analysis reveals implications for the formation of cold seep carbonates at Hydrate Ridge (off Oregon, USA), Biogeosciences, 5, 731–738, 2008.

Lizarralde, D., Soule, S. A., Seewald, J. S. and Proskurowski, G.: Carbon release by off-axis magmatism in a young sedimented spreading centre, Nat. Geosci., 4(1), 50–54, doi:10.1038/ngeo1006, 2010.

Lonsdale, P. and Becker, K.: Hydrothermal plumes, hot springs, and conductive heat flow in the Southern Trough of Guaymas Basin, Earth Planet. Sci. Lett., 73(2–4), 211–225, doi:10.1016/0012-821X(85)90070-6, 1985.

975 Lupton, J. E.: Helium-3 in the Guaymas Basin: Evidence for injection of mantle volatiles in the Gulf of
976 California, J. Geophys. Res., 84(B13), 7446, doi:10.1029/JB084iB13p07446, 1979.

977 McDermott, J. M., Seewald, J. S., German, C. R. and Sylva, S. P.: Pathways for abiotic organic synthesis
978 at submarine hydrothermal fields, PNAS, 112(25), 7668–7672, 2015.

979 Milkov, A. V., Claypool, G. E., Lee, Y. J. and Sassen, R.: Gas hydrate systems at Hydrate Ridge offshore
980 Oregon inferred from molecular and isotopic properties of hydrate-bound and void gases, Geochim.
981 Cosmochim. Acta, 69(4), 1007–1026, doi:10.1016/j.gca.2004.08.021, 2005.

982 Nauhaus, K., Treude, T., Boetius, A. and Krüger, M.: Environmental regulation of the anaerobic
983 oxidation of methane: A comparison of ANME-I and ANME-II communities, Environ. Microbiol, 7, 98–
984 106, 2005.

985 Niemann, H. and Elvert, M.: Diagnostic lipid biomarker and stable isotope signatures of microbial
986 communities mediating the anaerobic oxidation of methane with sulphate, Org. Geochem., 39,
987 1668–1677, 2008.

988 Peckmann, J., Birgel, D. and Kiel, S.: Molecular fossils reveal fluid composition and flow intensity at a
989 Cretaceous seep, Geology, 37, 847–850, 2009.

990 Pfender, M. and Villinger, H.: Miniaturized data loggers for deep sea sediment temperature gradient
991 measurements, Mar. Geol., 186(3–4), 557–570, doi:10.1016/S0025-3227(02)00213-X, 2002.

992 Schmidt, M., Hensen, C., Mörz, T., Müller, C., Grevemeyer, I., Wallmann, K., Mau, S. and Kaul, N.:
993 Methane hydrate accumulation in “Mound 11” mud volcano, Costa Rica forearc, Mar. Geol., 216(1–
994 2), 83–100, doi:10.1016/j.margeo.2005.01.001, 2005.

995 Schmidt, M., Linke, P., Sommer, S., Esser, D. and Cherednichenko, S.: Natural CO2 Seeps Offshore
996 Panarea : A Test Site for Subsea CO2 Leak Detection Limit, Mar. Technol. Soc. J., 49(1), 19–30, 2015.

997 Scholz, F., Hensen, C., Reitz, A., Romer, R. L., Liebetrau, V., Meixner, A., Weise, S. M. and Haeckel, M.:
998 Isotopic evidence (87Sr/86Sr, δ7Li) for alteration of the oceanic crust at deep-rooted mud volcanoes
999 in the Gulf of Cadiz, NE Atlantic Ocean, Geochim. Cosmochim. Acta, 73(18), 5444–5459,
1000 doi:10.1016/j.gca.2009.06.004, 2009.

1001 Scholz, F., Hensen, C., De Lange, G. J., Haeckel, M., Liebetrau, V., Meixner, A., Reitz, A. and Romer, R.
1002 L.: Lithium isotope geochemistry of marine pore waters - Insights from cold seep fluids, Geochim.
1003 Cosmochim. Acta, 74(12), 3459–3475, doi:10.1016/j.gca.2010.03.026, 2010.

