In the text below, our responses to the Reviewer' comments are shown in blue, whereas our resolve and modifications in the manuscript are shown in purple. Line numbers refer to the revised "no markup" document.

Interactive comment on "Quantity and distribution of methane entrapped in sediments of calcareous, Alpine glacier forefields" by Biqing Zhu et al.

David Archer (Referee) d-archer@uchicago.edu Received and published: 27 March 2020

This is an interesting, thorough characterization of the distribution of methane trapped within CaCO3 in glacial fore field deposits. The methane is released when the CaCO3 is dissolved in acid, a somewhat aggressive analog for chemical weathering. The authors are very careful not to overstate the implications of their data to the global methane cycle or climate, even though as they point out, the actual quantity of methane is rather high relative to other regional metrics. The primary motivation for investigating this is curiosity, which is a perfectly fine motivation for publication. I would be curious whether the methane has a measurable impact on the microbiology within the sediments; whether there is metabolic energy to be gained by reacting the methane with anything available, and whether RNA or proteomics of some other type of biotech characterization could detect this activity. Probably any methane-driven metabolic activity would be at low level, given the apparently conservative behavior of the methane that the paper documents. This is not a suggestion for idea for the current paper, obviously, which I would recommend for publication as is, with only one editorial suggestion, from line 73, "virtually omnipresent" could be changed to "found virtually everywhere" or something like that. The former phrase makes the methane itself seem virtual.

We would like to thank the Reviewer for the overall positive assessment of our manuscript.

We agree with the Reviewer that it would be highly interesting to investigate whether this entrapped CH_4 has an impact on the microbiology within the sediments, particularly on methane-oxidizing bacteria (MOB). In earlier studies (e.g., Chiri et al. 2017) we have confirmed the presence and activity of aerobic MOB utilizing atmospheric CH_4 in calcareous glacier-forefield sediments. This group of MOB is well adapted to utilizing CH_4 at low levels (< 2 $\mu L\ L^{-1}$ in gas phase) in this environment. Indeed, a set of recently conducted experiments in our laboratory yielded first indications that these MOB may utilize (i.e., oxidize) trace amounts of previously sediment-entrapped CH_4, which "leaks" from the calcareous sediments into the sediment-gas phase. However, we consider these experiments to be preliminary, additional experiments will have to be conducted for confirmation. But as indicated by the Reviewer, this topic is beyond the scope of the current manuscript.

We also agree with the Reviewer's editorial comment, and have re-phrased the sentence in question to now read:

"…we established that entrapped CH_4 was present in nearly all sediment and bedrock samples collected throughout this catchment…" (l. 66)

In the text below, our responses to the Reviewer' comments are shown in blue, whereas our resolve and modifications in the manuscript are shown in purple. Line numbers refer to the revised "no markup" document.

Interactive comment on "Quantity and distribution of methane entrapped in sediments of calcareous, Alpine glacier forefields" by Biqing Zhu et al.

Anonymous Referee #2 Received and published: 28 March 2020

GENERAL COMMENTS:

The topic of the reviewed manuscript (MS) is the occurrence spatial distribution and estimated total mass of methane (CH4) entrapped in calcareous sediment and bedrock in glacier forefields in the Swiss Alps. The topic is both novel and relevant for the improved understanding of terrestrial CH4 reservoirs and their potential source of emission to the atmposhere. The current study takes of where Zhu et al (2018) ends, with a clearly formulated aim (ll 87-89): "To extend the work of Zhu er at (2018) to other calcareous glacier forefields located in different regions of the Swiss Alps, and to assess the distribution of entrapped CH4 contents within and compare total mass of entrapped CH4 between all sampled glacier forefields". The study is well designed with clear descriptions of the work that has been done. However, since the study can be viewed as almost a part 2 of a larger study of entrapped CH4 in calcareous sediment in Alpine catchments, with the Xhu et al (2018) paper as part 1, it could benefit from reflecting this more clearly. In particular, I would recommend that the manuscript is abbreviated significantly, to sharpen the focus, novelty and importance of the extended study, making it as short and concise as possible using referencing to the Zhu et al (2018) paper when it comes to more general background information. Finally, I recommend that the use of sediment age and landform as explanatory variables for the potential amount of entrapped CH4 present in the sediment is revised according to the specific comments. In summary, I recommend publication of the study following a careful revision of the manuscript.

We would like to thank the Reviewer for a detailed review, and for the overall positive assessment of our manuscript. In the General Comments section, the Reviewer makes two recommendations, (i) to shorten the manuscript and (ii) to revise the use of sediment age and landform as explanatory variables. As both issues are also raised under Specific Comments, we will address these issues in the Specific Comments section below.

SPECIFIC COMMENTS:

1.) Ll 30-69: The two opening paragraphs are almost identical to the introduction of Zhu et al (2018) and does not mention subglacial/ glacial CH4. These two paragraphs could be shortening into a few referenced sentences with reference to Zhu et al (2018), in order for the MS to more quickly get to the essence of this study (from line 60 and onwards).

We agree with the reviewer that the first two paragraphs of the Introduction section can be shortened, and we shortened them from 29 to 18 lines of text. On the other hand, we strongly feel that core topics relevant to this manuscript such as the distinction between microbial, thermogenic, and abiotic CH_4 should be presented to readers in the Introduction section rather than just referring to our previous publication.

In addition, we feel that our introduction into the topic of subglacial CH_4 (third paragraph) may also be shortened, as subglacial CH_4 is not the topic of this manuscript. Moreover, we feel that the reviewer was confused with our use of the term "sediment age" (see also discussion of comments below), in that we use it to indicate time since deglaciation rather than "absolute" sediment age (time since the formation of sediments). We feel that a clarification regarding this term is needed prior to its (previously first) appearance in our objective statement. We previously provided such a statement in our Methods section, whereas we now introduce and provide a clarification of this term at the end of the third paragraph of our Introduction. The clarification reads:

"In this context, sediment age refers to the number of years sediment has been exposed to the atmosphere following glacier retreat. Note that both terms, sediment age and landform, serve as proxies for all edaphic variations present in these sediments at different locations within the glacier forefield. We will adopt this convention and use the terms sediment age and landform in this fashion throughout this paper." (l. 59)

2.) l.125. In this section the three steps of the fieldwork of stage I is described. However, the actual testing of the effect of sediment depth, sediment exposure age and landform on entrapped CH4 as well as total mass estimation comes after the fieldwork as it is based on data analysis. The text describing this should therefore be placed at a more appropriate stage in the MS.

There appears to be a misunderstanding. The Reviewer suggests that we conducted all stage 1 field sampling prior to analyses in the laboratory, and therefore the order of description in our method section should be changed. But this is incorrect. We conducted the work exactly as described in our Methods section 2.1.1. In other words, after collecting samples to test for sediment depth, these samples were analysed in the laboratory for CH_4 content. The results of this analysis was then used to adapt the sampling scheme of the subsequent step, in which we tested for the effects of sediment age and landform. This is mentioned in both the Methods section ("The sampling depth of 20 cm below ground surface was chosen based on our results from the previous step"; l. 138) and the Results section ("Thus, we subsequently proceeded to collect sediments from 20 cm depth only, and assumed these samples to be representative in terms of entrapped CH_4 content for the entire sediment thickness."; l. 272).
To further clarify this issue, we added the following sentence to the end of the Methods paragraph describing step 1: "The result of this analysis was then used to adapt the sampling scheme for the following step." (l. 127)

3.) l. 129. Is there a difference between a randomized design and a completely randomized design? If yes, please explain. If no, remove completely.

We agree with the Reviewer. As there is no difference, we deleted the word "completely".

4.) l. 152 What is the uncertainty on depth estimated based of the electrical resistivity tomography (ERT) method, and how does this uncertainty propagate into total CH4 mass best estimates? Section 2.2.1 in general. Can you absolutely rule out that no CH4 is chemically produced during the acid dissolution of the carbonate rock (by e.g. cold temperature version of similar processes as the high temperature conversion of CO2 into CH4 using reduced metals as catalyst as decribed in e.g. https://onlinelibrary.wiley.com/doi/full/10.1002/cssc.200900152)

The uncertainty of ERT on the estimate of mean sediment depth is documented in Table 1. It amounts to up to 50% of the respective mean depth value. This large uncertainty is dominated by the high variability in sediment depth encountered within the glacier forefield, rather than by measurement uncertainties in the field and uncertainties introduced during the inversion of apparent resistivities (typically <10% (Loke, 2000)). The propagation of this uncertainty into total CH_4 mass estimation is mathematically described in Eq. 2, and its contribution to the total uncertainty in estimated CH_4 mass is shown in Figure 7b. To better indicate the origin of the uncertainty in sediment depth, we modified a sentence in the results section to now read:

“Uncertainties in individual m_{CH4} values up to ~50% mostly arose from uncertainties in T_{sed} (dominated by the large variability in sediment thickness across the GRF sampling zone) and to a smaller degree from uncertainties in C_{CH4}.” (l. 293)

We are familiar with the process of “methanization” as described in the reference provided by the Reviewer, but not with a “cold-temperature version” under the prevailing experimental conditions. As noted by the Reviewer, methanization takes place at high temperatures (above 300°C) and/or pressures in the presence of a catalyst and in a H_2 atmosphere. None of these conditions are met during our acidification experiments. Apart from conducting these experiments at ambient temperature (21°C), we are certain that there is no H_2 (which would serve as the electron donor in the chemical reduction of CO_2 during methanization) present in our assays, as the headspace of all samples was flushed with N_2 gas prior to acidification treatment (l. 182).
But more importantly, we have previously provided unequivocal evidence that CH_4 release from these calcareous sediments can be induced by other means than acidification (Nauer et al., 2014). In that paper we demonstrated that similar amounts of CH_4 are released by mechanical disturbance (hammering) in the field, and that a substantial quantity of CH_4 is released in the laboratory by the addition of water and subsequent sonification treatment. None of these treatments involve the use of acid.

5.) L 178. Good example of efficient referencing to previous literature on the same topic, saving space in this MS.

We thank the Reviewer for this assessment.

6.) L. 179. Why where particles larger than 20 mm excluded?

We adopted this threshold in particle size from our previous work (Zhu et al., 2018) for compatibility, but also for the following reason: On the international (ISO) scale for soil classification, 20 mm marks the boundary between medium and coarse gravel. Apart from the topmost sediment layer (< 5 cm depth, not sampled), particles > 20 mm in size were rare in our samples, thus did not appear representative of the bulk sediment in these sediments.

7.) L. 189. Maybe expand a little on how the initial tests were conducted in order to reach your methodological conclusion

We agree with the Reviewer that some more information on this issue would be helpful to readers. In these initial tests we compared hammering with sawing. Using both methods we collected rock fragments both from the surface and from the core of larger rocks. Obtaining fragments from the core required substantially more hammering and more sawing, thus a much longer duration of the mechanical treatment. But subsequent analyses of these rock fragments showed that differences in geochemical parameters were insignificant. This we took as evidence that there was no adverse effect of sawing or hammering on the fragment’s geochemical parameters. To provide more information in concise fashion to readers, we replaced the sentence in question with the following statement:

“Initial tests, in which we compared hammering with sawing to obtain rock fragments both from the surface and from the core of larger rocks, showed insignificant effects on the fragments’ entrapped CH_4 contents and other geochemical parameters. As the duration of the respective mechanical treatment varied greatly between the collected fragments, we consider this as evidence that neither hammering nor sawing had an adverse effect on measured geochemical parameters.” (l. 182)

8.) L. 204. The number of samples used should be more clearly stated. Avoid using “About five samples. . .”

We fully agree with the Reviewer and have rephrased the sentence in question to read:

“A total of 31 sediment and bedrock samples from the five glacier forefields were selected for stable carbon-isotope analysis of entrapped CH_4 ($\delta^{13}C_{CH4}$).” (l. 199)

9.) L.232. Title of 2.3.2 should include a description of what is being estimated, e.g. “Estimation of XXXX for five glacier forefields”.

We agree with the Reviewer. However, for consistency we have included the description also in titles of sections 2.3.1 and 2.3.3. Title 2.3.2 now reads:

“Estimation of entrapped CH_4 mass for the five glacier forefields (IMG, GRF, GRI, WIL, TSA)” (l. 226)

10.) L. 237 and onwards. Natural chemical dissolution of carbonate rock from carbonic acid is an important weathering process over geological timescales and is also likely to be a process of relevance in the glacial forelands in which the study is performed. With this time perspective in mind, the reason for choosing the time difference between 1850 (asserted latest glacial maximum) and 2018 (same but minimum) as the boundary conditions for the CH4 upscaling appear somewhat arbitrary. I understand of course that it is an operational boundary condition for identifying the area of the current glacial forelands. But the temporal relevance of the phenomena that you investigate, where the natural chemical weathering rates are in fact the rate limiting factor for potential CH4 emissions needs to be justified on a bigger timescale. Especially the implied relationship the last glacial maximum could serve as a time zero for CH4 release (see also line 326) and that the current climatic development should in fact increase emission to the atmosphere, which may very well not be the case, if the overall rate limiting factor is not glacial coverage, but rather the kinetics of natural carbonate weathering, which can take place both in a warm-based subglacial environment as well as in the current pro-glacial settings.

We agree with the Reviewer that chemical weathering is indeed a slow process taking place over geologic timescales. However, with the transition from subglacial to proglacial sediment as a result of glacier retreat, forefield sediments undergo changes other than mere chemical weathering. As soil formation is initiated following deglaciation, microbial and pioneer plant colonisation may alter sediment characteristics, which are visually noticeable within a few decades following deglaciation, and certainly within a 100 to 150 year chronosequence. These changes may include chemical characteristics including TOC, nutrient levels, and pH (Stevens & Walker, 1970; Bernasconi et al., 2008; Lazzaro et al., 2009; Chiri et al., 2015). We strongly feel that it is a fair and worthy question to ask whether sediment age (used here as time since deglaciation and as a proxy for edaphic variations) affects sediment-entrapped CH_4 contents or not.

