

Bg-2019-41

Summary of earlier responses to reviewers and former Associate Editor

Detailed replies to the reviewers' comments were posted during the interactive discussion period and submitted to the Associate Editor Suzanne Anderson in September 2019. We did not receive any direct feedback but the Associate Editor suggested more minor alterations in November 2019. These were made and we received an email from the editorial office on November 16, 2019 that the manuscript was accepted for final publication in *Biogeosciences*. Evidently there was a problem with this decision in that one of the original reviewers was not involved in evaluation of the revised manuscript despite being willing to do so. All of the revisions have been available on the *Biogeosciences* web site since 17 November but for your convenience we have combined all of our responses into one file (below). As well as the comments in this file we include an annotated version of the manuscript showing the changes made, and a clean version of the final revised manuscript.

Summary of changes made in response to the initial comments of the three reviewers.

The major criticism of the manuscript was that, while it was a good *review*, it did not function as a *synthesis*. We have attempted to rectify this by being clearer about our own conclusions and by providing a clearer distinction between 1) work that was performed before 2009, 2) work that has been carried out in the following 10 years and 3) experiments that still need to be performed (where there are still knowledge gaps).

We agree that the final, concluding section was too short and we have now instead added a summary section *at the end of each of the first six sections highlighting remaining recent advances and remaining knowledge gaps*. We hope that the overall aim of the review is now clearer. *Almost all of the recommendations we received from the referees have been acted upon*. A number of additional references suggested by **Reviewer 1** have been added. There is some additional text on lichens and saprotrophic fungi.

Reviewer 2 considered the proportion of older references was too high so we have removed about 25 of the older references and replaced them with more modern work. Several of the submitted manuscripts we referred to are now published.

We have followed the recommendation of **Reviewer 2** and removed five of the original 11 figures and there are now six. Some of the missing references suggested by **Reviewer 3** have been added but most of the older ones were not – bearing in mind the criticism of **Reviewer 2**. The manuscript is still quite long, but this is necessary since it covers a broad range of fields from cell biology to ecosystem sciences. We hope that the re-ordering of the figures will make the manuscript (in particular Section 5) easier to follow. Five sections deal with different spatial scales. The sixth and seventh sections deal with stable isotope experiments and modelling respectively – two areas where further advances can be made in understanding.

In the conclusion we mention the important conclusions of Severdrup et al (2009) about the likely importance of referred to by **Reviewer 1** under his point 5.

We hope the manuscript is significantly improved now and that it will soon be acceptable for publication in *Biogeosciences*.

Roger Finlay.

Reply to Reviewer 1

Biological weathering and its consequences at different spatial levels – from nanoscale to global scale

Reviewer 1 makes a number of helpful comments that will no doubt greatly improve our manuscript if we are permitted to submit a revised version.

The ms is intended as a review of current progress made in understanding biological processes contributing to weathering. It is based on a very extensive reading in the literature (I counted 215 references) on a very wide range of topics, including chemistry, physics and biology, combining empirical and modelling approaches, based on a large range of experimental techniques. The authors also make a very laudable attempt to scale up, both spatially (as indicated by the title) and temporally, when they link past and current weathering processes as an evolutionary and ecological force. The ms is also very well written.

We are pleased the reviewer considers the text well written.

Despite all this initial praise, reading the ms did not fully satisfy me. In my view this is to a large extent due to the fact that it succeeds very well as a review, but succeeds to a lesser extent as a synthesis. Several empirical observations seem to contradict other observations, and one would like to read how much consensus has been reached on the biology of weathering. In that respect I found the final section (key questions and knowledge gaps) somewhat disappointingly short.

We agree fully that the final section is too short and intend to expand it. (see below).

Considering the lack of consensus on the importance or generality of several processes, a more cynical reader may easily be inclined to think that almost anything goes in biological weathering. In fact this kind of mild cynicism is almost encouraged by the authors: after having presented so many data the authors (p. 17, l. 33 – p. 18, l. 1; note that one of the authors of the paper referred to is also an author of this ms) state that "Smits & Wallander (2017) consider that there is *no clear evidence* [emphasis mine] that processes at the laboratory-scale play a significant role in soil-scale mineral dissolution rates". If so, what is the main message of this paper?

We do not agree that the lack of consensus reflects "cynicism". Indeed, one of the aims of this article was to examine differences in the degree of consensus about research conducted at different temporal and spatial scales. (Admittedly this is not very well explained at present, but one of the take-home messages was meant to be that there is greater consensus on the large-scale, systemic effects of microorganisms on weathering than on the overall significance of micro-/nano-scale observations). Science proceeds by first identifying conflicting opinions and then, often at a later stage, resolving conflicts by collecting additional data – often in newly designed experiments or by using new techniques. It would be surprising if the eleven authors of this article had exactly the same opinion about every single process discussed, but we do agree that we should have worked much harder to try to resolve conflicting results to provide the "synthesis" the reviewer wants. At any one point in time it is often not possible to resolve conflicts of information completely but, in that case we agree that it is important to identify new approaches or key questions to ask in new experiments and to provide clear guidance about the approaches required. We will re-write the text to improve this aspect and expand the final section – as suggested above.

Let me try to back up my dissatisfaction with a couple of general observations. Before providing more detailed comments.

1. The point of departure for the study is that weathering is the only or main supplier of base cations and phosphorus to compensate for losses through harvesting and leaching. However, on p. 17, l. 21 the reader is informed about atmospheric deposition (the only mention of this input source) where we are informed that a study found that atmospheric deposition was four times as important as weathering; and that the weathering flux was less than 0.3% of calcium uptake. This statement then raises questions about its quantitative importance over ecological time scales and evolutionary time scales, an issue treated very implicitly at best.

We agree that alternative sources of different nutrients and base cations should be discussed and that there may be significant input under some circumstances from atmospheric deposition – examples of significant P input from atmospheric deposition to coastal Fynbos systems (eg. Brown et al. 1984) and the Florida everglades (Redfield, 2002) have been shown. These possible alternatives are now included in our discussion. However, this does not call into question the validity of all weathering studies and the clear stable isotope results from our own mesocosm experiment suggest that in boreal forest soils mobilization of Mg is probably not primarily from litter re-cycling in surface soil as shown by Dijkstra and Smits (2002) for Ca.

2. Despite the generality of the title (biological weathering), the focus is almost exclusively on the role of mycorrhizal fungi plus associated mycorrhizosphere bacteria and the trees with which they associate (I like the focus on the plant as holobiont). Lichens, generally considering as major weathering agents in the first stages of primary succession, are mentioned only once (p. 12, l. 10-12). There the authors state that "the ubiquity and significance of lichens (...) as a model for understanding weathering (...) are well understood." However, the reader is not informed about this understanding, nor is (s)he informed whether fungal weathering is similar or dissimilar from lichen weathering in any significant respect. There is also very limited attention for fungi other than mycorrhizal fungi, however from an evolutionary perspective this is a missed opportunity. A fungus often used in weathering studies is *Paxillus involutus*, a species derived from a clade of brown- rotting fungi characterized by oxalate production. It could be possible that the ability to produce and excrete oxalate in the environment evolved for different purposes and was even maintained in the ectomycorrhizal groups in this clade for different purposes.

