

We would like to thank both reviewers and the editor for taking the time to review this manuscript, and for their evident engagement with the content. Their commentary has been very helpful in improving the manuscript. We have addressed their concerns either by amending the text or by, hopefully, pushing back constructively to others. A point-by-point response to each of the comment, with updated line numbers, is given below.

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#### Reviewer 1 comments:

“.....a big concern remains over the experimental design that did not consider realistic conditions of subglacial environments. More thorough descriptions and discussion of the methodological rationales and limitations would be required to tear down the big huddle for the publication of this well-written manuscript.

#### Major comments

- Experimental design: The information provided in section 2.4 made me wonder if the experimental design was adequate enough to simulate glacial environments in terms of temperature, moisture, pressure, etc. It looks like only manual shaking was employed to mix samples with water. Creating similar conditions, at least for some key conditions, would be a prerequisite for this type of simulation experiment. Please provide a more thorough description of the approach and methodological details, along with an in-depth discussion of the necessity and limitations of the employed approach.

The focus of this study was to investigate the potential for **abrasion** of sedimentary, pyrite containing rocks to impact the available nutrients within subglacial ecosystems. These are early days in the study of the release from crushed rock of trace gases via thermo-mechanically free radical reactions and volatiles in fluid inclusions into water. We are beyond the proof-of-concept stage, but we note that two key features of subglacial erosion processes are already present in the incubation studies. First, the rock has been crushed, which fractures mineral grains and promotes the surface free radical reactions, and water is in contact with the crushed rock. Rock is crushed under glaciers, and water is often present, albeit if only temporarily as the ice flows over bedrock irregularities and pressure melting occurs on the stoss side of higher standing bedrock and freezing occurs on the lee side. So-called regelation is a common process at glacier beds, even beneath those glaciers where geothermal heat fluxes are not sufficient to melt the bed slightly.

We acknowledge that these experiments are not perfect replicates of subglacial environments, but they still provide valuable data which illustrate the **potential** contribution of abrasion in these environments. As such, we have taken care throughout the text to make sure we refer to the “potential role” of abrasion and caution readers not to “over-extrapolate” these results.

To make these limitations more explicit we have added the following to section: “The experimental design for this study is consistent with previous subglacial abrasion studies. These experiments are not perfect analogues of subglacial environments, being conducted at slightly warmer temperature and lower pressure than real systems, but they illustrate the potential contribution of subglacial abrasion and wetting of crushed sediments to the chemical weathering and provision of chemicals that occur in biogeochemical reactions in these environments. We elaborate on these issues in

the discussion” (L110). This was further expanded on in the discussion, by adding the following two paragraphs (L460 –):

“A final consideration is how representative these experiments are of the production of crushed debris beneath glaciers and the potential for their reactivity during subsequent wetting. The mechanical crushing of rock in the laboratory is not analogous of subglacial comminution in many ways. First, the temperature is lower and the pressure is higher in the subglacial environment as a whole. The overall lower temperature may not be so much of an issue, since this is only a few degrees at most, but the temperatures that are reached during subglacial comminution, where rock fragments in ice may be dragged across the bed for example, are unknown, but may be locally high at rock-rock contact points. Likewise, the temperatures reached in laboratory crushing at rock-rock interaction points can be locally high, and potentially much higher than in a subglacial environment where ice may thermally buffer against higher temperatures. These higher temperatures may increase the reaction rates of surface free radicals, increasing rates of H• and H<sub>2</sub> (Kita et al., 1982) and H<sub>2</sub>O<sub>2</sub> (Stone et al., 2022) generation. The higher pressures of subglacial environments may not be of such great importance to the generation of free radicals, but they may influence the reaction pathways and products. Higher pressures favour interactions between gases which reduce the number of moles of gases in the system (e.g. 2CO + O<sub>2</sub> ----> 2CO<sub>2</sub>, three moles of gas have been converted into two moles of gas).