As hinted by the Reviewer, we indeed use the time interval from the end of the little ice age until present time *exclusively* to estimate the surface area of the glacier forefields, because the 1850 end moraine is often a visible feature in the landscape, defining the extent of the glacial advance at the end of the little ice age. However, we carefully checked our manuscript to assure that nowhere we imply a relationship that the last glacial maximum could serve as a time zero for CH_4 release, nor that current climatic development should increase emissions to the atmosphere.

11.) L. 273. Your conclusion that the gas must be of thermogenic origin and has not been altered by physical/chemical weathering appear correct. However, this particular conclusion supports the view that sediment age (i.e. time since last exposure) could be an irrelevant measure on the time scale that you operate, which also your statistical analysis show (l. 283).

We agree with the Reviewer. This is indeed an important result of this study, and it is in agreement with our finding that effects of sediment age on CH_4 contents were insignificant. The implications of these findings (entrapped CH_4 appears stable in its entrapped state) are discussed beginning on line 379. We see no inconsistency here.

12.) L. 283. The term Landform is a less exact term for the variable than e.g. mineralogy of the sediment, parent material for the sediment or similar. As stated in the MS in seems that you argue that the landform itself has a significant effect on the potential CH4 content, while I believe you mean that significant difference in entrapped CH4 content is observed between different landforms. The sediment in the different landforms (floodplain, terrase, sand hill, etc) could potentially originate in contrasting parent material, and the variation in entrapped CH4 is more likely an effect of this, rather than the landform itself, the time of deposition or the time since the most recent exposure to the atmosphere after year 1850. I recommend that both this section and the MS in general is revised to reflect this relationship.

We agree with the Reviewer that this issue requires clarification. We used "landform" as one variable to spatially discretize the glacier forefield sampling zone. The other variable we used is sediment age (time since deglaciation, see answer to comment 1). In doing so, we follow a previous spatial discretization of the forefield sampling zone (Chiri et al., 2017). Moreover, sediment age and landform is terminology commonly used in research papers dealing with studies in glacier forefields. For compatibility reasons we prefer to keep using these terms for the spatial discretization. However, we fully agree with the Reviewer that "landform" is not a causal variable, i.e., it is not the cause for the different sediment-entrapped CH_4 contents detected. Rather, and as is the case also for sediment age, both terms serve as proxies for all edaphic variations present in sediments at these locations in the glacier forefield. Therefore, we strongly feel that an up-front clarification on the use of these terms should be provided already in the Introduction (before they are used in the objective statement). This is why we now introduce these terms in our Introduction, and provide the following clarification:

"In this context, sediment age refers to the number of years sediment has been exposed to the atmosphere following glacier retreat. Note that both terms, sediment age and landform, serve as proxies for all edaphic variations present in these sediments at different locations within the glacier forefield. We will adopt this convention and use the terms sediment age and landform in this fashion throughout this paper." (l. 59)

Together with our (modified) statement in the Method section, we feel this provides adequate clarification:

"During stage I in summer 2016, we performed a detailed investigation on the spatial distribution of sediment-entrapped CH_4 within a designated sampling zone at the GRF glacier forefield, using high spatial-resolution sampling to determine variations in entrapped CH_4 contents in relation to sediment depth, sediment age, and glacier-forefield landforms. The GRF forefield was chosen for this purpose mainly because it features well-defined sediment-age classes and well-developed, clearly distinguishable landforms within a previously discretized and characterized sampling zone (Chiri et al., 2015; Chiri et al., 2017)." (l. 106)

To remind the reader on the use of these terms, we also modified the first sentence of the Results paragraph in question to read:

"The effects of the proxies sediment age and landform on entrapped CH4 contents were tested using…". (l. 274)

Finally, we fully agree with the Reviewer that observed differences in in entrapped CH_4 contents in different landforms may be related to differences in parent bedrock from which these sediments are derived. We modified a paragraph in our Discussion section to better address this issue:

"In contrast to sediment depth and sediment age, we detected a small but significant difference in mean sediment-entrapped CH_4 content between landforms within the GRF sampling zone. Specifically, mean entrapped CH_4 content in floodplain sediments was significantly higher than in terrace and sandhill sediments (Table 1). We can only speculate about possible reasons for this observation. One reason could be that floodplain sediments, intermittently removed and deposited by the glacial stream during and after flooding events, originate from locations outside of our sampling zone, i.e., from different parent bedrock (Fig. S2). It is therefore possible that we missed to sample parent bedrock types (e.g., from steep rock walls) with different (in this case higher) entrapped CH_4 contents in this or any of the other glacial catchments. An improved mineralogical investigation of sediments in the various landforms would aid in clarifying this issue." (l. 398)

13.) L.302 Similar to the comment above, the distance between landform and its relationship to entrapped CH4 is more likely to be a proxy of the parent material of the sediment and deposition history than the time elapsed since the areas were covered by glaciers, i.e. glacier extend and sediment age as defined could be irrelevant properties for explaining the inferred amount of entrapped CH4.

We agree with the Reviewer that distance is not a causal variable. But in our results section we merely state our finding with due caution in that we say "…with distance between the forefields playing an *apparently* important role." In the Discussion (l. 405), we then make the link to the parent material, i.e. the differences in lithology and tectonic settings. We have slightly modified the central statement to now read:

"This may be explained by the fact that sediments in glacier forefields located in close proximity to one another are, at least in part, derived from the same individual nappes and geological formations contained therein." (l. 406) … "Hence, this result supports our previous hypothesis that differences in lithology, mineralogy, and tectonic settings between individual nappes play an important role in determining bedrock- and thus sediment-entrapped CH_4 contents…". (l. 410)

14.) L. 319 Please use a quantative terms, rather than the qualitative term "little".

We agree with the Reviewer. The sentence in question now reads:

"Conversely, entrapped CH_4 contents, sediment porosity, and sediment-particle density together contributed $\leq$ 16% to the calculated uncertainties." (l. 314)

15.) L.326 as stated in the comment above, more arguments should be provided to back up the assumption that maximum glaciated area in year approx. 1850 is the original value as stated here. It seems that, the original value could more correctly be de- scribed as the start value for your estimate of the exposed proglacial area following the most recent major glacial retreat, which could or could not have a direct influence of the amount of CH4 stored in the sediment. However, the relevant age of the sediments CH4 content (i.e. the time the CH4 was trapped in the rock which by weathering became sediment) is not related to the point in time in which it most recently was ex- posed to the atmosphere (i.e. not covered by ice), nor to the point in time where the sediment was deposited in the current landform. It is highly likely that the sediment that you sample here and now, on several other points in tie have been exposed to the atmosphere without either incorporating more CH4 or releasing parts of the currently entrapped CH4.

This comment is similar to comment 10 and we refer to our answer to that comment. We strongly feel that there was a misunderstanding on our use of the 1850 maximum glaciated area. As stated above, the *only* purpose of using the 1850 glacial extent together with the extent of 2010 was to estimate the glacier-forefield area that has been exposed as a result of deglaciation since 1850. In that sense we follow the commonly used definition of a glacier forefield (“area between the moraines of modern (or post-glacial) advances (e.g. greatest extent as around 1850/60) and today's glacier outlines”; Glacier Monitoring of Switzerland (GLAMOS)). Please note that nowhere in the paragraph in question nor in the entire manuscript do we claim that 1850 marks an original value or a time zero for entrapped CH4 contents.

16.) L.329. Consider the wording in the sentence: “ From these numbers, the total mass of sediment-entrapped CH4 in all Swiss glacier forefields derived from calcareous bedrock was computed. . ..” I recommend that this sentence should be revised to more appropriately reflect what the study has done, namely to give a best estimate of the entrapped CH4 in an area of the glacier forefields corresponding to the area extending from the current position of the glaciers to their reconstructed position during the most recent glacial maximum, which is different from “all Swiss glacier forefields”. The findings and associated increase in scientific understanding is sufficiently strong, novel and interesting in itself, and I see no reason for trying to upscale the potential amount of CH4, which at the current level of understanding will be very uncertain.

The entire Results paragraph in question deals with the upscaling of the results we obtained in five glacier forefields to all calcareous glacier forefields in Switzerland. We agree with the Reviewer that the estimate from this upscaling must be associated with a large uncertainty. Nonetheless, we feel that providing a first albeit rough estimate is a worthy objective, particularly when an estimate of the associated uncertainty can be provided, which is what we have done. As suggested by the Reviewer, and to indicate that this is not a precise computation but just an estimate, we modified the last sentence of this paragraph to now read:

“From these numbers, we estimated the total mass of sediment-entrapped CH4 in all Swiss glacier forefields derived from calcareous bedrock to $1.04\times10^5 \pm 3.7\times10^4$ t CH_4.” (l. 324)

We note that in the discussion of these results, we intentionally state that we consider this a rough estimate only, repeating the substantial uncertainty involved. “Our first, rough estimate for the total quantity of CH_4 entrapped in sediments of all calcareous Swiss glacier forefields combined yielded a substantial mass of $1.04\times10^5 \pm 3.7\times10^4$ t CH_4, contained within a solid volume of ~2.1 km^3 glacier-forefield sediments.” (l. 421)

17.) L. 376 Little variation in entrapped CH4 across sediment depth and exposure age, indicate that the CH4 concentration is not dependent on recent transformations or release, but an inherent property reflecting the CH4 content of the parent material (as also indi- cated in L. 383). Again, sediment age as defined does not seem to be a very relevant explanatory variable.

This comment relates back to previous comments on sediment age. Indeed, sediment age even used in the sense of a proxy (see comments 1, 10, 11 above) showed no significant effect on entrapped CH_4 contents. This is one result of this study, which is here discussed.

18.) L.386/387. What “major alterations” do you suggest that the sediment has under- gone during and after the erosion of the parent materiel? Usually, physical erosion of bedrock primarily reduces the grain size of the material in question without any further alterations to the matrix of the grain (unless the material undergoes diagenesis). I believe your observations point towards the opposite, namely that the sediment has not undergone any significant alterations with respect to entrapped CH4 and that this property is indeed one of the key take-home messages of your story, i.e. that large quantities of entrapped CH4 is present, but not very likely to be quickly mobilized by natural weathering with following release to the atmosphere. The importance of this is of course linked to recent discoveries of subglacial CH4 emissions (as included in your references), in which the sediment entrapped CH4 is likely not a major contributor, unless there is significant subglacial dissolution of calcareous material with entrapped CH4.

We agree with the Reviewer that the sentence in question is misleading, as we argue in this paragraph that CH_4 in forefield sediments appears relatively stable in its entrapped state. To avoid misinterpretation, we rephrased the sentence in question to read:

“Thus, although sediments have undergone erosion from the parent bedrock and subsequent weathering, changes in entrapped CH_4 geochemical characteristics appeared negligible.” (l. 382)

The relevance to subglacial CH_4 emissions is less clear in our opinion and requires further study. In particular, several studies indicate that CH_4 in these systems is derived from microbial CH_4 production rather than being of thermogenic origin.

19.) L- 404/405 and 413/414. Yes, differences in CH4 content of the parent rock is likely the main explanation for the observed variability. An improved mineralogical investigation of the sediment in the various landforms would be able to test whether the sediment in the floodplain is significantly different that the other two landform, thereby providing a possible explanation for the observed differences in CH4 content.

We agree with the Reviewer. To indicate the value of such a mineralogical investigation to readers we have added a sentence to the end of the first paragraph in question to read:

“An improved mineralogical investigation of sediments in the various landforms would aid in clarifying this issue.” (l. 404)

20.) L 426/427 What is the relevance of comparing a large, entrapped, immobilized and thermogenic CH4 volume in sediment with no proven interaction with the atmosphere to a mobile, biogenic CH4 pool in lakes, wetland and wild animals? These are two completely different carbon cycles, with very contrasting element cycling times.

Here we wanted to provide a comparison of our estimate of entrapped CH_4 mass to other CH_4 inventory data available for Switzerland. However, most inventory data are available in the form of CH_4 fluxes. We agree with the Reviewer that it is debatable how relevant such comparisons are, but we feel it provides readers with a sense for the magnitude of the CH_4 pool in glacier forefields. As a compromise, we have removed the numbers on CH_4 flux from a Swiss lake, and only mention the estimate of total CH_4 flux from natural and semi-natural sources in Switzerland.

"At first glance, this number appears large when compared with an estimate of annual CH_4 emissions to the atmosphere (5.7×10^3 t CH_4) from natural and semi-natural sources in Switzerland." (l. 423)

21.) L 433 - 441. Why is it important to narrow down the uncertainty of how much CH4 is indeed present in the entire area going beyond your study area, if the CH4 is not mobile?

The reason for upscaling is described in the answer to comment 16, and we feel that reducing the uncertainty in our currently rough estimate is a worthy cause by itself. Moreover, at this time there is no experimental verification that entrapped CH_4 is truly immobile. On the contrary, a set of recently conducted experiments in our laboratory yielded first indications that trace amounts of sediment-entrapped CH_4 may slowly "leak" from the calcareous sediments into the sediment-gas phase (see our response to the comment of Reviewer 1). But these experiments are beyond the scope of this manuscript, and we consider them preliminary only, requiring experimental confirmation.

22.) L441 – L 453. CH4 emission release rates by chemical weathering is likely to be orders of magnitude lower than reported rates of microbial CH4 oxidation in soil and sediment. The described scenario is quite hypothetical and non-documented. To strengthen the scope of the study and highlight its importance, I recommend to remove this last section of the MS dealing with microbial oxidation and exchange with the atmosphere, as this is most likely not happening at a rate with any significance for biological CH4 turnover.

We feel that a speculative statement at the end of the Discussion section is permissible, and that it does not weaken the manuscript, particularly in light of the unresolved question if traces of CH_4 may leak from these sediments (see previous comment). Moreover, we feel that we were careful in phrasing this speculation. We note that bacteria mediating atmospheric CH_4 oxidation make indeed a living on traces of CH_4 in the sub-ppm range. On the other hand, we fully agree with the Reviewer that such speculation should be avoided in the Summary and Conclusions section (see comment below).