*Apart from ectomycorrhizal fungi in forests we do also mention 1. proteoid roots of in highly weathered soils, 2. calcicole plants in calcareous soils, 3. non-mycorrhizal fungi such as different *Aspergillus* species and 4. different bacterial species. However, we agree that a slightly better description of the potential role of bacteria, lichens and non-mycorrhizal fungi as weathering agents should be included and will include more information in the revised version of the manuscript. This will include evolutionary aspects (discussed by Fahad et al., 2016) and also the desired information about *Paxillus involutus* – recently discussed by Nicholás et al 2019. (ISME J. 13: 977-988).*

3. There are many parts in the ms where the possible difference in weathering ability between arbuscular mycorrhizal fungi+plants and ectomycorrhizal fungi+plants are mentioned. Some of these are quite explicit in suggesting

that the ectomycorrhizal symbiosis allows higher weathering rates than the arbuscular mycorrhizal symbiosis. However, we also learn that weathering evolved in the arbuscular mycorrhizal symbiosis (p. 11, l. 26) and that some studies did not find differences in weathering rates under ectomycorrhizal and arbuscular mycorrhizal vegetation (p. 21, l. 26-27). The reader of his paper will therefore remain in doubt what the current consensus view is (if there is consensus), what likely hypotheses exist to explain such different data and what kinds of research approaches exist to resolve that issue. (One option would be a common-garden experiment with sister clades of plants with the different mycorrhizal symbioses, in analogy of the approach by Koele et al. (New Phyt. 196: 845-852. 2012) when they tested for stoichiometric differences (leaf N:P ratio) between both guilds. I am sure there must be other ways to make progress as well.) Another group of mycorrhizal fungi + plants, which form the ericoid mycorrhizal symbiosis, is mentioned once (p. 7, l. 21) even though they have been suggested to be strong weathering agents as they can produce copious amounts of low-molecular-weight organic acids (Martino et al., Soil Biol. Biochem. 35: 133-141. 2003).

We agree that some of these ideas are not currently included and will mention them in the revised manuscript. One of the arguments about possible differences between arbuscular mycorrhizal and ectomycorrhizal fungi concerns evolutionary differences of the C-fixation properties of their plant hosts (work of KJ Field and D Cameron) and these ideas will be discussed in the revised manuscript.

4. Addressing (and putatively answering) the question of the role of different mycorrhizal symbioses in weathering is, in my view, particularly relevant when it comes to understanding mechanisms. If weathering is driven by the production of LMWOA and siderophores, then it should be clear that the ectomycorrhizal symbiosis is much more important for weathering than the arbuscular mycorrhizal symbiosis (as AMF have not been reported to produce LMWOA, the AMF symbiosis has been reported to downregulate LMWOA production by plants (Ryan et al., Plant Cell Environ. 35: 2170-2180. 2012), and AMF do not produce siderophores as far as I know). If other mechanisms are more important (e.g., acidification driven by excess uptake of cations over anions and proton exudation to maintain charge balance; or dissolved CO₂ as a consequence of respiratory activity), the contribution by both guilds could be more important – with differences still related to the amount of extraradical hyphal biomass and / or respiratory activity.

This is an interesting subject area and there are probably questions that cannot be fully resolved with currently available information but we will add some comments. Generalisations should always be made with care but one aspect that could be relevant is differences in decomposition rates. Since ectomycorrhizal (and ericoid) fungi typically dominate systems characterized by recalcitrant organic substrates and slow decomposition rates, whereas AM fungi dominate systems with higher decomposition rates in which the input from turnover of nutrients from organic residues may be higher. Possible future approaches include common-garden experiments, as mentioned above, as well as the use of mutant plants with altered regulation of proton-pumping and some of these ideas will now mentioned in the revised manuscript.

5. The issue about the relative importance of weathering mechanisms has been debated since mycorrhizal researchers entered that field in the early 2000s.

When enthusiastic claims were made for a major role of mycorrhizal fungi (and I admit having been such an enthusiast as well), these ideas were criticised by Sverdrup, who essentially claimed that weathering was driven by CO₂ flux and that the contribution by ectomycorrhizal fungi was around 2%. While his claim has been challenged (Van Schoi et al., Plant Soil 303: 35-47. 2008), I think this review would have been a good place to synthesise current understanding. Sverdrup (cited in the ms – pls note that the journal has Volume 23, Issue 4; not Volume 4) has maintained his suggestion about the major importance of respiration / CO₂ production, rather than the production of organic acids) as the driver for weathering, stating: “the growth of trees represents quantitatively largest single biological process that can affect weathering, followed closely by decomposition of organic matter.” It is evident that the authors of this ms disagree with Sverdrup, however, without fully discussing this alternative view. I think this is a missed opportunity. The same applies to the origin of pores, with Sverdrup claiming that they are of abiotic origin (as cited in p. 3, l. 30). How would the authors of this ms evaluate our current knowledge and understanding? (Note that because of the extent of tunnelling the contribution to weathering might be limited, irrespective of the question on their origin.)

We have discussed the fact that tunnelling may be both biotic and abiotic and that there are ways of distinguishing the two types of tunnels. ALL tunnelling is not abiotic. However, we also discuss the important studies of Smits et al. (2005) that showed that tunnelling is not quantitatively significant as the sole indicator of weathering. In fragmented mineral substrates weathering of surfaces may take place without formation of tunnels. We do fully understand that the growth of trees affects weathering of minerals and have explained that removal of weathering products from these sites (by hyphae) is an important process. We explain in the concluding section that the conclusion of Sverdrup et al. that “the growth of trees represents quantitatively largest single biological process that can affect weathering, followed closely by decomposition of organic matter” is entirely consistent with modern theories of ectomycorrhizal functioning.

6. While I agree about the importance of upscaling, both spatially and temporally, I think that progress depends on the extent to which we can quantify rates. Unfortunately, the paper is quite frugal in giving numbers. This may give the impression that despite such many studies there has been little progress in quantifying processes. That conclusion seems also implied in p. 1, l. 31-32 (“opinion appears to be divided with respect to the quantitative significance [of interactions between microbes and minerals]”). If opinions are divided, please give equal hearing to arguments from both sides. But if a clearer picture has emerged in the view of the authors, please provide more quantitative detail. In order to have feedback mechanisms to work over both ecological and evolutionary times, we need such data.

We agree that more quantitative estimates (rates) are necessary and will attempt to cite more quantitative estimates in the revised manuscript.

7. The authors refer (p. 2, l. 28) to twelve testable hypotheses on the geobiology of weathering. It would help the reader to list those (rather than to invite them to look up the paper themselves) and to indicate to what extent their review helps addressing these hypotheses. For instance

hypothesis 8 (elevated CO₂ will enhance weathering) seems to assume that weathering fluxes and its ultimate consequences of drawdown of CO₂ occur at very different time scales, which could put constraints on feedback mechanisms postulated in the ms. With respect to hypothesis 2, the importance of stoichiometry, I think that the studies done of mycorrhizal weathering provide much of the needed data. In none of their hypotheses they draw attention to different kinds of mycorrhizal symbiosis (but this could be a refinement of hypothesis 1), although it may not be coincidental that their figure 1 depicts an ectomycorrhizal conifer...

A full discussion of all 12 hypotheses discussed by Brantley et al is not possible within this article is not possible for reasons of space but some of the ideas cited in that article are now discussed in more detail in as much as they relate to biological weathering.

Some of these comments will make the manuscript longer, so I think it may help if I indicate cases were shortening of the ms is possible. I noted several digressions (also in the Abstract) that result in a less focused paper. Examples are: reference to acquisition of N and P by mechanisms other than weathering (p. 7, l. 18-34), hydraulic lift / redistribution (p. 9, l. 6-8), oxygenic and anoxygenic photosynthesis (p. 11, 14- 24), autotrophic and heterotrophic respiration in forests (p. 13, l. 30 – p. 14, l. 6; unless the authors think that Sverdrup is, essentially, right...), differential carbon storage in ectomycorrhizal and arbuscular mycorrhizal forests (p. 14, l. 4-28; note that of the two biomes where both guilds occur larger C storage per unit N was shown for the temperate biome, not for the (sub-)tropical biome – so we should not take Averill's claim too seriously), nitrogen in the rhizosphere (p. 24, l. 1-2).

We will make some of the suggested cuts to reduce the overall length of the article.

Page-by-page comments

p. 3, l. 9

Is the Finlay & Clemmensen paper on biogenic weathering? The title of the paper would suggest otherwise

The paper is on carbon flow in relation to both decomposition and weathering.

p. 5, l. 14 Please provide a reference for the suggestion about the importance of horizontal gene transfer in such microbial consortia in EPS.