Laboratory and in situ crushing beneath glaciers share at least one common element, that minerals are sheared, and so must have broken bonds on the surface. Comminution, and the deformation of pre-existing sediments, occurs often in the vicinity of meltwater beneath temperate-based and polythermal-based glaciers. Additionally, sediment entrainment onto cold based glaciers may involve regelation waters or waters under the glacier freezing onto the base, trapping sediment as a consequence. Regelation is a common process at glacier beds, when pressure melting occurs as ice flows over protuberances or bumps in the bed. The ice melts at the high pressure side of the bump, facing up flow, and meltwater travels around the bump and refreezes on the lower pressure down flow side. Hence, overall, there is a reasonable probability that comminuted rock, otherwise called glacial flour, will come into contact with meltwater. However, the timescale in which this happens cannot be known with certainty, given current understanding of glacial erosion. Timescales may range from almost instantaneously in some areas of the bed, particularly if regelation and comminution occur at the same place and at the same time, but equally there may be much longer delays. This begs the question of how much water, and indeed whether even water vapour, is needed to initiate the surface free radical catalysed reactions. Further, how comminuted minerals interact with ice during their entombment in debris-rich basal ice, for example, has yet to be examined. The simplicity of these experiments shows the potential of the comminution to supply chemicals for biogeochemical reactions in subglacial environments, but just how the experiments may map onto the production and wetting of subglacial sediment in real environments is more difficult to assess, because pertinent subglacial parameters, some of which have been discussed here, are poorly known and quantified.”

- Sediments sources: Rock samples from three glaciated and previously glaciated sites were compared in this experiment. The Jurassic Shale sample from the previously glaciated site may have been exposed to a quite different environment than the other glaciated environments. Please provide a more convincing rationale for the comparison. Otherwise, it would be more appropriate to present only the results of the samples from the glaciated sites.

We wanted to investigate the effect of abrasion on pyrite containing rocks, and since pyrite is known to produce considerable  $H_2O_2$  concentrations when crushed and wetted (Borda et al., 2001; Borda et al., 2003; Gil-Lozano et al., 2017; Gil-Lozano et al., 2014; Schoonen et al., 2010)), we wanted to examine the effect this abrasion would have on samples containing various amounts of organic matter, since some could be oxidised by the  $H_2O_2$ . We chose the Jurassic shale since it is known to have a high pyrite concentration, and since it had a mid-range organic matter content, it made a suitable positive control for these experiments. We have made this clearer by re-wording **L125-126** to read "...experiments as it is known to be relatively high in pyrite and has an organic matter content that is mid-range of the sample types chosen".

- Biotic vs. abiotic mechanisms: As alluded in Discussion (Lines 378-384 and section 4.4.), it appears that sample pre-treatments such as drying did not preclude biological processes affecting the abiotic abrasion. It should be explicitly stated whether the experiment was designed to allow for biological effects. Then, an ensuing question would be how to disentangle biological effects from the abrasion effects that constitute the overwhelming story throughout the manuscript.

Samples were dried at 75°C (pasteurisation temperature) to kill a significant proportion of any potential microbes present. This pasteurisation was done twice, once prior to breaking the rocks and again after breaking rocks into their "coarse" state. The washing and drying steps after breaking rocks into the coarse fraction were unintentionally excluded from the initial submitted manuscript, an oversight amended by including the following "The coarse samples were then washed with 18.2 MΩ cm<sup>-1</sup> water, transferred to a foil tray and covered with a loosely fitted foil cover, and dried at 75 °C overnight, or until there was no change in mass." (**L159-161**) This will have not completely eliminated all microbes in the sample, but it is unlikely that we see a microbial population establishing and producing chemical impacts within a 25 hour incubation. Furthermore, the compounds which are more likely to result from biological processes (such as acetate, formate and ammonium) did not show a temporal trend – and are unlikely to be produced instantly by microbes after the addition of water.