23.) L. 455-468. Very good summary of the presented work and conclusions.

We thank the Reviewer for this assessment.

24.) L. 469-474 Somewhat speculative when the data suggest the opposite, i.e. that CH4 is very stable within sediment and not released due to weathering at any significant rate (no significant difference with sediment depth+ entrapped CH4 in sediment reflect that of parent material). I suggest removing this part of the conclusion to make your story more focused, and not end on a speculatory note, when you in fact have quite strong and novel data.

We agree with the Reviewer that the manuscript should not end with a speculation. We have therefore removed the paragraph in question.

25.) Figure 2: Good idea to show sample point and profiles on a map. However As mentioned above, the concept of sediment age as an explanatory variable does not seem justified.

This issue was addressed in comments 1 and 12. To remind the reader on the use of these terms as proxies, we also modified the caption of Fig. 2 to read:

"Sampling zone at Griessfirn (GRF) glacier forefield showing (a) blocks and sampling locations to study the effect of sediment age and glacier-forefield landforms (used here as proxies for all edaphic variations present in these sediments) on entrapped CH_4 contents,…”. (l. 703)

26.) Figure 3: The difference between minimum and maximum glacial extend could be irrelevant as an explanatory variable.

This issue was addressed in comments 10 and 15. The difference between minimum and maximum glacial extent was never intended as an explanatory variable, but was only used to estimate glacier-forefield area.

27.) Figure 7: More info on mineralogy and parent material would be useful to better characterize and understand the shown differences in entrapped CH4. The absolute unit “Mass of entrapped CH4 (t)” is very dependent on your upscaling and its associated uncertainty. I suggest to revise figure 7a, the show entrapped CH4 in relative terms (could be g CH4 per ton sediment or similar) to better the variation span in entrapped CH4 per sediment type (i.e. what you call landform).

We agree with the Reviewer that data on CH_4 contents is important to show for the five glacier forefields. This information is shown in Table 2. But as the five glacier forefields not only differ in sediment-entrapped CH_4 contents, but e.g. also in spatial extent (area), we feel that the determination of CH_4 mass and associated uncertainties for each of the forefields provides important, additional information and insight. We also argue that there is no upscaling involved in the data presented in Fig. 7a. For each of the five glacier forefields, we computed entrapped CH_4 mass based on measurements of CH_4 contents, and estimates of sediment thickness and sediment-covered area. (Upscaling, on the other hand, was used to provide a first estimate of entrapped CH_4 mass contained in all calcareous glacier forefield sediments in Switzerland).

28.) Table 2: Sediment porosity: It is not clear if the the parameter “porosity” indicated intragrain porosity (i.e. amount of pore volume within the sediment) or intra-grain porosity (i.e. amount of pore volume between grains, which must be assumed to be occupied by atmospheric air at approximately 1.9 ppm CH4). Please clarify.

We agree with the Reviewer that this needs clarification. We provide this clarification at the first instance where the term is introduced in the manuscript:

“…and $\theta_{t,sed}$ is total inter-particle sediment porosity, hereafter referred to as sediment porosity.” (l. 210)

and also in the caption of Table 2:

“Mean values and uncertainties of sediment-entrapped CH_4 content, sediment-covered area, and total inter-particle sediment porosity …” (l. 756)

Quantity and distribution of methane entrapped in sediments of calcareous, Alpine glacier forefields

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Abstract. Aside from many well-known sources, the greenhouse gas methane (CH_4) was recently discovered entrapped in sediments of Swiss Alpine glacier forefields derived from calcareous bedrock. A first study performed in one glacial catchment indicated that CH_4 was ubiquitous in sediments and rocks, and was largely of thermogenic origin. Here we present results of a follow-up study, which aimed at (1) determining occurrence and origin of sediment-entrapped CH_4 in other calcareous glacier forefields across Switzerland, and (2) providing an inventory for this sediment-entrapped CH_4, i.e., determining contents and total mass of CH_4 present, and its spatial distribution within and between five different Swiss glacier forefields situated on calcareous formations of the Helvetic Nappes of the Central Alps.

Sediment and bedrock samples were collected at high spatial resolution from the forefields of Im Griess, Griessfirn, Griessen, Wildstrubel, and Tsanfleuron glaciers, representing different geographic and geologic regions of the Helvetic Nappes. We performed geochemical analyses on gas extracted from sediments and rocks, including determination of CH_4 contents, stable carbon-isotope analyses ($\delta^{13}C_{CH4}$), and determination of gas-wetness ratios (ratio of CH_4 to ethane and propane contents). To estimate the total mass of CH_4 entrapped in glacier-forefield sediments, the total volume of sediment was determined based on measured forefield area and either literature values of mean sediment thickness or direct depth measurements using electrical-resistivity tomography.

Methane was found in all sediments (0.08–73.81 $\mu g\ CH_4\ g^{-1}$ dry weight) and most rocks (0.06–108.58 $\mu g\ CH_4\ g^{-1}$) collected from the five glacier forefields, confirming that entrapped CH_4 is ubiquitous in these calcareous formations. Geochemical analyses further confirmed a thermogenic origin of the entrapped CH_4 (average $\delta^{13}C_{CH4}$ of sediment: -28.23 (± 3.42) ‰; average gas-wetness ratio: 75.2 (± 48.4)). Whereas sediment-entrapped CH_4 contents varied moderately within individual forefields, we noted a large, significant difference in CH_4 content and total CH_4 mass (range: 200–3881 t CH_4) between glacier forefields at the regional scale. Lithology and tectonic setting within the Helvetic Nappes appeared to be dominant factors determining rock and sediment CH_4 contents. Overall, a substantial quantity of CH_4 was found to be entrapped in Swiss calcareous glacier forefields. Its potential release and subsequent fate in this environment is the subject of ongoing studies.

1 Introduction

The atmospheric concentration of the greenhouse gas methane (CH_4) has increased from pre-industrial values < 0.8 µL/L to a current global average of ~1.86 µL/L (Dlugokencky, 2018), indicating an imbalance in strength between CH_4 sources and sinks during this time period (Kirschke et al., 2013; Saunois et al., 2016; Ciais et al., 2013). Methane sources are commonly classified as either natural (e.g., wetlands, inland waters, geological sources (Etiope et al., 2008; Kirschke et al., 2013; Bastviken et al., 2011)), or, in case they result from human activity, anthropogenic (e.g., ~~. Major natural CH_4 sources include wetlands, inland waters such as lakes, rivers, and reservoirs, as well as geological sources, e.g., gas seeps and geothermal/volcanic sources (Etiope et al., 2008; Kirschke et al., 2013; Bastviken et al., 2011). Major anthropogenic CH_4 sources include~~ rice paddies~~ (Saunois et al., 2016)~~, livestock husbandry~~ (Johnson et al., 2002)~~, fossil fuels (Bousquet et al., 2006), and biomass burning (Bousquet et al., 2006; Kirschke et al., 2013; Johnson et al., 2002; Saunois et al., 2016)).

An alternative way to categorize CH_4 sources is based upon the CH_4 production pathway: microbial, thermogenic, or abiotic (Conrad, 2009; Etiope and Sherwood Lollar, 2013; Joye, 2012; Whiticar, 1999). Microbial CH_4~~, which accounts for ~70 % of global CH_4 emissions to the atmosphere,~~ is produced by methanogenic archaea (methanogens) under anoxic conditions and in the absence of energetically more favorable terminal electron acceptors as the final step of organic matter degradation (Conrad, 1996; Conrad, 2009; Denman et al., 2007). Conversely, thermogenic CH_4 is produced in sedimentary deposits under elevated temperatures and pressures during sediment diagenesis by thermal decomposition of organic matter (Etiope, 2012; Martini et al., 2003; Schoell, 1988). ~~This type of CH_4 is dominant in natural-gas fossil fuel, and is often found in terrestrial and marine gas seeps and mud volcanoes (Etiope, 2012; Kirschke et al., 2013; Etiope, 2009).~~ Together, microbial and thermogenic CH_4 are frequently referred to as biotic CH_4, as in both cases the initial substrates are of biological origin (Etiope and Sherwood Lollar, 2013). Finally, CH_4 can also be formed via inorganic chemical reactions in the Earth's crust and mantle, e.g., in serpentinized, ultramafic rocks, and is therefore referred to as abiotic CH_4 (Etiope and Sherwood Lollar, 2013; Etiope and Schoell, 2014; Etiope et al., 2018). ~~Initial substrates of abiotic CH_4 production typically include CO, CO_2, and H_2 (Etiope and Schoell, 2014).~~ Stable isotope analyses and/or analyses of gas composition are commonly employed to distinguish between microbial, thermogenic, and abiotic CH_4 origins (Etiope and Schoell, 2014; Whiticar, 1999; Milkov and Etiope, 2018; Schoell, 1988).

Accelerated melting of ~~many~~ glaciers and ice sheets as a result of global warming (Haeberli et al., 2007; Paul et al., 2004; UNEP and WGMS, 2008) has prompted intense research activities in glacial environments~~ to become topics of intense research in recent years~~, including investigations on their role in the turnover of greenhouse gases. ~~Specifically, s~~Several studies have identified subglacial environments as habitats for methanogens, and consequently as a potentially important CH_4 source (Wadham et al., 2012; Wadham et al., 2013; Christner et al., 2012; Souchez et al., 1995; Stibal et al., 2012). Methane emissions from these locations have recently been confirmed and quantified in field measurements (Burns et al., 2018; Christiansen and Jørgensen, 2018; Lamarche-Gagnon et al., 2019). Conversely, other studies provided evidence that aerated glacier-forefield sediments can act as a sink for atmospheric CH_4 (Chiri et al., 2015; Nauer et al., 2012; Bárcena et al., 2010;

Hofmann et al., 2013). This function is mediated by a group of aerobic methane-oxidizing bacteria (MOB), which catalyze CH_4 oxidation at near-atmospheric concentrations (Curry, 2009; Zhuang et al., 2013; Dunfield, 2007). The strength of this CH_4 sink appears to vary between different glacier-forefield landforms, and increase with sediment age (Bárcena et al., 2010; Chiri et al., 2017; Hofmann et al., 2013). In this context, sediment age refers to the number of years sediment has been exposed to the atmosphere following glacier retreat. Note that both terms, sediment age and landform, serve as proxies for all edaphic variations present in these sediments at different locations within the glacier forefield. We will adopt this convention and use the terms sediment age and landform in this fashion throughout this paper.

~~Evidence thereof was provided from elevated CH_4 concentrations found in basal ice (Campen et al., 2003; Christner et al., 2012; Souchez et al., 1995), and from long-term incubation experiments that indicated a substantial methanogenic potential in subglacial sediments (Wadham et al., 2012; Stibal et al., 2012; Boyd et al., 2010). Emissions of CH_4 from subglacial environments to the atmosphere, in particular through meltwater discharge, have recently been confirmed and quantified in field measurements (Burns et al., 2018; Christiansen and Jørgensen, 2018; Lamarche-Gagnon et al., 2019).~~

~~A~~An alternative potential CH_4 source ~~in glacial environments~~ was recently detected in sediments of Swiss glacier forefields, in particular in those derived from calcareous bedrock (Nauer et al., 2012). Subsequent laboratory experiments revealed that ~~this~~ CH_4 ~~could be~~was released from ~~these~~glacier-forefield sediments upon mechanical impact and during acidification (Nauer et al., 2014). In a recent study focusing on one particular Swiss glacial catchment (Wildstrubel catchment, Canton Valais), we established that entrapped CH_4 was present in nearly all~~virtually omnipresent in~~ sediment and bedrock samples collected throughout this catchment, but that CH_4 contents exhibited substantial variation between sampling locations (Zhu et al., 2018). We also provided robust evidence based on stable-isotope and other geochemical data that CH_4 entrapped in sediment and bedrock samples was predominantly of thermogenic origin, and that microbial CH_4 production was likely of minor importance at this site. However, as the focus of that study was on the occurrence and origin of entrapped CH_4 in different regions of the catchment, the number of samples collected was insufficient to rigorously assess spatial distribution and total quantity (here defined in terms of content, i.e., concentration, and total mass) of entrapped CH_4 within the forefield sediments (Zhu et al., 2018). Yet, to better characterize this potential CH_4 source, it is important to assess its spatial distribution and total quantity, particularly in glacier-forefield sediments, as we expect the potential for CH_4 release from these sediments to far exceed that from large bedrock surfaces due to the much higher specific surface area of the former (André et al., 2009; Michel and Courard, 2014). Moreover, as calcareous glacier-forefield sediments throughout the Swiss Alps are of similar origin (Weissert and Stössel, 2015), sediment-entrapped CH_4 may be a feature common to most if not all Swiss glacier forefields derived from calcareous bedrock. Whereas this hypothesis remains to be tested, its confirmation would greatly increase the magnitude of this potential CH_4 source.

Therefore, the overall goal of this study was to extend the work of Zhu et al. (2018) to other calcareous glacier forefields located in different regions of the Swiss Alps, and to assess the distribution of entrapped CH_4 contents within and compare total mass of entrapped CH_4 between all sampled glacier forefields. Specific objectives included to (1) test occurrence and origin of sediment-entrapped CH_4 in four additional calcareous glacier forefields. Furthermore, we wanted to (2) assess the spatial distribution of sediment-entrapped CH_4 contents in detail within one glacier forefield, testing for dependencies on sediment depth, sediment age, and glacier-forefield landforms, and based on the results obtained to (3) efficiently sample sediments of the other glacier forefields to quantify contents and total mass of sediment-entrapped CH_4. Finally, we wanted to (4) upscale these results and derive a first estimate of the total mass of sediment-entrapped CH_4 contained in all Swiss glacier forefields situated on calcareous bedrock.