Reference is now provided.

p. 7, l. 1

Here I disagree. In such habitats, in case of a low pH, plants with cluster roots (or proteoid roots; I think they are the same) or dauciform roots produce carboxylates that *desorb* phosphorus from mineral surfaces. But desorption is not weathering, dissolution of minerals. Weathering would happen in the case of high-pH with calcium phosphates; in low-pH soils P is far too scarce to form substantial amounts of Fe- and Al-phosphates that are weathered.

We agree with the reviewer and have re-written the text more carefully

p. 9, l. 14

In the light of current criticisms of humic and fulvic acids as large molecules (Lehmann & Kleber claim these to be aggregates of essentially small molecules)

this statement may need reconsideration in terms of underlying mechanisms.
Agreed – we have altered the text to reflect this

p. 15, l. 21

When introducing the Blum et al. hypothesis, they should also refer to contradictory data by Dijkstra and Smits (now only referred to on p. 17, l. 18-22; however I interpret that paper as showing that Blum et al.'s conclusion is grossly overstated – but I would love to see the opinion of the authors of this ms).

Agreed – we have altered the text to reflect this. We originally discussed the Blum paper in more detail but removed the text because of this overstatement.

p. 17, l. 19

Please provide a reference to that further study.

The reference is now added – the comparable forest referred to is actually mentioned in the same study by Dijkstra & Smits.

p. 19, l. 17

Note that exudation of carboxylates / organic anions can also have a major function in the desorption of iron-oxide bound soil organic matter and the subsequent acquisition of carbon (Keiluweit et al., *Nature Clim. Change* 5: 588-595. 2015) and nitrogen (Jilling et al., *Biogeochemistry* 139: 103-122. 2018) (and possibly phosphorus, as both inorganic and organic P are sorbed on such surfaces).

Agreed – we have altered the text to reflect this

Thomas W. Kuyper

Reply to Reviewer 2

Interactive comment on “Biological weathering and its consequences at different spatial levels – from nanoscale to global scale” by Roger D. Finlay et al.

Anonymous Referee #2

Received and published: 26 March 2019

In General:

The authors of the paper propose a review of current (last 10 years) of advancement made in the understanding of biological weathering, specifically focusing on the boreal forest, in response to an interdisciplinary project called “Quantifying weathering rates for sustainable forestry.” This topic fits well the scope of BG and it is needed to help us move forward in this area of research.

Good that the topic fits and that an article like this is needed.

The manuscript cites more than 200 references that span a wide range of topics from physical, chemical and biological approaches, and scales from nano-scale empirical studies to global scale modeling, and emphasizing an evolutionary viewpoint on biological weathering. However, I was disappointed seeing that about 1/3rd of the references are prior to 2009 and

have been widely cited and reviewed in the past, thus these do not give “anything new” especially in some sections of the manuscript (see details below) and it also contradicts with the authors aim of summarizing the last 10 years of advancement.

We understand this reasoning but inclusion of some older references is necessary to provide perspective and to explain the development of different types of experiments. We will try to reduce the proportion of older references by cutting some of the older ones.

The manuscript is a well-written review/summary of more than the last 10 years of biological weathering research with a heavy emphasis on mycorrhizae mediated weathering (which is the ecosystem in the boreal forest). However, there is no synthesis of the reviewed literature, there is no agreement stated on what is the current understanding, or state of this biological weathering in the boreal forest, and how it applies to sustainable forestry or simply how to move forward. The manuscript is a review, but it lacks a synthesis.

We agree that the aims of the article are not clearly stated and that the final take home message is not made clearly enough. We will try to provide the desired synthesis more clearly by re-structuring of the manuscript.

Regardless of great writing, it was not an easy read, because I could not find/follow the purpose of this manuscript, it presents a lot of data on both side of the arguments that contradict each other, which is fine, however, there are no directions, there is a lot of rambling on without focus – what is the underlying message? What do the authors want to achieve with this review? Key questions and knowledge gaps section is underdeveloped and it seems like it was an afterthought and stuck to the end.

We are pleased that the reviewer considers the writing was good but agree the take-home message was not stated clearly enough. In the revision we will address this problem and try to provide more focus. We agree that the last section is too superficial and under-developed. It was included too close to the initial deadline and will be expanded to provide clearer guidance about key knowledge gaps and necessary approaches to resolving conflicting opinions in future experiments. (Separate summary sections have now been added at the end of each section)

In addition, I think that the title is misleading, as the review is really about weathering in the boreal forest. Most cited work was done by researchers related to the boreal or other forests (field), in the laboratory using mostly conifers and mycorrhizal fungi, and there are couple of “side topics” that seems to be out of place in this bigger scheme (for example, the hydraulic lift study for drought-prone ecosystems).

*We agree that the main emphasis is on boreal forests, although the section on evolutionary aspects includes a discussion of processes that took place before the evolution of terrestrial plants. Other components of different ecosystems are also mentioned in this section including 1. proteoid roots of in highly weathered soils, 2. calcicole plants in calcareous soils, 3. non-mycorrhizal fungi such as different *Aspergillus* species and 4. different bacterial species. If the handling editor considers it appropriate we can add a secondary part to the title such as “- with particular emphasis on boreal forests.” Extra information has been added about lichens and saprotrophic fungi*

Some specifics:

Abstract and 1. Introduction – no specific comments.

2. Microscale/nanoscale observations of physical alteration of minerals: This section is

heavily based on older findings and mention some new studies, but it is unclear what advances were made in the last 10 years – new techniques? New understanding of processes? Or just supporting previous findings? Or all above? It needs a refocus, and it can be shortened by about half and still convey the same message.

We agree, in part, with this assessment and will try to emphasize more recent studies involving the application of new techniques, and to explain more clearly what advances have been made – where appropriate. This section is only about 880 words (6.8 % of the article) and not excessively long but we will attempt to reduce the length.

3. Biofilms and small-scale microbial interactions with consequences at higher spatial scale: how are these differently categorized than the next section, which is about microbial and plant secretions? EPS, biofilm, oxalic acids etc. are secretions, are not? What are the consequences at higher spatial scale? Do we know? Or is it a challenge to scale things up? Again, what is the new advancement in the last 10 years? The section needs some clarifications and/or refocus.

The interactions in this section take place at a smaller spatial scale than those discussed in the subsequent section where plants or microorganisms are cultured in micro- or mesocosms. Admittedly there is some overlap between these sections since these small-scale processes also take place in single plant-scale interactions studied in microcosms, but we will re-write to improve clarity and focus.

4. Microbial and plant secretions – evidence from microcosms and mesocosms: long section – rambling on without focus, lots of info and data about various roles, functions, and processes of mycorrhizal fungi, but no other components of the ecosystem, and the hydraulic lift section seems irrelevant in the boreal forest. Bringing in drought may be something we want to think about as climate shifts, but it most likely causing larger problems in drought-prone parts of the world.

*We disagree about other components not being mentioned in this section. Other components of (different) ecosystems **ARE** mentioned in this section including 1. proteoid roots of plants growing in highly weathered soils, 2. calcicole plants growing in calcareous soils, 3. non-mycorrhizal fungi such as different *Aspergillus* species and 4. different bacterial species. We will try to add some more comments about other non-mycorrhizal fungi and lichens. We will also try to reduce the rambling and improve focus. We can remove the reference to hydraulic lift if necessary.*

5. Systemic consequences of microorganism-mineral interactions in an ecological and evolutionary context: this is really important and interesting, however, it is too long, have some repetition – I am not sure why the 5.1. section is separated (elevated) from the rest of 5. – Weathering, nutrient acquisition, carbon allocation, and sequestration are the key elements of the evolutionary viewpoint – perhaps, this section could be rearranged and shortened to synthesize our current understanding of the evolution of plants and associated fungi in the context of carbon and nutrient cycling. Bob Berner did the pioneering work in this field with his carbon models, but it got a lot of attention in the last 10 years, so a focused synthesis would help us to identify future directions.

We agree that this section can be made more concise and can be re-arranged. We want to retain the evolutionary focus to underline the fundamental nature of the interactions between microorganisms and minerals but we can provide more of a focused synthesis about future directions of research and outstanding questions.