1004 Simoneit, B. R. T., Leif, R. N., Sturz, A. A., Sturdivant, A. E. and Gieskes, J. M.: Geochemistry of shallow
1005 sediments in Guaymas Basin, gulf of California: hydrothermal gas and oil migration and effects of
1006 mineralogy, Org. Geochem., 18(6), 765–784, doi:10.1016/0146-6380(92)90046-Z, 1992.

1007 Sommer, S., Linke, P., Pfannkuche, O., Schleicher, T., Deimling, J. S. V, Reitz, A., Haeckel, M., Flögel, S.
1008 and Hensen, C.: Seabed methane emissions and the habitat of frenulate tubeworms on the Captain
1009 Arutyunov mud volcano (Gulf of Cadiz), Mar. Ecol. Prog. Ser., 382, 69–86, doi:10.3354/meps07956,
1010 2009.

1011 Środoń, J.: Nature of Mixed-Layer Clays and Mechanisms of Their Formation and Alteration, Annu.
1012 Rev. Earth Planet. Sci., 27(1), 19–53, doi:10.1146/annurev.earth.27.1.19, 1999.

1013 Svensen, H., Planke, S., Malthe-Sorenssen, A., Jamtveit, B., Myklebust, R., Eidem, T. R. and Rey, S. S.:
1014 Release of methane from a volcanic basin as a mechanism for initial Eocene global warming, Nature,
1015 429(June), 3–6, doi:10.1038/nature02575.1., 2004.

Teske, A., Callaghan, A. V. and LaRowe, D. E.: Biosphere frontiers of subsurface life in the sedimented hydrothermal system of Guaymas Basin, Front. Microbiol., 5(JULY), 1–11, doi:10.3389/fmicb.2014.00362, 2014.

Teske, A., De Beer, D., McKay, L. J., Tivey, M. K., Biddle, J. F., Hoer, D., Lloyd, K. G., Lever, M. A., Røy, H., Albert, D. B., Mendlovitz, H. P. and MacGregor, B. J.: The Guaymas Basin hiking guide to hydrothermal mounds, chimneys, and microbial mats: Complex seafloor expressions of subsurface hydrothermal circulation, Front. Microbiol., 7(FEB), 1–23, doi:10.3389/fmicb.2016.00075, 2016.

Timmers, P. H., Widjaja-Greefkes, H.A. Ramiro-Garcia, J., Plugge, C. M. and Stams, A. J.: Growth and activity of ANME clades with different sulfate and sulfide concentrations in the presence of methane, Front. Microbiol., 6, 988, 2015.

Wallmann, K., Drews, M., Aloisi, G. and Bohrmann, G.: Methane discharge into the Black Sea and the global ocean via fluid flow through submarine mud volcanoes, Earth Planet. Sci. Lett., 248(1–2), 544–559, doi:10.1016/j.epsl.2006.06.026, 2006.

Wegener, G., Krukenberg, V., Ruff, S. E., Kellermann, M. Y. and Knittel, K.: Metabolic capabilities of microorganisms involved in and associated with the anaerobic oxidation of methane, Front. Microbiol., 7, 46, 2016.

Welhan, J. A.: Origins of methane in hydrothermal systems, Chem. Geol., 71(1–3), 183–198, doi:10.1016/0009-2541(88)90114-3, 1988.

Whiticar, M. J.: Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, , 161, 291–314, 1999.

Zachos, J. C., Wara, M. W., Bohaty, S., Delaney, M. L., Petrizzo, M. R., Brill, A., Bralower, T. J. and Premoli-Silva, I.: A transient rise in tropical sea surface temperature during the Paleocene-Eocene thermal maximum., Science, 302(5650), 1551–1554, doi:10.1126/science.1090110, 2003.