2 Methods

2.1 Field sites and field-work stages

Field work was conducted in five different glacier forefields: Im Griess (IMG), Griessfirn (GRF), and Griessen (GRI) glaciers located in Central Switzerland in Cantons Uri (IMG, GRF) and Obwalden (GRI), and Tsanfleuron (TSA) and the previously investigated Wildstrubel (WIL, Zhu et al. (2018)) glaciers located in Canton Valais (Figs. 1 and S1). These forefields were selected for two main reasons. Foremost, their sediments are mainly derived from calcareous bedrocks of the Helvetic Nappes (green shaded area in Fig. 1), which consist of a series of nappes (sheets of thrusted rocks) largely composed of Mesozoic limestones, shales, and marls of Jurassic to Eocene age (Pfiffner, 2014; Weissert and Stössel, 2015). They were originally deposited on the shallow northern shelf of the ancient Alpine Tethys Ocean (Weissert & Mohr, 1996), and subsequently deformed, folded, and stacked on top of each other during Alpine orogeny (Herwegh and Pfiffner, 2005). Whereas individual nappes within the Helvetic Nappe system therefore share a similar origin, lithology and tectonic settings between individual nappes can be quite diverse (Weissert and Stössel, 2015). This was suggested to be a dominant factor determining rock CH_4 contents in the WIL catchment (Zhu et al., 2018). Consequently, we chose to investigate ~~distant~~ glacier forefields ~~within the Helvetic Nappes~~distant from one another (e.g., distance TSA to IMG ~136 km), for which sediments are derived from different ~~individual~~ nappes, but also glacier forefields in close proximity to each other (e.g., distance IMG to GRF ~3.8 km; TSA to WIL ~24 km), for which sediments are derived, at least in part, from the same nappe. A second important reason for selection was that all five glacier forefields are relatively easy to access, facilitating sample collection and transport to the laboratory.

We conducted our field work in two stages. During stage I in summer 2016, we performed a detailed investigation on the spatial distribution of sediment-entrapped CH_4 within a designated sampling zone at the GRF glacier forefield, using high spatial-resolution sampling to determine variations in entrapped CH_4 contents in relation to sediment depth, sediment age, and glacier-forefield landforms. The GRF forefield was chosen for this purpose mainly because it features well-defined sediment-age classes and well-developed, clearly distinguishable landforms within a previously discretized and characterized sampling zone (Chiri et al., 2015; Chiri et al., 2017). We also conducted measurements of sediment thickness (distance between the ground surface and the underlying bedrock) to estimate sediment volumes and thus the total mass of entrapped CH_4 present in these sediments. Results of the GRF field work were then used to adapt our sampling strategies for field-work stage II performed in summer 2017, to quantify contents and total mass of sediment-entrapped CH_4 in the IMG, GRI, TSA, and WIL glacier forefields. During both field-work stages, selected sediment and rock samples were used to identify the origin of the entrapped CH_4 based on CH_4 stable carbon-isotope analyses and analyses of entrapped gas composition (see below).

2.1.1 Field-work stage I (GRF glacier forefield)

Sampling and measurements during stage I in the GRF forefield was conducted in three steps. First we tested the effect of sediment depth, then the effects of sediment age and glacier-forefield landforms on entrapped CH_4 contents. Finally, we estimated the total mass of sediment-entrapped CH_4 based on measured CH_4 content, sediment thickness, and sediment-covered area.

To study the effect of sediment depth on entrapped CH_4 contents, we implemented a ~~completely~~ randomized design, selecting 14 random locations within our sampling zone (not shown). We collected a total of 52 sediment samples (each ~500 g) by excavation from depths ranging from 20 to 70 cm below ground surface. All sediment samples were stored in clean plastic bags, transferred to the laboratory, and kept in the dark at 4 °C before further treatment. Following the extraction of entrapped gas and subsequent quantification of CH_4 contents in sediment samples (see below), the effect of sediment depth on entrapped CH_4 contents was studied using a one-way ANOVA. The result of this analysis was then used to adapt the sampling scheme for the following step.

To study the effect of sediment age and glacier-forefield landforms on entrapped CH_4 contents, we implemented a randomized block-sampling design. We first divided the GRF sampling zone into nine blocks (a combination of three sediment-age classes and three landforms, Fig. 2a), ~~adopting~~using ~~a~~the ~~previous~~ spatial discretization of Chiri et al. ~~classification~~ (2017). The three sediment-age classes were: A (0–20 yr), B (20–50 yr) and C (50–100 yr). ~~In this context, sediment age refers to the number of years since the sediment has been exposed to the atmosphere as a result of glacier retreat.~~ The three forefield landforms at GRF were floodplain, terrace, and sandhills. A floodplain refers to the frequently flooded area in the immediate vicinity of the glacial stream, which commonly consists of sediments of fine particle size (mostly silt) and a lack of vegetation. A terrace refers to an elevated, previously flooded area, i.e. a former floodplain, usually featuring some vegetation coverage. Finally, sandhills consist of un-oriented, hummocky glacial-debris deposits, typically featuring poorly sorted, well-aerated sediments of sandy loam to sandy clay-loam texture. We collected a total of 78 sediment samples (each ~500 g) by excavation from a depth of 20 cm below ground surface, with 8–12 samples collected at random locations from within each block (Fig. 2a). The sampling depth of 20 cm below ground surface was chosen based on our results from the previous step. Following laboratory analyses (see below), the impact of sediment age and landforms on entrapped CH_4 contents was studied using a two-way ANOVA.

In addition to sediments, we also collected a total of 17 bedrock samples from outcrops and large boulders within the GRF glacier forefield. These samples were used to determine the CH_4 content of the parent material (Zhu et al., 2018). All bedrock samples were stored in plastic bags, transferred to the laboratory, and stored in dark at 4 °C before further treatment.

Estimation of the total mass of CH_4 entrapped in glacier-forefield sediments also requires information on sediment thickness. For the GRF sampling zone we employed the electrical resistivity tomography (ERT) method (e.g., Kneisel, 2006;

Reynolds, 1997; Scapozza et al., 2011). Five two-dimensional, vertical ERT profiles (ERT1–ERT5) were measured during two field campaigns, covering the three sediment-age classes and the three landforms (Fig. 2b). Two profiles were measured parallel to the glacier stream (ERT2 and ERT5), and three perpendicular to the glacier stream (ERT1, 3, and 4). For each profile, 48 stainless-steel electrodes (30 cm long, 1.2 cm dia.) were hammered into the sediment to a depth of ~15 cm and connected to two 24-core copper cables, which were linked to the ERT instrument (SYSCAL Pro; Iris Instruments, Orléans, France) at the profile's midpoint. To improve electrical coupling of the electrodes with the skeleton-rich glacier-forefield sediments, water-soaked sponges were positioned at the sediment surface surrounding each electrode. Profile ERT1 was measured with an electrode interspacing of 2.5 m (total profile length 120 m), the other four with 5 m distance between the electrodes (240 m profile length). Using a so-called Wenner-Schlumberger configuration (Loke, 2001), an electrical current was sent to the subsurface using a pair of electrodes. The voltage difference measured across the other pairs of electrodes was used to calculate the electrical resistivity of the subsurface. To infer the location of the sediment-bedrock interface, inversion of apparent resistivities was performed using the 2-D program RES2DINV (Loke and Barker, 1996). The average sediment thickness and its uncertainty within the GRF forefield was then analyzed in R. Electrical resistivities >2000 Ωm were considered indicative of solid bedrock, whereas resistivities < 2000 Ωm were considered indicative of unconsolidated sediment (Kneisel, 2006; Reynolds, 1997). Portions of the ERT profiles, for which the sediment-bedrock interface could not be detected, were omitted from further analyses.

2.1.2 Field-work stage II (IMG, GRI, WIL, and TSA glacier forefields)

During stage II, we collected a total of 111 sediment samples at 20 cm depth, 25 samples from IMG, 25 from GRI, 33 from WIL, and 28 from TSA glacier forefields (sampling locations shown in Fig. 3). Based on results obtained during field-work stage I, and given that glacier-forefield landforms were much less prominent at IMG, GRI, WIL, and TSA, we divided each of the four forefields into six blocks, and collected four to eight sediment samples (each ~500 g) from each block at random locations. We also collected 55 bedrock samples from outcrops and boulders; 13 from IMG, 14 from GRI, 12 from WIL, and 16 from TSA glacier forefields (locations also shown in Fig. 3).

2.2 Laboratory procedures

2.2.1 Extraction of entrapped gas

We extracted entrapped gas from sediments and rocks using the acidification method described in Nauer et al. (2014) and Zhu et al. (2018). Before acid treatment, sediments were sieved with a clean 20 mm mesh sieve. Particles >20 mm were excluded from subsequent analyses. For each sample, ~3–5 g of sediment was weighed and transferred into a 117 mL serum bottle, sealed with a butyl rubber stopper and crimped with an aluminum cap. The vial's headspace was then flushed with N_2 gas. Thereafter, 5 mL deionized water was added into the vial, followed by ~50 mL of 6 N HCl to dissolve carbonate minerals. The headspace of each vial was connected to one or multiple 1 L gas bags (Tesseraux GmbH, Bürstadt, Germany). Sediment samples released large amounts of gas immediately after the acid was added. When bubbling stopped, an additional 2 mL 6N HCl was added to each vial to confirm that the carbonate minerals were fully dissolved. Full dissolution of all carbonate minerals took ~4 h. After gas extraction, ~200 mL of gas were removed from the gasbags with syringes and stored in glass vials for further analysis. The total volume of gas remaining in gas bags was measured with a mass-flow meter (Bronkhorst, Reinach, Switzerland). Rocks were first hammered or sawed into ~1 cm diameter ~~pieces~~fragments and then dissolved in the same way as sediments. Initial tests, in which we compared hammering with sawing to obtain rock fragments both from the surface and from the core of larger rocks, showed insignificant effects on the fragments' entrapped CH_4 contents and other geochemical parameters. As the duration of the respective mechanical treatment varied greatly between the collected fragments, we consider this as evidence that neither hammering nor sawing had an adverse effect on measured geochemical parameters. ~~Initial tests indicated that rock hammering or sawing had no adverse effect on measured entrapped CH_4 contents, nor on other geochemical parameters.~~

2.2.2 Quantification of methane, ethane, and propane

Concentrations of CH_4 were measured with a gas chromatograph equipped with a flame-ionization detector (GC-FID; Trace GC Ultra, Thermo Electron, Rodano, Italy) and a Porapak N100/120 column. The column-oven temperature was 30 °C, runtime was 36 s. Nitrogen carrier-gas flow was set to 26 mL/min. The FID was operated at 150 °C in high sensitivity mode. Concentrations of ethane (C_2H_6) and propane (C_3H_8) were quantified in selected gas samples using the same GC-FID system, but with oven temperature at 40 °C for 2 min, an increase to 140 °C at a rate of 25 °C/min, and constant oven temperature of 140 °C for another 9 min. Gas contents were calculated as the mass of CH_4, C_2H_6, and C_3H_8 released during acidification, normalized to the dry weight of the sample. The dry weight of sediments was determined by oven-drying of subsamples at 60 °C for 72 h. Computed entrapped gas contents C_{CH4}, C_{C2H6}, and C_{C3H8} were subsequently used to calculate the gas-wetness ratio as $C_{CH4}/(C_{C2H6} + C_{C3H8})$ (Jackson et al., 2013), a commonly used indicator of CH_4 origin (a value >1,000 is considered evidence for microbial CH_4, whereas a value <<1,000 is considered indicative of thermogenic CH_4 (Rowe and Muehlenbachs, 1999)).

2.2.3 Stable carbon-isotope analysis of entrapped methane

A total of 31 ~~About five~~ sediment ~~samples~~ and ~~five~~ bedrock samples from ~~each~~the five glacier forefields were selected for stable carbon-isotope analysis of entrapped CH_4 ($\delta^{13}C_{CH4}$). To determine $\delta^{13}C_{CH4}$ we used a modified acidification protocol for gas extraction, which consisted of flushing the vials' headspace with He instead of N_2 to remove ambient air. Gas released during the acidification treatment was passed through two 1 M NaOH solutions to remove the majority of CO_2, an Ascarite trap to remove final traces of CO_2, a Drierite trap to remove H_2O vapor, and a 1 M $ZnCl_2$ trap to remove potential H_2S (all chemicals from Sigma Aldrich, Buchs, Switzerland). The purified gas samples were subsequently analyzed by GC-IRMS (Isoprime, Elementar Ltd., Stockport, UK).

2.3 Estimation of total mass of CH_4 entrapped in glacier-forefield sediments

2.3.1 Estimation of entrapped CH_4 mass for the GRF sampling zone

The mass of CH_4 (m_{CH4}) entrapped in a specific volume of porous sediment may be calculated using:

$$m_{CH4} = C_{CH4}\,\rho_{sed}\left[A_{sed}\,T_{sed}\left(1-\theta_{t,sed}\right)\right] \tag{1}$$

where C_{CH4} is sediment-entrapped CH_4 content (mass of CH_4 per mass of sediment), ρ_{sed} is sediment-particle density, A_{sed} and T_{sed} are sediment-covered area and sediment thickness in the glacier forefield, and $\theta_{t,sed}$ is total inter-particle sediment porosity, hereafter referred to as sediment porosity. To determine m_{CH4} for the GRF sampling zone, we applied Eq. (1) separately to each landform, but also used averaged values for entrapped CH_4 contents (from laboratory analyses), sediment thickness (from ERT field measurements), and sediment-covered area estimated from aerial maps (https://map.geo.admin.ch). In Eq. (1), the term in brackets represents the sediment's solid volume. To compute the latter, we assumed a mean $\overline{\theta}_{t,sed} = 0.42 \pm 0.02$, as determined for this site by Nauer et al. (2012). To convert solid volume to sediment mass, a mean value of $\overline{\rho}_{sed} = 2.71 \pm 0.15$ g cm^{-3} was used, as derived by Daly (1935) from measurements of a variety of calcite rock samples.