6. Methods using stable isotopes: The section is interesting, provide laboratory evidence of the usefulness of these techniques in addition to field studies, however, the last paragraph states that the “there is no clear evidence that processes observed at the laboratory-scale play a significant role in “soil-scale” mineral dissolution rates.” This indicates that laboratory studies are useless, why do we bother then? Is there anything we learned from the laboratory studies? Also, the last paragraph is a repetition of statements on page 12 lines 13-15.

We have agreed to remove this statement from the last paragraph. We will also re-write this section to avoid any repetition.

7. Modelling of weathering in forest soils: this whole section is unfocused. It starts with the PROFILE and ForSAFE models, then it talks about information needs and possible improvements (in 7.1.) and then it returns to talk about a bunch of other models in too much detail without getting to a point. This section should synthesize what are the main outcomes of the different modeling approaches (probably in half of the length), and identify what is missing (information) and how to tackle the shortcomings.

We agree with these comments and will re-write this section according to the recommendations. It will be re-organized and shorted substantially.

8. Conclusions: I was expecting to find the key questions, knowledge gaps and future directions (or call for specific areas of research) in this section.

We agree that this section could be usefully combined with Section 9 (which is much too short). We will expand the key conclusions and have a clear presentation of the major knowledge gaps as well as clear recommendations about how these can be solved. – To identify the key questions and what future approaches/measurements are needed to answer them.

Figures: Not all necessary – Figure 1, 2, 4, 6, 7 do not add new information to the summary (synthesis) or not necessary to understand the text. Figure 9 and 10 are a good representation of specific examples for laboratory approaches. Figure 3, 5, 8, and 11 are great illustrations of processes and their interactions from small to large scales.

We agree with this assessment of the necessity (or not) of the figures. The non-essential ones were provided to make the article more self-contained but can be omitted to make the article shorter. Figures 4 and 6 at least show what mycorrhizas look like and show a pictorial representation of what they do (in terms of C allocation). Potentially the article may be read by many people who have limited knowledge of mycorrhizal structures and these would improve understanding.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2019-41>, 2019.

Reply to Reviewer 3

Interactive comment on “Biological weathering and its consequences at different spatial levels – from nanoscale to global scale” by Roger D. Finlay et al.

Anonymous Referee #3

Received and published: 29 April 2019

General comments:

Finley and coauthors provide here an interesting and timely review on biological weathering across scales. It is well written and meets current questions and gaps of knowledge in this field. The general organization of the manuscript might on the other hand be significantly improved. I do not doubt however that some restructuring will enable this discussion paper to reach a wide audience and the large impact it deserves.

We are grateful for these positive comments and agree that some re-structuring will improve the paper

I would first like to acknowledge the fact that covering such a wide topic is challenging, and I would like to congratulate the authors for their effort to try to bring together various aspects of the study of biological weathering in one single review paper. In that respect, I found the general organization according to spatial scales very attractive in the first place. The resulting sections, however, lack of focus, while the last sections do not seem to follow this original plan (e.g. section 6 on insights from stable isotope methods). As a result, the reader might get easily lost or distracted by some of the digressions.

From the introduction (section 1) we review processes and experimental analyses at successively larger spatial and temporal scales (sections 2,3,4 & 5). Thereafter we discuss new possible methodological approaches using stable isotopes (section 6) and modelling (section 7) before presenting some concluding remarks (section 8) and finally (section 9) outlining some key questions, knowledge gaps and suggested future approaches. We think this structure is logical and will now explain it at the beginning of the revised manuscript so there is less likelihood of readers getting lost. Section 9 will also be expanded.

I think that the richness of ideas and concepts gathered here is a real originality of this review, but the author may want to be careful that the reader keeps track of the point that they are trying to make in a given paragraph. Section 5, which gathers a main section introducing concepts as diverse as “mineral evolution”, the geological carbon cycle or plants as holobionts and another subsection on carbon allocation and sequestration including carbon cycle and geoengineering concepts is for instance a little hard to digest.

We agree that that the review includes ideas from diverse disciplines (and also that this contributes to the originality of the review) but we also accept that these ideas can be introduced in a way that makes them more “digestible” and we have tried to do that in the revised manuscript.

To improve this point, I could first suggest gathering the different processes and links existing between them in a dedicated introductory section to make sure all readers are on the same page before tackling more detailed aspects of each scale. For instance, the relevance of allusions to

long-term sequestration of carbon (e.g. lines 7-9 p. 8 and lines 24-26 p. 6) for the general topic of the paper might be unclear to some readers until they reach section 5.1. Another example is the geological cycle of carbon, the presentation of which is scattered across section 5 and somewhat redundant (e.g. p. 11 and 14). An introductory section could also enable to present the order of magnitude of the different processes and elemental fluxes to be considered here (e.g. typical elemental flux derived from primary mineral weathering vs. typical plant uptake and potential export related to forestry practices vs. typical atmospheric input for a given type of system) which is something missing here. Second, I would recommend organizing sections into subsections to keep the reader oriented. I would also avoid sections including a sort of single small subsection, e.g. 5->5.1->6 or 7->7.1->8.

We agree with these helpful suggestions and will re-write the introduction to describe the structure of the article and introduce the key concepts to be discussed. We will change the section divisions to make them more consistent between chapters and try to avoid single small subsections.

Another general point is that I find that the manuscript is lacking a few but quite important references. I try to provide a couple of them in the specific comments section below, which I hope the authors will find helpful. Aside from those points, I am enthusiastic about this interesting manuscript and I would recommend its publication provided that a couple of modifications and restructuring are done.

We are pleased this reviewer recommends publication, welcome the suggestions concerning re-structuring and will try to follow the helpful advice to make the article clearer.

Specific comments:

-Section 2: Alt and Mata (2000), Benzerara et al. (2007), Furnes et al. (2001) and Torsvik et al. (1998) are additional references on the biotic origin of tubular structures that the authors might find useful to include. l.12 p.4: the effect of turgor pressure on biomineral weathering is also discussed by Li et al. (2016)

Thanks for these helpful suggestions

-Section 3: Maybe the first paragraph might be strengthened by adding a couple of references when presenting common biofilm features to guide the reader, especially if some studies are relating these biofilm properties (e.g. retention of water) to mineral weathering (e.g. fluid-mineral contact time). In the second paragraph, Barker et al. (1998) is probably another classical reference on biofilms and microenvironments that might be added. In the last paragraph dealing with the interplay between bacteria and mineral weathering should be strengthened in my opinion. Some recent references including Mitchell et al. (2013), Montross et al. (2013), Wild et al. (2018) and Wild et al. (2019) are missing here and should be included at this point I think. l.19 p.6: "Burial" is referred to as "incubation" in Uroz et al. (2012). I would recommend sticking to this latter term. l.23 p.6: I am not completely sure of the relevance of the position of the last sentence (l. 23-26). I would move it upward or delete it.

Thanks for these helpful suggestions

-Section 4: l.29 p.6: the statements of the production of acidifying substances (H⁺, organic acids) and ligands that complex with metals in the minerals may need to be supported by quotations. l.30 p.6: "that retard weathering rates" reduce or decrease weathering rates would be more accurate l.7 p.7: "uptake of positively charged nutrients such as NH₄⁺ and K⁺, result in exudation of protons" may benefit from the support of a quotation. **OK**

-Section 5: This section is a little bit dense, I would suggest dividing it into subsections. C3

Agreed – we will use sub-section titles to improve readability.

-Section 6: This section is thematic, not intrinsically associated to a given scale. Also, I am questioning the scientific relevance of specifically distinguishing studies from the QWARTS project from other studies.

Hopefully the re-structuring of the introduction will improve the readability and make it easier to understand our approach. Theoretically stable isotope measurements could be discussed within each scale section but we thought it was easier to group these studies together – especially as we introduced new results from a hitherto unpublished study. The fact that these results are so far un-published is one reason for distinguishing them and the idea behind the special issue was to highlight the recent research done within this interdisciplinary project but we can remove the reference to the project if the Editor thinks this is more appropriate.