#### Minor comments

- L 154: Please specify the approximate size range of the crushed samples.  
We have added this information in the updated manuscript to read: "After crushing, the size of rock and sediment samples ranged from 6 to 806 μm (measured using a Malvern Mastersizer 3000 laser particle size analyser (Malvern Panalytical, Worcestershire, UK))" (**L161-164**)
- L 234-239: Are the relationships to examine some causality or just correlations? If the latter is the case, correlation coefficient (r), not r<sup>2</sup>, would work. Otherwise, the relationships need to be described to indicate causality. Another question is about how to evaluate the strength of relationships. I would suggest that r or r<sup>2</sup> values be presented with P values.  
R<sup>2</sup> indicates the association of one variable with another, which does not necessarily imply causation. In this case, we are using it to indicate the fit of a linear regression line, as is standard practice. We have added p values to the figures for all R<sup>2</sup> values (these were all p<0.05 or p<0.01).
- L 248: This non-parametric test and its necessity, together with other tests, can be better explained in an ending section of Methods.

The following section has been added to the Methods section (L225-):  
**“2.9 Statistical Analysis**

Simple regression lines were fitted to infer potential correlations between the concentration of H<sub>2</sub>O<sub>2</sub> produced by crushed and coarse samples and sulphate, iron or specific surface area using Sigma-Plot. An R<sup>2</sup>-value of 0.7 or above was considered to indicate a strong correlation between two variables (Moore et al., 2013). A Kruskal-Wallis test was conducted followed by a post-hoc Wilcoxon test using RStudio to determine significant differences in the concentrations of NH<sub>4</sub><sup>+</sup>, acetate, formate and pH, between crushed and coarse samples. The data for these compounds and pH did not show a temporal trend, thus the values were pooled into one population and the Kruskal-Wallis test determined the distribution of the data was non-parametric. Due to this, and the low number of samples, a Wilcoxon test was then used to determine statistical differences in the concentrations of these compounds and pH in crushed and coarse samples.”

- L 313: Do you mean there are no sulfate minerals found in glacial environments?  
There are many sulfate rocks around.  
The descriptions of the rock outcrops at these particular sites (taken from McMechan, 1998; Elvevold et al., 2007) include pyrite bearing rocks, but no sulphate minerals or evaporitic rocks were described.
- L 341: Again, provide the criterion for the ‘strong’ relationship.  
Typically, an R value of 0.7 or above is considered to be a strong correlation (Moore et al., 2013), this has been made explicit in the additional suggested section 2.9 (see above).
- L 358-361: It is worthwhile to discuss in more detail the effects of temperature differences and more importantly wide ranges of temperature variations found in real glacial environments.  
To date, there are no publications which address this issue. We feel that the temperature of the incubations (4°C) is sufficiently close to that of wet subglacial environments at the ice pressure melting point (typically -2 to 0 °C) to avoid undue speculation of temperature impacts at the moment. We have made this explicit in the final two paragraphs of the discussion (see above).
- L 377- (Section 4.3): What is the main mechanism under this specific setting? Please sum up your thoughts, not just list up potential sources.  
Even the simple rocks we use in this study suggest that there are multiple sources of gases. Therefore, we offer all the potential factors influencing gas generation. We clarify that the gases detected are likely sourced from the combination of all of these mechanisms by adding the following sentence to this section: “The gases measured during crushing and, in the case of RMC, during the 25 h incubation, are likely a result of a combination of these mechanisms.” (L422-423)
- L 425-: As mentioned in a major comment, it is crucial to disentangle biological effects from the abrasion effects. If you want to assess the potential for nitrification, you need to compare your results with the previous studies that were conducted under similar conditions. Dried samples must be totally different from those under natural conditions.  
We mentioned above that if NH<sub>4</sub><sup>+</sup> was due to nitrification, we would expect the concentration of NH<sub>4</sub><sup>+</sup> to increase over time – not appear instantly after the reaction of crushed sample with water.
- Figure captions lack some crucial information. For instance, in Fig. 1, what samples is this experiment about? (sedimentary rocks). What about so many site (sample) labels? Captions need to be sufficient enough to allow the figures and tables to

stand alone.

The captions have been clarified as requested.

- 1: Is there any reason for showing original triplicate measurements? I wondered if presenting means and error bars would help readers identify differences among the treatments.