The total uncertainty in the estimated mean CH_4 mass $\overline{m}_{CH4}$, expressed as standard error (SE) of the mean ($\sigma_{\overline{m}_{CH4}}$), was computed using:

$$\sigma_{\overline{m}_{CH4}} = \overline{m}_{CH4}\sqrt{\left(\frac{\sigma_{\overline{C}_{CH4}}}{\overline{C}_{CH4}}\right)^2 + \left(\frac{\sigma_{\overline{\rho}_{sed}}}{\overline{\rho}_{sed}}\right)^2 + \left(\frac{\sigma_{\overline{A}_{sed}}}{\overline{A}_{sed}}\right)^2 + \left(\frac{\sigma_{\overline{T}_{sed}}}{\overline{T}_{sed}}\right)^2 + \left(\frac{\sigma_{\overline{\theta}_{t,sed}}}{\overline{\theta}_{t,sed}}\right)^2} \tag{2}$$

where $\sigma_{\overline{x}}$ represents the SE associated with any parameter's mean value $\overline{x}$. The individual contribution of any parameter x ($frac_x$, in %) to the total uncertainty in $\overline{m}_{CH4}$ was then computed using:

$$frac_x = \left(\frac{\overline{m}_{CH4}}{\sigma_{\overline{m}_{CH4}}}\left(\frac{\sigma_{\overline{x}}}{\overline{x}}\right)\right)^2 \times 100 \tag{3}$$

We note that throughout this manuscript SE values (reported as $\overline{x} \pm \sigma_{\overline{x}}$) are used as a measure of uncertainty of any parameter's mean value $\overline{x}$, whereas standard deviations (SD, reported as $\overline{x}(\pm\sigma_x)$) are used as a measure of general parameter variability.

2.3.2 Estimation of entrapped CH_4 mass for the five glacier forefields (IMG, GRF, GRI, WIL, TSA)

To compute total mass and associated uncertainty of sediment-entrapped CH_4 for all five glacier forefields, we employed Eqs. (1) and (2), but with partially modified parameters. For C_{CH4} we used mean values of sediment-entrapped CH_4 contents determined for each glacier forefield. In addition we determined mean values $\bar{A}_{sed}$ from estimates of the maximum and minimum extents of sediment-covered area within each glacier forefield. As maximum we used the areas exposed as a result of glacier retreat since the last glacial maximum (Little Ice Age, ~1850). The latter was estimated from the difference in glacial extent as taken from the most current (2018) and historic (~1850) topographic maps (Swisstopo; https://map.geo.admin.ch; Fig. S2). Minimum areas were directly estimated from the 2018 aerial maps. Also, data on sediment thickness was unavailable for the IMG, GRI, WIL, and TSA glacier forefields, as well as for the GRF forefield outside of the designated sampling zone. We therefore used the average value of $T_{sed} = 10.0 \pm 3.0$ m obtained from our ERT measurements in the GRF sampling zone (see below) as an average T_{sed} for all five glacier forefields. We note that our average T_{sed} value agrees well with previous measurements performed in another Swiss glacier forefield, in which T_{sed} ~8 m was obtained by borehole drilling (Kneisel and Kääb, 2007). Finally, we used values of $\bar{\theta}_{t,sed}$ for GRF, GRI, and WIL forefields as determined for these sites by Nauer et al. (2012). As such values were unavailable for the IMG and TSA forefields, we used a value of $\bar{\theta}_{t,sed} = 0.44 \pm 0.05$ for the latter, averaged from data reported for five calcareous glacier forefields (Nauer et al., 2012).

2.3.3 Estimation of entrapped CH_4 mass for sediments in all Swiss glacier forefields derived from calcareous bedrock

We again used Eq. (1) and (2) to upscale results and to compute a first estimate of the total mass of sediment-entrapped CH_4 contained in all Swiss glacier forefields derived from calcareous bedrock. In this case, we used the mean $\bar{C}_{CH4}$ of the five glacier forefields. Calcareous glacier-forefield surface area in Switzerland (A_{sed} in Eq. (1)) was estimated from available data on the decrease in glaciated area in the Swiss Alps between the Little Ice Age (~1850; Zemp et al. (2008)) and the year 2010 (Fischer et al., 2014), together with an estimate of the fraction of calcareous bedrock area to the total area of the Swiss Alps taken from the Tectonic Map of Switzerland 1:500.000 (Federal Office of Topography, swisstopo). Mean values for ρ_{sed}, T_{sed}, and $\theta_{t,sed}$ were used as described above.

3 Results

3.1 Geochemistry of gas entrapped in sediment and bedrock samples

Of the 271 sediment samples from the five glacier forefields we analyzed 256 samples for entrapped CH_4 contents. All analyzed sediments contained detectable amounts of CH_4 ranging from 0.08 to 73.81 µg CH_4 g^{-1} dry weight (d.w.; Fig. 3), with an average of 14.9 (± 17.0) µg CH_4 g^{-1} d.w.. Gas released from 225 samples was analyzed for C_2H_6 and C_3H_8 contents, of which 215 contained detectable amounts of C_2H_6 ranging from 0.002 to 1.67 µg C_2H_6 g^{-1} d.w., with an average of 0.25 (± 0.32) µg

C_2H_6 g^{-1} d.w.. In addition, 146 out of 225 samples contained detectable amounts of C_3H_8 ranging from 0.001 to 0.82 µg C_3H_8 g^{-1} d.w., with an average of 0.11 (± 0.15) µg C_3H_8 g^{-1} d.w. (not shown).

The average gas-wetness ratio for all sediment samples was 75.2 (± 48.4), and the average $\delta^{13}C_{CH4}$ was -28.23 (± 3.42) ‰. Plotting $\delta^{13}C_{CH4}$ values vs. gas-wetness ratios in a so-called Bernard diagram (Fig. 4; Bernard et al. (1978)) indicated a thermogenic origin for sediment-entrapped CH_4, derived from ancient terrestrial or marine organic matter (kerogen types III and II, Fig. 4). Although CH_4 extracted from sediments collected in the IMG glacier forefield showed a higher variability in gas-wetness ratios than CH_4 extracted from sediments of other glacier forefields, it still fell into the same origin type in the Bernard diagram.

All 72 bedrock samples were analyzed for CH_4 content, and 64 contained detectable amounts of CH_4 ranging from 0.06 to 108.58 µg CH_4 g^{-1}, with an average of 11.4 (± 20.0) µg CH_4 g^{-1} (Fig. 3). The average $\delta^{13}C_{CH4}$ value of -29.21 (± 2.77) ‰ was similar to that of sediment-entrapped CH_4. Likewise, the average gas-wetness ratio of gas extracted from rocks was 78.45 (± 121.84), similar in value but with higher variability than gas-wetness ratios for sediment-entrapped CH_4 (Fig. 4). Together, these data suggest a common, thermogenic origin of entrapped CH_4 in sediments and rocks, with little apparent alteration from physical/chemical weathering. Moreover, our data suggest that entrapped CH_4 is of similar origin in all five glacier forefields.

3.2 Spatial distribution of sediment-entrapped CH_4 contents in the GRF sampling zone

Methane contents in 52 samples collected from 20–70 cm depth ranged from 1.19 to 11.24 µg CH_4 g^{-1} d.w., with one exceptionally high value at 40 cm depth (Fig. 5). Based on these data, there was no clear correlation between sediment depth and entrapped CH_4 contents (one-way ANOVA, $p = 0.9$). Thus, we subsequently proceeded to collect sediments from 20 cm depth only, and assumed these samples to be representative in terms of entrapped CH_4 content for the entire sediment thickness.

The effects of the proxies sediment age and landform on entrapped CH_4 contents were tested using sediments collected from 20 cm depth at 99 locations (Fig. 2a). The CH_4 contents in these samples ranged from 0.59 to 34.82 µg CH_4 g^{-1} d.w. (Fig. 3b), with an average of 5.30 (± 4.86) µg CH_4 g^{-1} d.w.. Two-way ANOVA analysis indicated that landform had a significant effect on sediment-entrapped CH_4 contents ($p = 0.03$), whereas effects of sediment age ($p = 0.19$) and the combined effects of sediment age and landform on entrapped CH_4 contents ($p = 0.37$) were insignificant. Post-hoc comparisons using the Tukey HSD test indicated that mean values for sediment-entrapped CH_4 content (Table 1) were significantly different between floodplain and sandhill ($p = 0.03$), and weakly different between floodplain and terrace ($p = 0.10$). The difference between terrace and sandhill with respect to mean sediment-entrapped CH_4 content was insignificant ($p = 0.88$).

3.3 Mass of sediment-entrapped CH_4 in the GRF sampling zone

To estimate the mass of sediment-entrapped CH_4 stored within the GRF sampling zone, we used Eq. (1) with mean values on entrapped CH_4 contents, sediment thickness, and sediment-covered area determined for each of the three landforms (Table 1). Whereas $\overline{C}_{CH4}$ varied by a factor <1.4 between landforms, sediment thickness was highly variable along the five measured ERT profiles (range 1.0–31.5 m; Fig. 6, Fig. S3), and $\overline{T}_{sed}$ varied by a factor of ~2 between landforms (Table 1). Sediment-covered area also showed substantial variation between the different landforms. Within the GRF sampling zone, the sandhill landform comprised the largest sediment-covered area with $\overline{A}_{sed} \approx 10^5$ m^2, about 5 times larger than for floodplain and terrace. Consequently, the largest sediment mass was contained in the sandhill landform (factor 2–3 larger than floodplain and terrace, Table 1). All three landforms combined featured a surface area of ~1.5×10^5 m^2, and contained an estimated mass of ~2.~~3~~4×10^6 t sediment. Adding up the masses of sediment-entrapped CH_4 for each landform yielded a total $\overline{m}_{CH_4} = 9.7 \pm 3.0$ t CH_4. When calculated using average values for entrapped CH_4 contents~~,~~ and sediment thickness, and combined sediment-covered area, the estimated $\overline{m}_{CH_4}$ within the GRF sampling zone was 12.~~3~~7 ± ~~3.9~~4.0 t CH_4 (last row in Table 1). Uncertainties in individual $\overline{m}_{CH_4}$ values up to ~50% mostly arose from uncertainties in $\overline{T}_{sed}$ (dominated by the large variability in sediment thickness across the GRF sampling zone), and~~,~~ to a smaller degree~~,~~ from uncertainties in $\overline{C}_{CH_4}$.

3.4 Contents and total mass of sediment-entrapped CH_4 in five glacier forefields

Methane contents varied substantially between different glacier forefields (Table 2), with distance between the forefields playing an apparently important role. Specifically, the IMG, GRF, and GRI glacier forefields are located in the Northeast of the Helvetic Nappes relatively close to each other (Fig. 1) and featured similar, low sediment-entrapped CH_4 contents. Likewise, the WIL and TSA glacier forefields are located close to each other in the Southwest of the Helvetic Nappes and featured similar, but high sediment-entrapped CH_4 contents. Indeed, our ANOVA results indicated that differences in sediment-entrapped CH_4 contents were insignificant between the IMG, GRF, and GRI glacier forefields ($p = 0.36$) and between the WIL and TSA glacier forefields ($p = 0.18$). Conversely, differences in entrapped CH_4 contents between the two groups of glacier forefields were highly significant ($p < 0.0001$).

The total mass of CH_4 entrapped in sediments of the five glacier forefields was calculated using estimated values for sediment thickness (10.0 ± 3.0 m; the thickness measured in the GRF sampling zone (see above)) and sediment-particle density (2.71 ± 0.15 g/cm^3; Daly (1935)) that were assumed identical for all five forefields, as well as specific data for each glacier forefield on entrapped CH_4 contents, sediment-covered area, and sediment porosity (Table 2). Whereas $\overline{\theta}_{t,sed}$ values varied only little between the five forefields, $\overline{A}_{sed}$ varied up to a factor of ~3 (IMG vs. WIL), and $\overline{C}_{CH_4}$ up to a factor of ~7 (GRF vs. WIL). This led to substantial ~~variability~~differences in the estimated total mass of sediment-entrapped CH_4 between the five forefields, which ranged from 200 ± 74 t CH_4 for the GRF glacier forefield to 3881 ± 1367 t CH_4 for the WIL forefield (Fig. 7a). Estimates of sediment-entrapped CH_4 mass for the WIL and TSA glacier forefields were significantly larger than for IMG, GRF, and GRI. For all five forefields, sediment thickness and sediment-covered area contributed most to uncertainties in the quantification (Fig. 7b). Conversely, ~~E~~entrapped CH_4 contents, sediment porosity, and sediment-particle density together contributed ≤ 16%~~little~~ to the calculated uncertainties.

3.5 Mass of sediment-entrapped CH_4 in all Swiss glacier forefields on calcareous bedrock

The first estimate of the total mass of sediment-entrapped CH_4 in all calcareous ~~Swiss~~ glacier forefields in Switzerland was based on published data on glacier retreat in the Swiss Alps, an estimation of the fraction of calcareous glacier-forefield surface area, mean values for sediment thickness, sediment-particle density and ~~total~~ sediment porosity, as well as a mean value for sediment-entrapped CH_4 content obtained from the five investigated glacier forefields (18.5 ± 4.4 µg CH_4 g^{-1} d.w.; Table 3). Between the end of the Little Ice Age (~1850) and 2010, the glaciated area within the Swiss Alps has decreased by ~676 km^2 to less than 60 % of its original value (data sources see Table 3). When multiplied by the fraction of calcareous bedrock area in the Swiss Alps (54.6 ±1.7 %), this yielded an exposed calcareous glacier-forefield area of ~369 km^2. The total sediment mass contained within this exposed calcareous glacier-forefield area was then computed as $5.62\times10^9 \pm 1.46\times10^9$ t. From these numbers, we estimated the total mass of sediment-entrapped CH_4 in all Swiss glacier forefields derived from calcareous bedrock ~~was computed as~~ to $1.04\times10^5 \pm 3.7\times10^4$ t CH_4.