-Section 7: Direct in situ measurements using gravimetric approaches by Augusto et al. (2000) or Turpault et al. (2009) or interferometry methods by Wild et al. (2019) are not reported by Akselsson et al. (2019) but might be worth mentioning since they directly meet some of the challenges implicitly pointed out in this manuscript regarding the validation of weathering models and the transposition/upscaling of laboratory mesocosms to field systems. In the second paragraph, I find the description of the influence of the different processes on the dissolution rate a little bit unclear, and I feel that the clarity of this section might be improved. Otherwise, readers who are not familiar with that type of models will be easily lost. I would suggest reorganizing this section and starting by presenting the different parameters controlling the dissolution rate (temperature, pH, chemical affinity, ...) and then, in a second step, describing the influence of plant metabolism on these factors and thus on the dissolution rate. I would also strongly recommend using an equation (e.g. developed from equation 3 in Erlandsson et al. (2016), equation 3 in Godderis et al. (2006) or equation 1 in Palandri and Kharaka (2004)) to visually support this discussion. I would also avoid mentioning the concepts of "weathering brakes" or "transition state theory" if they are not explained. This might be more confusing than useful for readers, depending on their background.

We thank the reviewer for these detailed, helpful suggestions and will do our best to incorporate them in our revised manuscript. We aim to shorten section 7 substantially and to re-structure and simplify it so that it is more directly relevant to the weathering processes described in the rest of the manuscript.

Thank you for these additional references

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Additional changes in response to a request for minor revision received on 20 Oct 2019

Further minor revision was requested on 20 October 2019 and a revised version of the manuscript was submitted on Nov 17 2019. The main purpose of the revision was to reduce the length of Section 5 by 10%.

The earlier main revisions (with changes)

[bg-2019-41_author_response-version1.pdf](#)

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and “clean” manuscript versions

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[bg-2019-41-manuscript-version5.pdf](#)

[bg-2019-41-manuscript-version6.pdf](#)

are all available for download from the file upload page of the *Biogeosciences* web site.

For some reason which is unclear to us the box at the bottom of the page entitled “File History BG Discussions (latest Versions only)” contains a link to a very early version of the manuscript which is NOT the latest version.

The latest version of the manuscript – showing changes is pasted below.

5 Natascha Töpfer
Copernicus Publications
Editorial Support
editorial@copernicus.org

10 Dear Editor

10 Thank you for the comments of the associate editor on our manuscript **bg-2019-41**.

15 We agree that section 5 had become a little long, following incorporation of the material that the referees considered we should mention. We have followed the recommendation of the associate editor and reduced the length of this section by 10%. We have also made a number of other small changes and deletions in other sections of the manuscript and tried to improve the clarity of the text in several places.

The changes are listed below in this document and we have uploaded a clean version of the revised manuscript.

20 We hope that the revised version is more suitable for publication.

With best regards,

25 Roger Finlay.

Biological weathering and its consequences at different spatial levels – from nanoscale to global scale

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Abstract. Plant nutrients can be recycled through microbial decomposition of organic matter but replacement of base cations and phosphorus, lost through harvesting of biomass/biofuels or leaching, requires *de novo* supply of fresh nutrients released through weathering of soil parent material (minerals and rocks). Weathering involves physical and chemical processes that are modified by biological activity of plants, microorganisms and animals. This article reviews recent progress made in 20 understanding biological processes contributing to weathering. A perspective of increasing spatial scale is adopted, examining the consequences of biological activity for weathering from nanoscale interactions, through *in vitro* and *in planta* microcosm and mesocosm studies, to field experiments and finally, ecosystem and global level effects. The topics discussed include: the physical alteration of minerals and mineral surfaces, the composition, amounts, chemical properties and effects of plant and microbial secretions, and the role of carbon flow (including stabilization/sequestration of C in organic and inorganic forms). 25 Although the predominant focus is on the effects of fungi in forest ecosystems, the properties of biofilms, including bacterial interactions, are also discussed. The implications of these biological processes for modelling are discussed and we attempt to identify some key questions and knowledge gaps, as well as experimental approaches and areas of research in which future studies are likely to yield useful results. A particular focus of this article is to improve the representation of the ways in which biological processes complement physical and chemical processes that mobilize mineral elements, making them available for 30 plant uptake. This is necessary to produce better estimates of weathering that are required for sustainable management of forests in a post fossil-fuel economy. While there are abundant examples of nm- and μ m-scale physical interactions between microorganisms and different minerals, opinion appears to be divided with respect to the quantitative significance of these observations to overall weathering. Numerous *in vitro* experiments and microcosm studies involving plants and their associated microorganisms suggest that the allocation of plant-derived carbon, mineral dissolution and plant nutrient status are tightly 35 coupled but there is still disagreement about the extent to which these processes contribute to field-scale observations. Apart

from providing dynamically responsive pathways for the allocation of plant-derived carbon to power dissolution of minerals, mycorrhizal mycelia provide conduits for the long-distance transportation of weathering products back to plants that are also quantitatively significant sinks for released nutrients. These mycelial pathways bridge heterogeneous substrates, reducing the influence of local variation in C:N ratios. The production of polysaccharide matrices by biofilms of interacting bacteria and/or 5 fungi at interfaces with mineral surfaces and roots, influences patterns of production of antibiotics and quorum sensing molecules, with concomitant effects on microbial community structure, and the qualitative and quantitative composition of mineral solubilizing compounds and weathering products. Patterns of carbon allocation and nutrient mobilization from both organic and inorganic substrates have been studied at larger spatial and temporal scales, including both ecosystem and global 10 levels and there is a generally wider degree of acceptance of the 'systemic' effects of microorganisms on patterns of nutrient mobilization. Theories about the evolutionary development of weathering processes have been advanced but there is still a lack of information connecting processes at different spatial scales. Detailed studies of the liquid chemistry of local weathering sites at the μm -scale, together with up-scaling to soil-scale dissolution rates, are advocated, as well as new approaches 15 involving stable isotopes.

1 Introduction

15 Modelling of base cation supply using the PROFILE/FORSAFE modelling platform (Kronnäs et al., 2019) suggests that planned intensification of Swedish forestry, involving increased harvesting of organic residues for biofuel, will not be sustainable in a long-term perspective without compensatory measures such as wood ash recycling (Akselsson et al., 2007; Klaminder et al., 2011; Futter et al., 2012; Moldan et al., 2017). The base cations and phosphorus that are essential for forest 20 growth can be re-cycled from organic residues through microbial decomposition but if they are lost through removal of organic material the only way they can be replaced is by weathering of rocks and minerals, or deposition from the atmosphere. There is a need to improve the available estimates of weathering and to improve our knowledge of the ways in which biological 25 processes may complement physical and chemical processes that mobilize mineral elements, making them available for plant uptake.

The role of fungi in biological weathering in boreal forest soils was reviewed by Höffland et al. in 2004 and by Finlay et 25 al. in 2009. More recent reviews of the more specific roles of mycorrhizal symbiosis in mineral weathering and nutrient mining from soil parent material (Smits and Wallander, 2017), pedogenesis (Leake and Read, 2017) and immobilization of carbon in mycorrhizal mycelial biomass and secretions (Finlay and Clemmensen, 2017) have also been published. Twelve testable 30 hypotheses on the geobiology of weathering were outlined by Brantley et al. (2011). These authors concede that some of the outlined hypotheses have been implicit in scientific research conducted since the late 1800's but argue that there are now new analytical, modelling and field opportunities to test these hypotheses. The aim of the present article is to review recent advances in the understanding of biological weathering, particularly with respect to nutrient and carbon cycling within boreal forests, including findings made within the interdisciplinary project *Quantifying Weathering Rates for Sustainable Forestry*

(QWARTS, 2012-2016). One major motivation for this study was the concern that the modelling tools used to determine the long-term supply of weathering products for sustainable forest growth may have been missing biological processes that allow a forest ecosystem to alter the rate of weathering in response to the biological demand for these weathering products (Klaminder et al., 2011).

Deleted: funded by FORMAS, the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning.