We cannot assume a normal distribution of the data (which is what a mean and error bars would imply) since  $n = 3$  for each time point. Therefore, we felt that displaying all data points would show the data distribution most accurately. Data will be displayed by mean and error bars if the editor and reviewers think this would make the figure easier to follow.

- Editorial suggestion: A thorough proofreading would clear out many typos such as unchecked subscripts in H<sub>2</sub>O<sub>2</sub> throughout the manuscript.

These (cut and paste) typos have been addressed in the updated manuscript.

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#### Simon Bottrell comments:

This study uses simplified model lab experiments to assess the potential of comminution of materials by glacial abrasion as a source of hydrogen peroxide and nutrients to the subglacial environment. This is presented in the context of “standard” models for subglacial solute acquisition. The manuscript is well organized and written and the processes and logic are clear and easy to follow. This is work that will be significant to those interested in subglacial weathering and biogeochemistry as it opens up the potential of some novel possibilities. In this respect this seems to me to be a valuable “reconnaissance” study that should inspire future work on these possibilities.

#### Major comments:

LL 234-239 – the r-values presented don’t carry much weight without associated P-values! We have added p values to the figures for all R<sup>2</sup> values (these were all  $p < 0.05$  or  $p < 0.01$ ).

L330 et seq. This discussion about the fate of radicals is a kind of “post-hoc” discussion. It relies quite heavily on the mineralogical composition of the materials tested but I don’t see that data clearly presented – was there petrographic and/or XRD characterization? Or does this rely on previous studies? (and NB: these may have been made with very different objectives in mind). To my mind this needs to be clarified and reported much more explicitly here (indeed, future work might require experiments on single minerals/model mixtures to unambiguously identify mechanisms but this present work has great value in identifying that these interesting new possibilities exist in “real” materials).

The mineralogical composition of these samples was not characterized via XRD, identification was conducted using established physical properties of minerals that were visible with the naked-eye or with a hand-lens (x10 magnification) and further informed by descriptions of the rock outcrops in the respective catchments. We used the data provided by the elemental analyser to quantify the inorganic and organic carbon fractions in the sample as well as the S content. This, together with the mapped geologic data provide a reasonable estimate for the pyrite content of these rocks.

#### Minor comments:

L60 . . . of which is . . . (NOT . . . of which, are . . .) (knowledge is singular)  
This has been corrected in the updated manuscript.

L157 – I'm not sure that the word "furnace" can be used as a verb in this way. This has been changed in the updated manuscript to "then maintained at 450 °C for 4 hours in a muffle furnace." (L167-168)

L304. Lab air contamination is mentioned – at what stage in the process was this entrained in the sample and what background/blank analyses were made??

These experiments were conducted under lab air, procedural blanks (consisting of serum vials which underwent the same treatment and sampling as those containing rock and sediment samples) were taken at each stage of the incubation. Gas samples were also taken from the headspace of the ball mill prior to crushing and interpreted as blanks. These data can be added to the data repository if the reviewers and editor think it will be useful.

LL354-5 – Previous crushing experiments . . . S L Whillans . . . provide appropriate reference to the source of these data here.

The data source has been added.

LL378-380. This is the one place where the otherwise excellent organization of the text breaks down. There is a hierarchy of links here that is presented in an ambiguous and confusing way. Apparently the hydrological system of SLM is fed by the Whillans ice stream, and glaciers on Svalbard!! Need to make it clear that:

1. methanogens have been found in (geographically) diverse subglacial environments (Robertson, Svalbard, SLW);
2. SLW and SLM share a similar hydrological regime.

Simply putting the Svalbard example first in the current structure would help.

This has been re-arranged to make it clearer, it now reads :

"Methanogens have been found in many subglacial systems, including glaciers on Svalbard (Stibal et al., 2012; Kaštovská et al., 2007), Robertson Glacier (Boyd et al., 2010), SLW (Michaud et al., 2017), which is within the same broad hydrological system as SLM (Carter et al., 2013)." (L401-403)

We hope the amendments suggested and replies to these comments will satisfy the concerns highlighted.

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