4 Discussion

4.1 Widespread occurrence of sediment-entrapped, thermogenic CH_4 in calcareous glacier forefields

We detected substantial quantities of sediment-entrapped CH_4 in all sampled glacier forefields. Entrapped CH_4 was ubiquitously encountered at different sediment depths, and in different forefield landforms and sediment-age classes. We also detected entrapped CH_4 in most bedrock samples obtained from these glacial catchments. Furthermore, our data indicated that both sediment- and rock-entrapped CH_4 are of thermogenic origin. Thus, the results presented here extend our previous studies (Nauer et al., 2012; Zhu et al., 2018) by providing a more detailed survey on entrapped CH_4 contained in glacier-forefield sediments across the Helvetic Nappes, and support our hypothesis on its widespread occurrence and thermogenic origin in calcareous, Swiss Alpine glacier forefields. On the other hand, we cannot entirely reject the possibility for the presence of microbial CH_4 sources in certain parts of glacier forefields, particularly in water-logged sediments. Methanogenic potential in isolated hotspots of water-logged sediments was previously confirmed for the WIL glacier forefield, but considered to be of minor importance under field conditions (Zhu et al., 2018). In the present study, no attempt was made to specifically identify potential methanogenic hotspots in sediments of the other four glacier forefields.

Methane is commonly found in organic-rich sedimentary rocks such as shales, marls, and limestones as a product of the thermal maturation of buried organic matter (Etiope, 2017; Horsfield and Rullkötter, 1994). Previous studies on fluid inclusions in quartz and calcite minerals collected from Alpine fissures and veins within the Helvetic Nappes revealed the existence of four fluid zones, including a large thermogenic CH_4 zone (Gautschi et al., 1990; Mazurek et al., 1998; Mullis et al., 1994; Tarantola et al., 2007). The five glacier forefields we sampled in this study were all located within or near the border of this thermogenic CH_4 zone (see Fig. 1 in Tarantola et al. (2007)). Our results thus agree with previous findings on the occurrence of thermogenic CH_4 in this region, including the occurrence of thermogenic CH_4 detected in gas seeps near Giswil, Central Switzerland, which lies on Penninic Flysch underlain by Helvetic Nappes (Etiope et al., 2010). On the other hand, our results also show that CH_4 entrapment within the Helvetic Nappes is not restricted to fluid inclusions in fissure minerals, but that substantial quantities of CH_4 are entrapped within the matrix of the sedimentary bedrock and sediment particles themselves, presumably within inter- and intragranular m~~a~~icro- and m~~i~~acroporosity (Hashim and Kaczmarek, 2019; Moshier, 1989; Léonide et al., 2014; Abrams, 2017).

Our geochemical data further indicate a common origin for CH_4 entrapped in bedrock and glacier-forefield sediments, derived from ancient terrestrial and marine organic matter (kerogen types III and II, respectively; Fig. 4). This provides further evidence that CH_4 entrapped in the forefield sediments of the Helvetic Nappes has its origin in the calcareous parent bedrock. Moreover, terrestrial and marine organic matter as the ultimate source of sediment- and rock-entrapped CH_4 agrees with the origin of the Helvetic Nappes: their sediments and organic matter were originally deposited under highly variable climatic conditions on the shallow northern shelf of the ancient Alpine Tethys Ocean (Weissert and Mohr, 1996; Weissert and Stössel, 2015).

4.2 Spatial distribution of sediment-entrapped CH_4 within and between glacier forefields

Sediment-entrapped CH_4 contents showed moderate variability within each glacier forefield (Fig. 3a-e). As sediments were largely derived by glacial erosion from the surrounding calcareous bedrock (Chesworth et al., 2008; Fu and Harbor, 2011), the observed variability in sediment-entrapped CH_4 contents reflects the variability in entrapped CH_4 contents of the various geological formations and associated mineralogy present in each catchment (Fig. 3f). Entrapped CH_4 contents in sedimentary bedrocks is typically affected by three main factors: the quantity and quality of organic matter buried during sediment deposition, the thermal history during sediment diagenesis and subsequent organic matter catagenesis, and the resulting permeability of the calcareous bedrock, which affects potential gas migration (e.g., Dayal, 2017; Horsfield and Rullkötter, 1994; Mani et al., 2017). Whereas geological formations contained within the same nappe are expected to possess a similar thermal history, the quantity and quality of organic matter buried may vary substantially between individual formations depending on prevailing conditions during the period of sediment deposition (Weissert and Mohr, 1996; Weissert et al., 1985). Thus, variability in rock- and sediment-entrapped CH_4 contents is to be expected for glacial catchments featuring geological formations from different time periods, as was observed for all of the glacier forefields sampled in this study (Table 2).

Our study in the GRF forefield sampling zone indicated that sediment-entrapped CH_4 content varied little with sediment depth (Fig. 5) and sediment age. However, we cannot exclude the possibility that such variations could be somewhat larger outside of the sampled depth interval, e.g., in top-layer sediments at depths < 5 cm as a result of enhanced chemical, physical, or biological weathering (Bernasconi et al., 2011; van der Meij et al., 2016; Lazzaro et al., 2009). We refrained from collecting top-layer sediments because in all five glacier forefields they were generally much coarser and thus did not appear representative of bulk sediments present at greater depth. We assume that sediment fines are continuously removed from the top layer as a result of physical (wind and water) erosion.

On the other hand, we consider the lack of significant variation with sediment age as an indication that CH_4 in glacier-forefield sediments is relatively stable in its entrapped state. This hypothesis is supported by results of our geochemical analyses for all five glacier forefields, which mostly indicated high similarity between sediment- and rock-entrapped CH_4 in terms of the range of measured CH_4 contents (Fig. 3f), as well as gas-wetness ratios and $\delta^{13}C_{CH4}$ values (Fig. 4). Thus, although sediments have ~~likely~~ undergone ~~great alteration during and after~~ erosion from the parent bedrock and subsequent weathering, changes in entrapped CH_4 geochemical characteristics appeared negligible. This indicates that a potential release of entrapped CH_4 from sediment particles by molecular diffusion, or oxidation of CH_4 in its entrapped state within sediment particles, ~~should~~ may be ~~of minor importance~~small in magnitude, as these processes would be expected to cause a noticeable change in CH_4 geochemical characteristics (Schloemer and Krooss, 2004; Whiticar, 1999; Zhang and Krooss, 2001). Our findings therefore suggest that CH_4 entrapped in bedrock and sediment matrices resides largely in inaccessible, occluded rather than connected pore spaces. However, a potential release of entrapped CH_4 from occluded pore spaces may yet occur via sediment erosion processes, in particular by means of physical and/or chemical weathering of calcareous minerals (Emmanuel and Levenson, 2014; Ryb et al., 2014; Trudgill and Viles, 1998). As these processes act on rock surfaces, they are of great important to sediments with large specific surface areas, the latter being inversely related to particle size (Michel and Courard, 2014). Although we are aware that similar erosion processes will act upon large bedrock surfaces, e.g., rock walls and other outcrops within glacial catchments, we have so far refrained from considering CH_4 release from these locations because of the much smaller specific surface areas involved. Unfortunately, the release of entrapped CH_4 as a result of sediment erosion may not be detectable in the sediment's entrapped CH_4 contents, as both CH_4 and sediment mass is lost as a result of erosion. Hence, our present data set yields no information on the relevance of erosion processes for CH_4 release.

In contrast to sediment depth and sediment age, we detected a small but significant difference in mean sediment-entrapped CH_4 content between landforms within the GRF sampling zone. Specifically, mean entrapped CH_4 content in floodplain sediments was significantly higher than in terrace and sandhill sediments (Table 1). We can only speculate about possible reasons for this observation. One reason could be that floodplain sediments, intermittently removed and deposited by the glacial stream during and after flooding events, originate from locations ~~far~~ outside of our sampling zone, i.e., from different parent bedrock ~~, where sampling of the parent bedrock, e.g., from steep rock walls, was not feasible~~ (Fig. S2). It is therefore possible that we missed to sample parent bedrock types (e.g., from steep rock walls) with different (in this case higher) entrapped CH_4 contents in this or any of the other glacial catchments. An improved mineralogical investigation of sediments in the various landforms would aid in clarifying this issue.

Finally, our data revealed large regional differences in mean sediment-entrapped CH_4 contents between glacier forefields (Table 2). This may be explained by the fact that sediments in glacier forefields located in close proximity to one another are, at least in part, derived from the same individual nappes and geological formations contained therein. For example, both the WIL and TSA glacier forefields harbor sediments derived from the Wildhorn nappe, featuring several identical geological formations. Hence, this result supports our previous hypothesis that differences in lithology, mineralogy, and tectonic settings between individual nappes play an important role in determining bedrock- and thus sediment-entrapped CH_4

contents (Zhu et al., 2018). Regional differences in entrapped CH_4 contents paired with differences in sediment-covered area led to significant variation in the estimates for total mass of CH_4 stored in sediments of the five glacier forefields (Fig. 7a). Uncertainties associated with these estimates were reasonably small, and arose largely from uncertainties in sediment thickness and sediment-covered area (Fig. 7b). To further reduce these uncertainties, measurements of these parameters across entire glacier forefields would be of help using, e.g., geophysical methods for sediment thickness (such as the ERT method used in the GRF sampling zone), and field mapping of sediment-covered area in combination with GIS based methods utilizing digital elevation models (e.g., Geilhausen et al., 2012; Smith and Clark, 2005; Zemp et al., 2005). Unfortunately, field measurements in the rugged alpine environment are typically time-consuming, expensive, and challenging to perform.

4.3 A substantial quantity of sediment-entrapped CH_4 with yet unknown fate

Our first, rough estimate for the total quantity of CH_4 entrapped in sediments of all calcareous Swiss glacier forefields combined yielded a substantial mass of $1.04\times10^5 \pm 3.7\times10^4$ t CH_4, contained within a solid volume of ~2.1 km^3 glacier-forefield sediments. At first glance, this number appears large when compared with an estimate~~s~~ of ~~annual CH_4 release from lake sediments into the lower, anoxic water column of a Swiss lake (1.7×10^3 t CH_4; Schubert et al. (2010)), and~~ annual CH_4 emissions to the atmosphere (5.7×10^3 t CH_4) from ~~all~~ natural and semi-natural sources in Switzerland, including emissions from lakes, reservoirs, wetlands, and wild animals (Hiller et al., 2014). However, whereas the latter data represent annual CH_4 fluxes, the fate of sediment-entrapped CH_4 remains elusive to date (see below). On the other hand, our number is in good agreement with a previous estimate on CH_4 content for Valanginian marl, a geological formation within the Helvetic Nappes, containing calcite fracture fill (~0.7×10^5–2.1×10^5 t CH_4 km^{-3} bedrock; Gautschi et al. (1990)).

Our estimate for total sediment-entrapped CH_4 mass is subject to substantial uncertainty. The two largest contributors to the calculated uncertainty are sediment-entrapped CH_4 content and sediment ~~depth~~thickness. In addition, there is considerable uncertainty in the exposed calcareous glacier-forefield area, as the latter was only roughly estimated based on glacier retreat and the fraction of calcareous bedrock area in the Swiss Alps. As discussed above for individual glacier forefields, field measurements and GIS based methods may help to reduce uncertainties related to sediment ~~depth~~thickness and exposed area. An important way to reduce uncertainty related to entrapped CH_4 contents would be to generate a database of CH_4 contents for different geological formations present within the Helvetic Nappes, as lithology and tectonic settings appear to control CH_4 contents. Determination of the areal extent of different geological formations would likely help to reduce uncertainties in sediment-entrapped CH_4 mass.

Whether or not sediment-entrapped CH_4 plays a role as an emission source to the atmosphere will largely depend upon its rate of release from sediment particles and its potential consumption by MOBs in aerated sediments. Whereas we produced some evidence that CH_4 is stable in its entrapped state (see discussion above), further investigations will be required to specifically elucidate possible mechanisms and fluxes of CH_4 release in forefield sediments, in particular during periods of enhanced physical/chemical weathering, e.g., during rainstorms or snow melt (Winnick et al., 2017). ~~On the other hand~~Notably, atmospheric CH_4 oxidation was previously detected in several glacier forefields including our GRF site (Bárcena et al., 2011;

Chiri et al., 2015; Hofmann et al., 2013). These studies indicated that MOB activity in forefield sediments establishes quickly (within the first 10 years after glacier retreat), and fluxes of CH_4 uptake from the atmosphere increase to values comparable to mature soils within a few decades (Chiri et al., 2015). Nonetheless, intermittent CH_4 emissions to the atmosphere were also observed in GRF floodplain sediments (Chiri et al., 2017). Hence, we hypothesize that traces of CH_4 released from sediment particles may be consumed by MOB, at least under favorable environmental conditions, and serve as an additional source of energy and carbon to this group of microorganisms. This hypothesis, of course, awaits experimental confirmation.

5 Summary and Conclusions

Our results provide new evidence for the widespread occurrence of sediment-entrapped, thermogenic CH_4 in Swiss calcareous glacier forefields. As entrapped CH_4 with highly similar geochemical characteristics was also detected in most bedrock samples collected from nearby geological formations, we conclude that CH_4 entrapped in forefield sediments of the Helvetic Nappes has its origin in the calcareous parent bedrock. Hence, spatial variability in sediment-entrapped CH_4 contents within glacier forefields largely reflects the variability in entrapped CH_4 contents of the surrounding bedrock types.

Within glacier forefields, sediment-entrapped CH_4 contents and other geochemical characteristics showed little systematic variation with sediment age and thus time of exposure to the atmosphere following glacier retreat. Together with the noted similarity in geochemical characteristics we took this finding as evidence that CH_4 in glacier-forefield sediments is relatively stable in its entrapped state, presumably because it resides in occluded pore spaces within bedrock and sediment matrices. This further indicates that CH_4 entrapment within the Helvetic Nappes is not restricted to fluid inclusions in fissure minerals, but that substantial quantities of CH_4 are entrapped within the matrix of the sedimentary bedrock and sediment particles themselves. On the other hand, our results revealed large regional differences in mean sediment-entrapped CH_4 contents between glacier forefields, supporting our previous hypothesis that differences in lithology and tectonic settings between individual nappes play an important role in determining bedrock- and thus sediment-entrapped CH_4 contents.