5 Biological weathering involves the weakening and disintegration of rocks and dissolution of minerals, caused by the activity of plants, animals and microorganisms. Biological weathering takes place in conjunction with physical and chemical processes but there is still disagreement about the quantitative contribution of biogenic weathering to overall weathering (see Leake and Read, 2017; Smits and Wallander, 2017). The first of Brantley et al.'s 12 hypotheses is that "*Solar-to-chemical conversion of energy by plants regulates flows of carbon, water, and nutrients through plant-microbe soil networks, thereby controlling the location and extent of biological weathering*". The supply and transport of photosynthetically derived carbon through roots and mycorrhizal hyphae to organic and inorganic substrates is a fundamental biogeochemical process (Jones et al., 2009), influencing both decomposition and mineral weathering, and these two processes influence each other. This flow of carbon and the role of plant-microbe-soil interactions in the rhizosphere have been reviewed in an evolutionary perspective (Lambers et al., 2009) and with respect to their potential applications in sustainable agriculture, nature

10 conservation, the development of bio-energy crops and the mitigation of climate change (Philippot et al., 2013). Since there is disagreement about whether biological processes demonstrated at small spatial scales contribute significantly to field scale processes, but a greater degree of consensus about the importance of systemic effects of biological weathering at larger spatial and temporal scales, we have adopted a spatial perspective. We start by reviewing processes occurring at the nm- and μm -scale before discussing *in vitro* microcosm experiments, mesocosm studies with plants, field experiments and finally

15 studies of effects at the ecosystem and global scale. Biological weathering is also discussed within an evolutionary perspective and some recent experiments using stable isotopes are presented. Each section is followed by a short summary in which we attempt to list the main conclusions and some of the remaining questions and knowledge gaps. Finally, different modelling approaches are discussed in relation to how we can incorporate the biological features discussed earlier and improve the reliability of models.

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25 2 Microscale/nanoscale observations of physical alteration of minerals

The idea that microorganisms may alter rocks and minerals is not new and biogenic etching of microfractures in borosilicate glass and crystalline silicates (olivine) by microfungi (*Penicillium notatum* and *Aspergillus amstelodami*), presumed to be producing both organic acids and siderophores, was demonstrated by Callot et al. in 1987. Early studies by Paris et al. (1995, 1996) demonstrated *in vitro* weathering of phlogopite involving displacement of non-exchangeable interlayer K^+ and alteration

30 of the crystal lattice structure, as well as stimulated accumulation of oxalate under simultaneous K^+ and Mg^{2+} deficiency. The widespread occurrence of tubular pores, 3-10 μm in diameter, has been demonstrated in weatherable minerals in podzol surface soils and shallow granitic rock under European coniferous forests (van Breemen et al., 2000; Jongmans et al., 1997; Landeweert

et al., 2001). Some of these pores were found to be occupied by fungal hyphae and the authors speculated that they could be formed by the weathering action of hyphae (possibly in association with bacteria) releasing organic acids and siderophores. The aetiology of pore formation has been questioned however, with some authors claiming that (all) the observed pores are of abiotic origin (Sverdrup, 2009). Studies of feldspar tunnelling along chronosequences created by post-glacial rebound

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5 (Hoffland et al., 2002) revealed that the tunnels were more frequent in the uppermost 2 cm of the E horizon, that the frequency of tunnelling increased with soil age, and that there was a lag period of up to 2000 years when tunnels were absent or rare, postulated by the authors to coincide with the time taken for the disappearance of the more easily weatherable K and Ca containing biotite and hornblende. Parallel studies along productivity gradients (Hoffland et al., 2003) have also revealed a significant positive correlation between the density of ectomycorrhizal root tips and the density of tunnels in the E horizon.

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10 However similar tunnels in feldspars across a sand dune chronosequence at Lake Michigan have been estimated to contribute less than 0.5% of total mineral weathering (Smits et al., 2005) suggesting either that fungal weathering is negligible, or that tunnel formation reflects only a small proportion of the total weathering effect of the fungi. The total mineral surface area available for mineral weathering in most mineral soils is clearly much larger than the internal surface area of the observed tunnels and small tunnel-like features were observed in mineral surfaces by Smits et al. (2005). Different biomechanical

15 mechanisms used by fungi to penetrate rock have received increasing attention. Ultramicroscopic and spectroscopic observations of fungus-biotite interfaces during weathering of biotite flakes have revealed biomechanical forcing, and altered interlayer spacing associated with depletion of K by an ectomycorrhizal fungus (*Paxillus involutus*) (Bonneville et al., 2009). It appears that physical distortion of the lattice structure takes place before chemical alteration through dissolution and oxidation. Fungal hyphae colonizing fractures and voids in minerals can exert substantial mechanical force and have been

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20 demonstrated to build up turgor pressure in excess of 8 MPa that is sufficient to penetrate Mylar and Kevlar and widen existing cracks in rocks (Howard et al., 1991). Recent studies of biotite colonization by *P. involutus* (Bonneville et al., 2016) have revealed extensive oxidation of Fe(II) up to 2 µm in depth and the increase in Fe(III) implies a volumetric change that is sufficient to strain the crystal lattice and induce the formation of microcracks, which are abundant below the hypha-biotite interface.

25 The observations of Jongmans et al. (1997) stimulated interest in biogenic weathering and led to a large number of subsequent studies. The endolithic biosignatures of rock inhabiting microorganisms can be distinguished from purely abiotic microtunnels (McLoughlin et al., 2010). Biological tubular microcavities can be distinguished by their shapes, distribution, and the absence of intersections which excludes an origin by chemical dissolution of pre-existing heterogeneities such as, radiation damage trails, gas-escape structures, or fluid inclusion trails. Atomic force microscopy and scanning transmission 30 electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX) have been used to demonstrate nanoscale alteration of surface topography and attachment and deposition of organic biolayers by fungal hyphae (Bonneville et al., 2011; McMaster, 2012; Gazzè et al., 2013, 2014; Saccone et al., 2012). More recent studies of lizardite dissolution by fungal cells, using confocal laser scanning microscopy (Li et al., 2016), suggest that biomechanical forces of hyphal growth are indispensable for fungal weathering and strong enough to breach the mineral lattice. The data from these studies suggest that

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bio-mechanical forcing takes place with μm -scale acidification mediated by surface-bound hyphae and subsequent removal of chemical elements due to fungal action. However, so far, the quantitative significance of these effects to total weathering rates is still unclear. Comparative studies of forests with either ectomycorrhizal or arbuscular mycorrhizal host tree species (Koelle et al., 2014) have revealed the presence of tunnel like structures in minerals in both types of forest, suggesting that mineral 5 weathering can be caused by acidification of the rhizosphere by both types of mycorrhizal fungus and/or saprotrophic fungi. Investigations of silicate mineral surfaces, buried in proximity to roots of trees that would normally host arbuscular mycorrhizal fungi and were growing in an arboretum (Quirk et al., 2012, 2014), suggest that arbuscular mycorrhizal fungi may also form weathering trenches, although the associated fungi were not identified in these particular studies. Nanoscale channels in chlorite flakes colonized by ectomycorrhizal fungi have also been demonstrated (Gazzè et al., 2012) using atomic force 10 microscopy, and suggested as evidence that fungal activity, fuelled by plant photosynthate, can enhance mineral dissolution.

Summary:

Many new studies, published during the past ten years, using atomic force microscopy, laser confocal microscopy, energy dispersive X-ray spectroscopy and vertical scanning interferometry, have revealed the structural alteration of mineral substrates 15 by fungi. The endolithic signatures of rock-inhabiting microorganisms can now be distinguished from structures of abiotic origin but the proportional contribution of tunnels and voids with respect to total biological weathering is probably low since their volume and internal surface area is small in comparison to the total mineral surface area exposed to microbial contact. The capacity of different vegetation systems, hosting different types of mycorrhizal symbionts, to cause structural alteration 20 of different minerals should be investigated in further studies, combined with DNA-based methods to identify the fungi (and bacteria) involved *in-situ*. The influence of environmental factors such as atmospheric CO_2 concentration, nitrogen deposition and mineral composition should be investigated.