~~Our first estimate for the total quantity of CH_4 entrapped in sediments of all calcareous Swiss glacier forefields suggests the presence of a substantial CH_4 mass. Whereas we have provided evidence for its stability in its entrapped state, we cannot exclude the possibility that sediment-entrapped CH_4 is being emitted into the sediments' pore space as a result of physical or chemical weathering. Whether this would lead to emissions into the atmosphere will largely depend upon the rate of release from sediment particles and its potential consumption by MOBs in aerated sediments. Experiments are needed and currently ongoing in our laboratory to quantify these two processes under variable environmental conditions.~~

Data availability. The data used in this manuscript will be made available on ETH Zurich Research Collection after the manuscript is published.

Supplement. The supplement related to this article is available online at: …..

Author contribution. BZ, MR, MK, and MHS helped with sample collection and/or geochemical measurements, and substantially contributed to the interpretation of data. DB helped with ERT measurements and subsequent ERT data analyses. BZ and MHS wrote the manuscript. MHS designed the study and acquired the funding for the project. All authors commented on the manuscript and approved the final version of the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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Figures

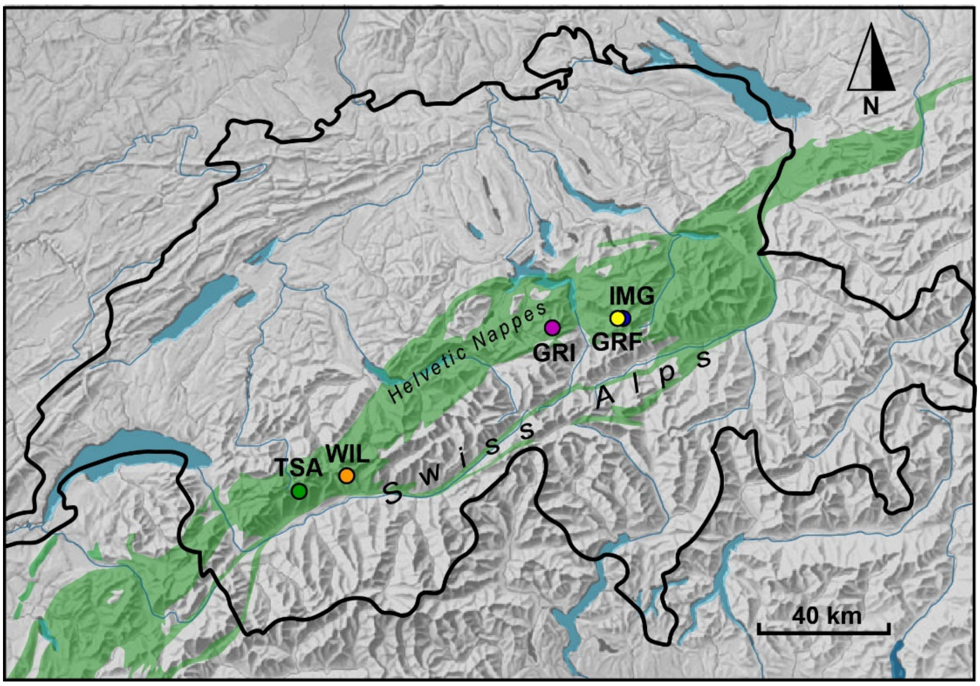

Figure 1. Map of Switzerland showing five glacier forefields from which sediment and bedrock samples were collected (Central Switzerland: Im Griess, IMG; Griessfirn, GRF; Griessen, GRI; Canton Valais: Wildstrubel, WIL; Tsanfleuron, TSA). All forefields are located within the Helvetic Nappes (green-shaded area), which consist largely of Mesozoic limestones, shales, and marls (map modified from Weissert and Stössel (2015)).

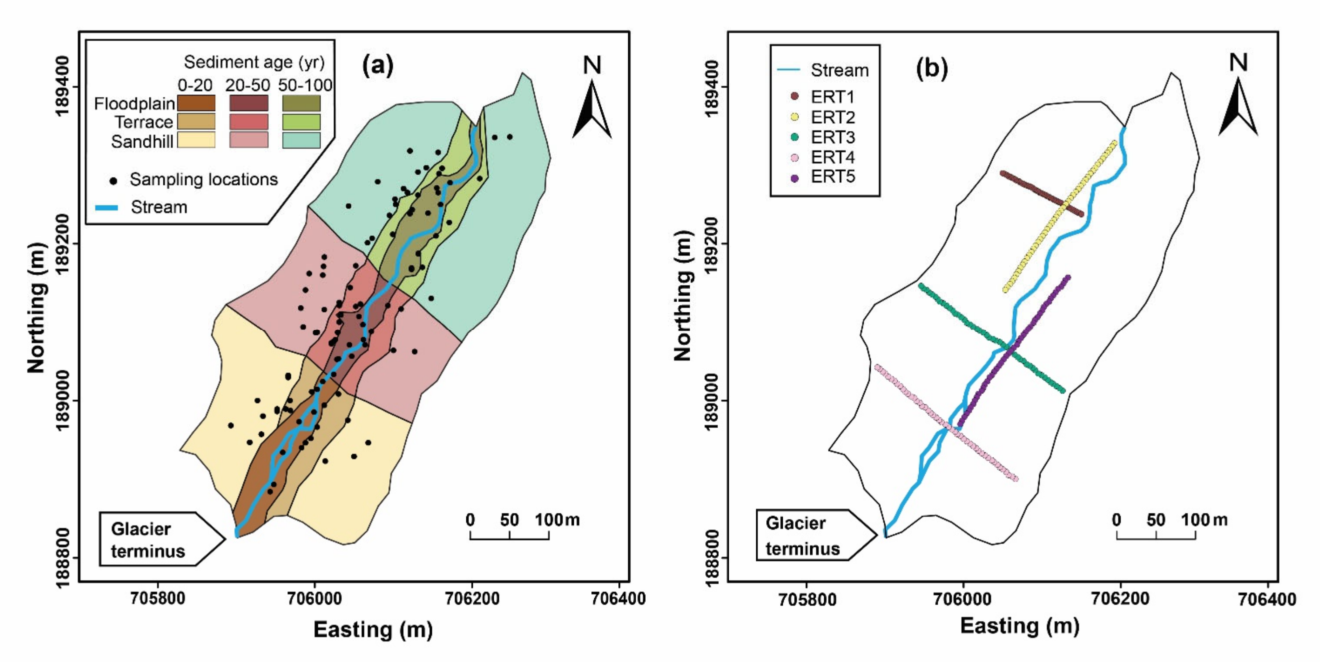

Figure 2. Sampling zone at Griessfirn (GRF) glacier forefield showing (a) blocks and sampling locations to study the effect of sediment age and glacier-forefield landforms (used here as proxies for all edaphic variations present in these sediments) on entrapped CH_4 contents, and (b) locations of five electrical resistivity tomography (ERT) profiles to measure sediment thickness. Axes show the Swiss CH1903/LV03 coordinate system (units in meters).

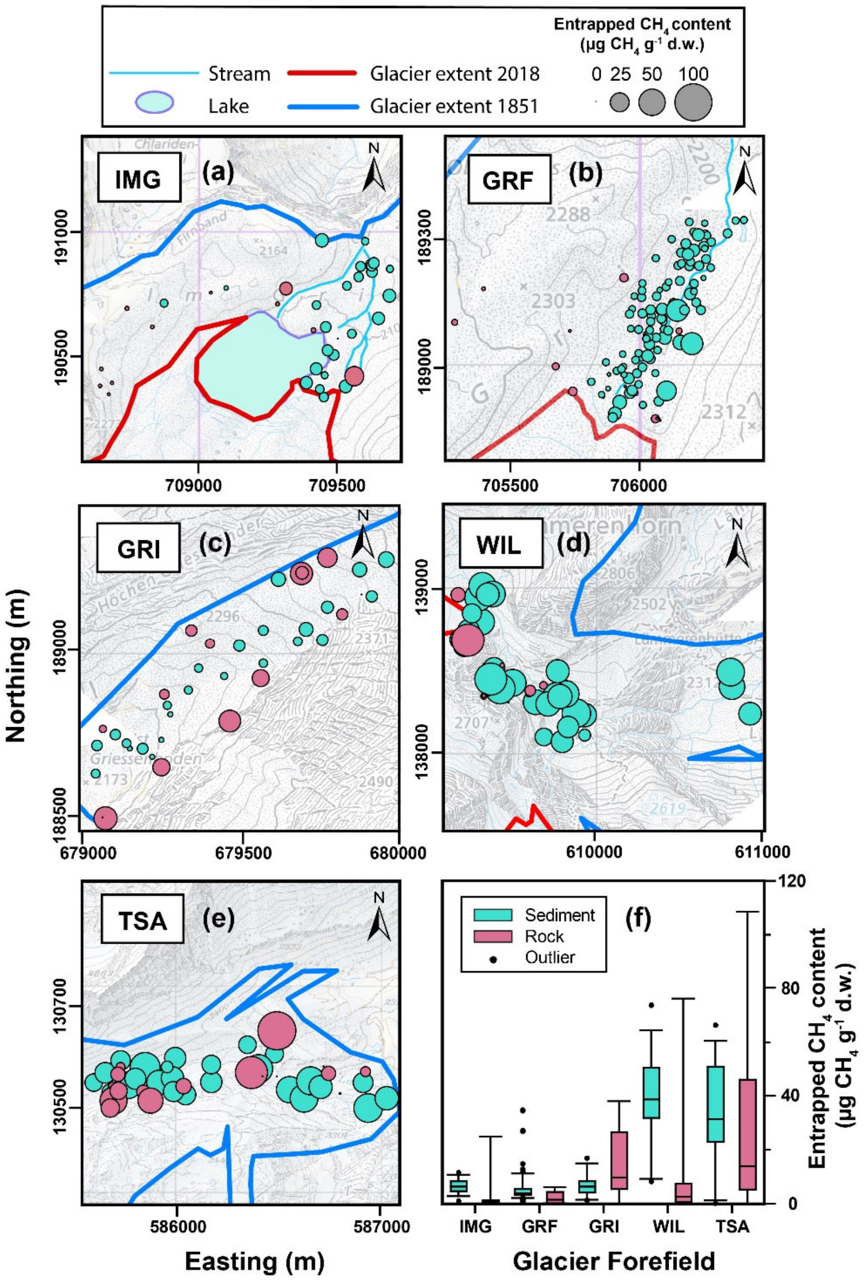

Figure 3. Spatial distribution of entrapped CH4 contents in sediments (blue bubbles) and rocks (red bubbles) collected from (a) Im Griess (IMG), (b) Griessfirn (GRF), (c) Griessen (GRI), (d) Wildstrubel (WIL), and (e) Tsanfleuron (TSA) glacier forefields (bubble size proportional to entrapped CH4 content). Background elevation data modified from swisstopo (Swiss Federal Office of Topography; maps.geo.admin.ch); axes show the Swiss CH1903/LV03 coordinate system (units in meters). (f) Box-whisker plot showing the range of entrapped CH4 contents in sediments and rocks for each glacier forefield. Boxes represent 25th, 50th (median), and 75th percentile; whiskers indicate 5th and 95th percentile, outliers are marked as dots.

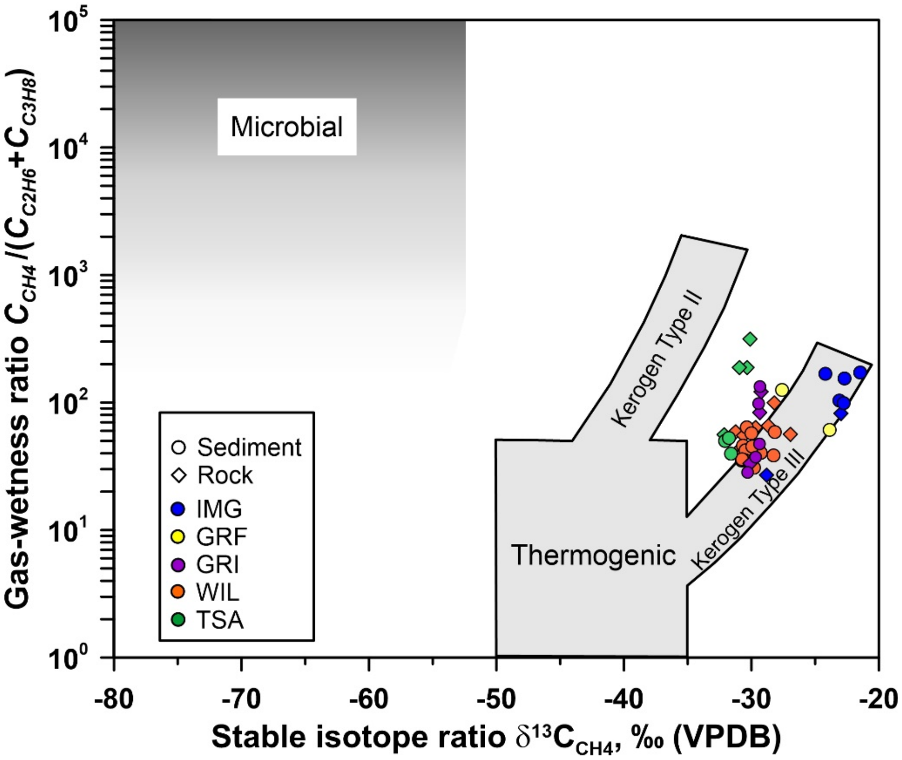

Figure 4. Adapted Bernard diagram (Bernard et al., 1978) showing gas-wetness ratio (C_{CH4} / (C_{C2H6} + C_{C3H8})) versus $\delta^{13}C_{CH4}$ for gas released from selected sediment and rock samples collected from Im Griess (IMG), Griessfirn (GRF), Griessen (GRI), Wildstrubel (WIL), and 745 Tsanfleuron (TSA) glacier forefields. Grey-shaded areas indicate different CH_4 origins (microbial vs. thermogenic).