3 Biofilms and small-scale microbial interactions with consequences at higher spatial scales

Most microorganisms do not live as pure cultures of dispersed single cells in soil solution. Instead they aggregate at 25 interfaces – on surfaces of roots, organic matter, rocks and minerals, forming biofilms or microbial mats (Flemming and Wingender, 2010; Flemming et al., 2016). Biofilms consist of a hydrated matrix of extracellular polymeric substances (EPS), mostly produced by the organisms they contain. This matrix can account for 90% of the dry mass of the biofilm and provides a structural scaffold responsible for adhesion to surfaces and cohesion of the biofilm, enabling interactions that are entirely different from those of planktonic bacteria. The EPS matrix isolates microorganisms from the bulk soil solution, maintaining them in close proximity to each other and to substrate surfaces, concentrating weathering agents and allowing cell to cell 30 communication and quorum sensing by containing and concentrating signal molecules. This permits the formation of synergistic microbial consortia, production, accumulation, retention and stabilization of extracellular enzymes through binding

interactions with polysaccharides, sorption of organic compounds and inorganic ions, as well as permitting redox activity in the matrix (Liu and Lian, 2019), and facilitating horizontal gene transfer (Savage et al., 2013; Borgeaud et al., 2015). The retention of water maintains a hydrated microenvironment, protecting against desiccation, and proteins and polysaccharides can provide a protective barrier against specific and non-specific host defences during infection, antimicrobial agents and some 5 grazing protozoa (Fig. 1a) (Flemming and Wingender, 2010).

Biofilms and microbial mats have been studied from different perspectives that are relevant to interactions between microorganisms and minerals in a biogeochemical context. Subaerial biofilms occur within solid mineral surfaces exposed to the atmosphere and are dominated by fungi, algae, cyanobacteria and heterotrophic bacteria (Gorbushina, 2007). These communities are known to penetrate the mineral substrates and induce chemical and physical changes contributing to 10 weathering. Effects of biofilms containing the phototrophic cyanobacterium *Nostoc punctiforme* and the rock-inhabiting ascomycete *Knufia petricola* have been quantified using inductively coupled plasma optical emission spectrometry/mass spectrometry as well as scanning electron microscopy/transmission electron microscopy-energy dispersive X-ray spectrometry (Seiffert et al., 2014), demonstrating clear effects of the biofilms on mineral dissolution and leaching. Mats of hypogeous ectomycorrhizal fungi have been studied by Griffiths et al. (1994) who found that colonization by *Gautieria monticola* notably 15 increased the amount of oxalic acid in soil. Calcium oxalate (CaOx) can accumulate in forest soils and deposition of Ca from the weathering of apatite as CaOx crystals on the hyphal surfaces of *Rhizopogon* sp. growing from *Pinus muricata* seedlings has been shown in microcosm studies (Wallander et al., 2002). More CaOx is formed under higher P levels (Tuason et al., 2009). Bulk soil solution concentrations of organic acids are considered to be too low to have a large effect on mineral 20 dissolution, and modelling (Smits, 2009) suggests that local concentrations of weathering agents such as oxalate will not have a major effect on feldspar weathering unless the weathering agents remain within a few microns of the mineral surface. However, several authors (Balogh-Brunstad et al., 2008; Finlay et al., 2009) have suggested that higher concentrations of 25 organic acids may accumulate within EPS matrices that are in close proximity to mineral surfaces, so that mineral dissolution is influenced, and have called for more experiments to confirm this possible effect. More recent studies by (Gazzè et al., 2013) using atomic force microscopy have demonstrated the presence of EPS halos (Fig. 1b) surrounding *Paxillus involutus* hyphae colonizing phyllosilicate surfaces. In addition to increasing the surface area for hyphal interaction with mineral surfaces these 30 hydrated EPS layers presumably enhance mineral weathering by promoting accumulation of weathering agents such as organic acids and acidic polysaccharides, but further detailed studies of the local concentrations of these molecules are still necessary. Fungi and bacteria live together in a wide range of environments (Deveau et al., 2018) and the exudation of carbon compounds from roots and fungal hyphae into biofilms undoubtedly influences bacterial growth and activity (Guennoc et al., 2018). Priming of bacterial activity may occur through supply of exudates from vital hyphae (Toljander et al., 2007) but may also include recycling of C from damaged or senescent hyphae. Carbon supply from arbuscular mycorrhizal hyphae can provide energy for associated bacteria to solubilize phosphate (Zhang et al., 2014, 2016). Different ectomycorrhizal fungi colonizing lateral roots of tree seedlings have been shown to influence the community structure of associated bacteria (Marupakula et al., 2016, 2017) and differences in the richness and composition of bacterial communities have been demonstrated between the

hyphosphere of ectomycorrhizal fungi and that of saprotrophic fungi (Liu et al., 2018). Although the role of bacteria in mineral weathering has been less widely studied than that of fungi in recent years, progress has been made in understanding the identity and mechanisms of bacteria involved in weathering of minerals in acidic forest soils. Bacteria in the genera *Burkholderia* and *Collimonas* appear to have significant mineral weathering ability (Uroz et al., 2011) and incubation of different minerals in 5 forest soils appears to result in selection of different bacterial communities, that are distinct from those of the bulk soil (Uroz et al., 2012), confirming the concept of mineralogical control of fungal and bacterial community structure (Gleeson et al., 2005; Hutchens, 2010). Uroz et al. (2015) contrasted the rhizosphere with the “mineralosphere” in which bacteria are selected, not by organic nutrients originating from roots, but by the physiochemical properties of different minerals. Microorganisms can also drive weathering of bedrock in subglacial environments and the ubiquitous nature of pyrite in many common bedrock 10 types and high SO_4^{2-} concentrations in most glacial meltwaters has been interpreted to suggest (Mitchell et al. 2013) that pyrite may be a dominant lithogenic control on subglacial microbial communities and that mineral-based energy may therefore serve a fundamental role in sustaining these microbial populations over glacial-interglacial time scales. Studies by Montross et al. (2013) demonstrated an up to eight-fold increase in dissolved cations in biotic systems containing glacial sediments and meltwater compared with abiotic systems, suggesting that microbial processes can maintain terrestrial chemical weathering 15 rates in cooling climates during glacial advance. Recent experiments attempting to investigate *in-situ* mineral dissolution rates and structure/diversity of bacterial communities colonizing silicate minerals (Wild et al., 2018, 2019) have revealed development of mineral-specific bacterial communities and large discrepancies between predicted and measured dissolution rates, which were attributed to “heterogeneity of fluid circulation and local variation of reaction conditions”.

20 **Summary:**

Consequences of the ecophysiological heterogeneity and spatial organization of plant-microbe-soil interactions in natural environments need to be incorporated into new models and experimental systems. The effects of biofilms at microbial-mineral interfaces include EPS haloes that increase the surface area of contact, increased concentrations of weathering agents through protection by antibiotic compounds secreted into the EPS matrix, rapid removal of feedback-inhibiting weathering products 25 by mycorrhizal hyphae attached to plants that act as strong sinks for mobilised products, and changed patterns of microbial activity due to the facilitation of quorum sensing and other types of signalling. Retention of water within the biofilm matrix may allow weathering to be maintained at higher rates than would otherwise be possible during periods of soil drying. The extremely fine spatial scale of biofilms necessitates further development of sampling at a μm -scale to capture the steep chemical gradients and micro-scale variation in chemical and biological diversity and composition. These measurements are 30 essential in order to gain an accurate picture of the chemical and biological conditions existing at weathering interfaces.

4 Microbial and plant secretions – evidence from microcosms and mesocosms

Plants play a fundamental role in soil formation since root activity and decomposing plant material enhance weathering rates by producing acidifying substances (H^+ , organic acids), and ligands that complex with metals in the minerals. In addition, uptake of ions released from weathering reduces the likelihood of saturating conditions that retard weathering rates. Many of 5 these effects are mediated by mycorrhizal fungi and in temperate and boreal forests the vast majority of fine tree roots are colonized by symbiotic ectomycorrhizal fungi.