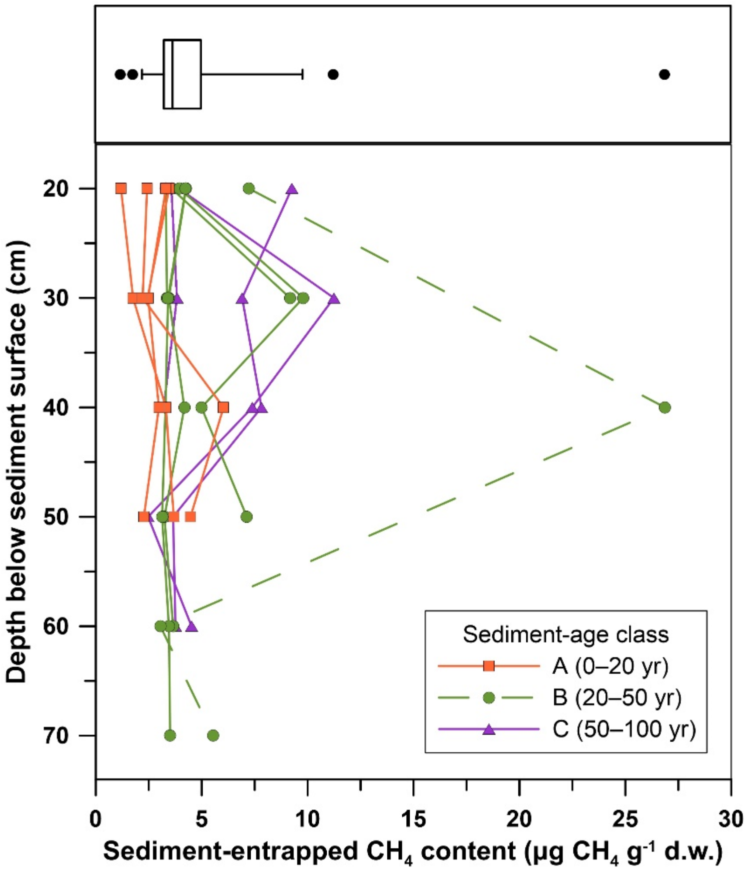

Figure 5. Sediment-entrapped CH$_4$ contents as a function of sediment depth for samples collected in three sediment-age classes in the Griessfirn (GRF) sampling zone. The box-whisker plot on top shows the range of entrapped CH$_4$ contents displayed below, with the box representing 25th, 50th (median), and 75th percentile; whiskers indicate the 5th and 95th percentile, outliers are marked as dots. 750

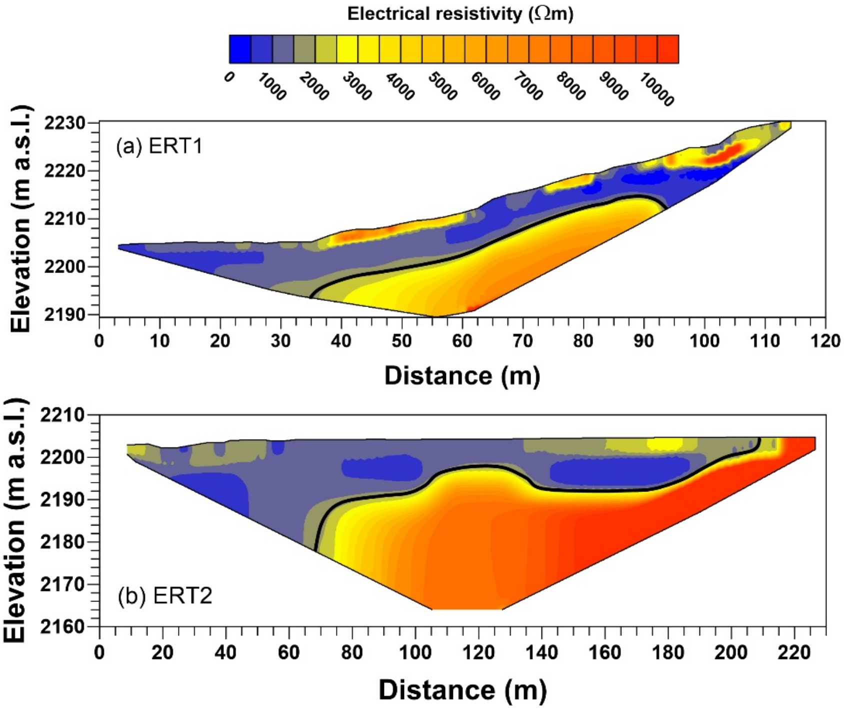

Figure 6. Vertical, two-dimensional electrical-resistivity-tomography (ERT) cross sections of profiles (a) ERT1 and (b) ERT2 collected in 755 the sampling zone of Griessfirn (GRF) glacier forefield. Solid black lines indicate the approximate location of the interface between unconsolidated sediment and the bedrock underneath. Lines were omitted at locations where the sediment-rock interface was too deep to be detected.

760

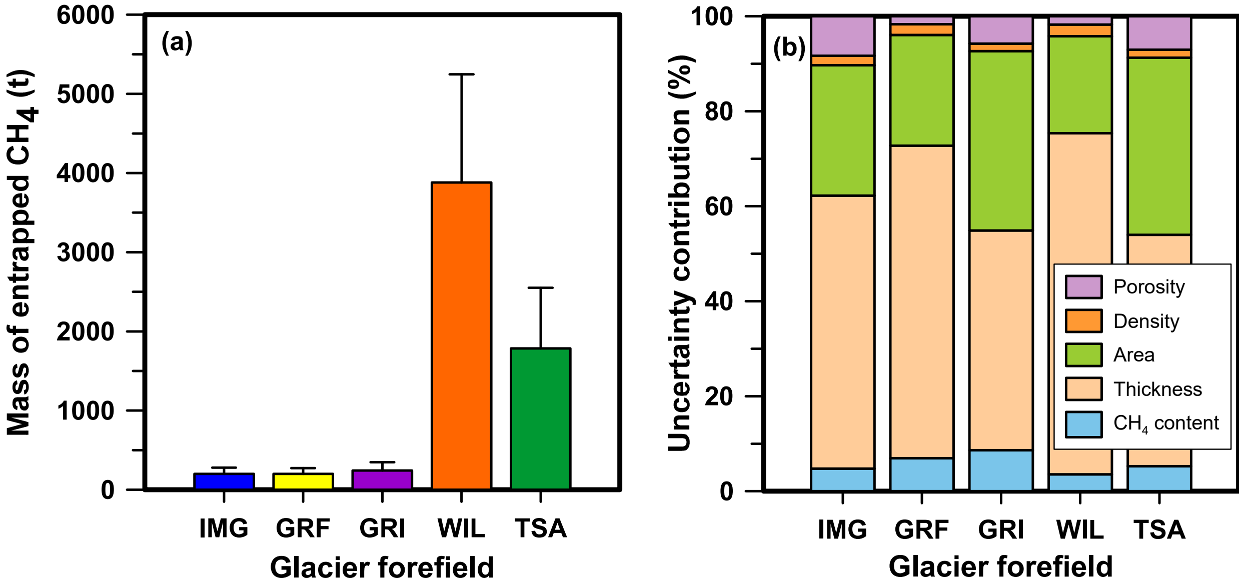

Figure 7. a) Estimated mass of CH_4 entrapped in sediments of Im Griess (IMG), Griessfirn (GRF), Griessen (GRI), Wildstrubel (WIL), and Tsanfleuron (TSA) glacier forefields. b) Contribution of sediment-entrapped CH_4 contents, sediment thickness and area, sediment-particle 765 density, and total porosity to total uncertainties in the estimation of the mass of sediment-entrapped CH_4 (error bars in a)) for each of the five glacier forefields.

Tables

Table 1. Mean values and uncertainties for sediment-entrapped CH_4 content, sediment thickness, sediment-covered area, sediment mass, and estimated mass of entrapped CH_4 in three different landforms of the Griessfirn (GRF) glacier-forefield sampling zone.

Landform	Entrapped CH_4 content (µg CH_4 g^{-1} d.w.)	Sediment thickness (m)	Sediment-covered area (m^2)	Sediment mass (t sed.)	Entrapped CH_4 mass (t CH_4)
	$\bar{C}_{CH4} \pm \sigma_{\bar{C}_{CH4}}$ [a]	$\bar{T}_{sed} \pm \sigma_{\bar{T}_{sed}}$	$\bar{A}_{sed} \pm \sigma_{\bar{A}_{sed}}$	$\bar{m}_{sed} \pm \sigma_{\bar{m}_{sed}}$	$\bar{m}_{CH4} \pm \sigma_{\bar{m}_{CH4}}$
Floodplain	6.37 ± 0.55	11.8 ± 3.0	$2.07\times10^4 \pm 2.0\times10^2$	$3.84\times10^5 \pm 1.0\times10^5$	2.4 ± 0.7
Terrace	4.72 ± 0.97	12.5 ± 4.0	$2.06\times10^4 \pm 2.0\times10^2$	$4.04\times10^5 \pm 1.3\times10^5$	1.9 ± 0.7
Sandhill	5.04 ± 0.78	6.4 ± 3.2	$1.05\times10^5 \pm 1.0\times10^3$	$1.06\times10^6 \pm 5.4\times10^5$	5.4 ± 2.8
Combined	5.3~~0~~8 ± 0.49	10.~~0~~2 ± 3.0	$1.47\times10^5 \pm 1.4\times10^3$	2.3~~1~~6×10^6 ± 7.~~9~~1×10^5	9.7 ± 3.0[b] 12.~~3~~7 ± ~~3~~4.~~9~~0[c]

[a] standard error of the mean (SE).

[b] calculated by adding up estimated mass of entrapped CH_4 from each landform.

[c] calculated using average values for entrapped CH_4 contents, sediment thickness, and sediment-covered area.

Table 2. Mean values and uncertainties of sediment-entrapped CH_4 content, sediment-covered area, and total inter-particle sediment ~~total~~ porosity for Im Griess (IMG), Griessfirn (GRF), Griessen (GRI), Wildstrubel (WIL), and Tsanfleuron (TSA) glacier forefields located within the Helvetic Nappes of Switzerland. Also listed are individual nappes and major geological formations, from which glacier-forefield sediments are derived.

Glacier forefield	Entrapped CH_4 content (µg CH_4 g^{-1} d.w.)	Sediment-covered area (km^2)	Sediment porosity[a] (-)	Sediment origin[b]	
	$\bar{C}_{CH4} \pm \sigma_{\bar{C}_{CH4}}$ [c]	$\bar{A}_{sed} \pm \sigma_{\bar{A}_{sed}}$	$\bar{\theta}_{t,sed} \pm \sigma_{\bar{\theta}_{t,sed}}$	Nappes	Geological formations[d]
IMG	6.51 ± 0.56	2.03 ± 0.42	0.44 ± 0.05	Kammlistock	Quinten, Schrattenkalk, Stad, Zementstein
GRF	5.59 ± 0.54	2.27 ± 0.40	0.42 ± 0.02	Kammlistock Griessstock	Betlis, Helvetic Siliceous Limestone, Öhrli, Quinten, Zementstein
GRI	7.03 ± 0.91	2.04 ± 0.55	0.38 ± 0.04	Axen	Bommerstein, Hochstollen, Quinten
WIL	39.41 ± 2.62	6.35 ± 1.01	0.43 ± 0.02	Wildhorn Doldenhorn	Garschella, Öhrli, Quinten, Schilt, Schrattenkalk, Seewen, Tierwis
TSA	33.74 ± 3.31	3.48 ± 0.91	0.44 ± 0.05	Wildhorn Diablerets	Betlis, Helvetic Siliceous Limestone, Öhrli,Schrattenkalk, Tierwis, Tsanfleuron Member, Pierredar

[a] adopted from Nauer et al. (2012).

[b] information obtained from the Geological Atlas of Switzerland 1:25.000 (online at maps.geo.admin.ch), Swiss Federal Office of Topography (swisstopo).

[c] standard error of the mean (SE).

[d] in alphabetical order.

Table 3. Data used for upscaling the mass of sediment-entrapped CH_4 from five sampled glacier forefields (Im Griess (IMG), Griessfirn (GRF), Griessen (GRI), Wildstrubel (WIL), and Tsanfleuron (TSA)) to all calcareous glacier-forefields in Switzerland.

Parameter	Value	Data source
Total Alpine area in Switzerland	$2.29\times10^4 \pm 504$ km^2	Tectonic Map of Switzerland 1:500.000 (swisstopo)
Area of calcareous bedrock	$1.25\times10^4 \pm 275$ km^2	Tectonic Map of Switzerland 1:500.000 (swisstopo)
Total glaciated area in 1850	$1.62\times10^3 \pm 36$ km^2	Zemp et al. (2008)
Total glaciated area in 2010	$9.44\times10^2 \pm 21$ km^2	Fischer et al. (2014)
Mean entrapped CH_4 content, $\overline{C}_{CH4}$	18.5 ± 4.4 µg CH_4 g^{-1} d.w.	Mean of averages for five glacier forefields
Mean sediment thickness, $\overline{T}_{sed}$	10.0 ± 3.0 m	Measurements in GRF glacier forefield
Mean sediment-particle density, $\overline{\rho}_{sed}$	2.71 ± 0.15 g cm^{-3}	Daly (1935)
Mean ~~total~~inter-particle sed.~~iment~~ porosity, $\overline{\theta}_{t,sed}$	0.44 ± 0.05	Derived from data of Nauer et al. (2012)
Mass of sediment-entrapped CH_4, $\overline{m}_{CH4}$	$1.04\times10^5 \pm 3.7\times10^4$ t CH_4	Eq. (1), this manuscript