In ancient, highly weathered soils, P is the primary nutrient limiting plant growth, whereas N is the main growth-limiting nutrient in young soils. Plant nutrient acquisition in nutrient-impoverished soils often involves specialized root structures such as cluster roots or symbiotic structures such as mycorrhizas or root nodules (Lambers et al., 2008). In ancient soils with very 10 low P availability ‘dauciform’ (carrot-shaped) roots are produced by monocots in the Cyperaceae and ‘proteoid’ roots are produced by numerous dicot families, including the Proteaceae. Both types of roots are hairy and produce large amounts of carboxylates that desorb P from mineral surfaces. Phosphatases are also produced to release P from organic sources. Protons are quantitatively important weathering agents and many biotic processes, including uptake of positively charged nutrients such as NH_4^+ and K^+ , result in exudation of protons. Organic acids such as oxalic acid and citric acid are produced by plant 15 roots as well as fungi and bacteria and contribute to proton-driven weathering, but their deprotonated forms also act as strong weathering agents complexing with metals, including Fe^{3+} and Al^{3+} (Ma et al., 2001). In acidic environments, organic acid complex formation with Al^{3+} may free P, making it available for plant uptake, whereas in Ca rich environments organic acid exudation by plant roots and subsequent complexation with Ca also increases P availability. Soil P and N change as a function of soil age and in younger- and intermediate-aged soils with adequate amounts of nutrients, mycorrhizal mycelia provide an 20 effective strategy for nutrient acquisition (Lambers et al., 2008). Experiments using dual isotopic tracers of (^{14}C and ^{33}P) suggest that evolution of land plants from rootless gametophytes to rooted sporophytes with larger arbuscular mycorrhizal hyphal networks enabled enhanced efficiency of P capture as atmospheric CO_2 concentrations fell during the mid-Palaeozoic (480-360 Ma ago), (Field et al., 2012).

Strategies of mycorrhizal symbiosis differ depending upon the plant host. The majority of plant species form arbuscular 25 mycorrhizas with Glomeromycotan fungi that are efficient at scavenging nutrients such as P, and transporting it to their plant hosts across the depletion zones around roots formed by the slow diffusion of P through soil. However, these fungi are less efficient than proteoid roots at ‘mining’ P and releasing it from sorbed forms. Ericoid mycorrhizas are formed by plants in the Ericaceae, Empetraceae and Ericaceae, and ectomycorrhizas are formed by many woody plants and trees (Smith and Read, 2008). The fungi forming these two types of symbiosis vary in their enzymatic competence but in general they have a more 30 highly developed capacity to both scavenge and ‘mine’ N and P than arbuscular mycorrhiza, releasing N and P from organic forms (in the case of ectomycorrhizal fungi) by different combinations of hydrolytic and oxidative enzymes and non-enzymatic Fenton chemistry (Lindahl and Tunlid, 2015; Nicolás et al., 2019), and P and other mineral elements from inorganic forms via proton, organic acid, and siderophore exudation. In boreal forests with stratified podzol soils, many ectomycorrhizal fungal

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species produce extensive fungal mycelia that colonize both organic soil horizons and mineral horizons to an equal extent on a land area basis (Söderström, 1979), although data expressed on a soil dry weight basis often suggest that colonization of the mineral soil is lower since the mineral soil has a dry weight approximately 10 times higher than the organic soil. Studies of vertical distribution of different functional guilds of fungi (Lindahl et al., 2007; Sterkenburg et al., 2018) suggest that 5 ectomycorrhizal fungi are more abundant than saprotrophs in deeper organic and mineral horizons, presumably because they receive supplies of carbon from their plant hosts and are less reliant on local sources of carbon that are less abundant in the deeper horizons.

Mycorrhizal fungal mycelia secrete a wide range of molecules and the secretome has been shown to include low molecular weight (LMW) organic acids, amino acids, polyols, peptides, siderophores, glycoproteins and a diverse range of enzymes such 10 as proteases, phosphatases, lignin peroxidases and laccases. The production of these substances is highly variable both within and between different types of mycorrhizal fungi and influenced by different environmental conditions. **Figure 2** illustrates the flow of plant-derived carbon compounds through the fungal mycelium, the secretion of compounds into extracellular polysaccharide matrices and the soil solution and the longer-term immobilization processes that result in storage of stable C in organic and mineral pools. Although many of the molecules produced by the mycelium and its associated bacteria are labile 15 and subject to rapid turnover, they play a collective role in mobilization of nutrients that can lead to a longer-term sequestration of C in recalcitrant substrates that are both organic (Clemmensen et al., 2013) and inorganic (Sun et al., 2019a).

Low molecular weight organic acids are frequently identified as important components of the exudates produced by ectomycorrhizal fungi. Simple carboxylic acids are often present in soil solution and implicated in pedogenic processes. Their 20 sorption characteristics were studied by van Hees et al. (2003) who found adsorbed to solution ratios as high as 3100. Organic acids are readily adsorbed to the solid phase and sorption provides an important buffering role in maintaining soil solution concentrations at low organic acid concentrations, inhibiting microbial degradation. Concentrations of LMW organic compounds in soil solution are typically low (<50 μ M) but the flux through this pool is extremely rapid and microbial mineralization to CO₂ results in mean residence times of 1-10 hours (van Hees et al., 2005). These labile compounds may thus 25 make a substantial contribution to the total efflux of CO₂ from soil. Direct measurements of oxalate exudation from hyphal tips of the ectomycorrhizal fungus *Hebeloma crustuliniforme* (van Hees et al., 2006) have led to calculated exudation rates of 19 \pm 3 fmol oxalate per hyphal tip per hour, suggesting that concentrations of 30 mM oxalate could occur within one hour inside feldspar tunnels occupied by fungal hyphae. This would represent a concentration 10 000 times higher than in the surrounding 30 soil solution. Production of the hydroxamate siderophore ferricrocin was also detected and calculated to be able to reach a concentration of 1.5 μ M, around 1000 times higher than in the surrounding soil solution. Interestingly, the steady-state dissolution of goethite by 2'-deoxymugineic acid (DMA) phytosiderophores has been demonstrated to be synergistically enhanced by oxalate (Reichard et al., 2005), and it is possible that synergistic interactions between other combinations of organic acids and siderophores may exist. Organic acid production by intact ectomycorrhizal fungal mycelia colonizing *Pinus sylvestris* seedlings was studied by Ahonen-Jonnarth et al. (2000), using axenic, *in vitro* systems. In this study, production of oxalic acid by seedlings exposed to elevated (0.7 mM) Al and colonized by *Suillus variegatus* or *Rhizopogon roseolus* was up

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to 39.5 and 26 times, respectively, higher than in non-mycorrhizal control plants. The same type of lab system was used by Johansson et al. (2009) to investigate the effect of different mycorrhizal fungi on production of LMW organic acids, amino acids and DOC. However, in these experiments the identifiable LMW organic acids constituted only a small proportion (3-5%) of the total DOC fraction but DOC production was increased in mycorrhizal treatments relative to the non-mycorrhizal

5 controls.

Studies of mycorrhizal hyphal exudates using NMR spectroscopy (Sun et al., 1999) have revealed exudation of fluid droplets at the hyphal tips of the ectomycorrhizal fungus *Stilulus bovinus* and found that sugars and polyols comprised 32%, and peptides 14% of the exudate mass. Oxalic acids and acetic acid were also found, and polyols such as mannitol and arabitol are thought to be important for retaining turgor in fungal hyphae during C translocation along hydrostatic pressure gradients.

10 High internal pressures in hyphae are thought to be an evolutionary adaptation to facilitate penetration of both plant tissues as well as rock surfaces (Jongmans et al., 1997). This exudation of droplets may play an important role in conditioning the immediate environment of hyphal tips, facilitating interactions with substrates and associated microorganisms, even in drier soils. Similar observations have been made by Querejeta et al. (2003) who demonstrated that water obtained by *Quercus agrifolia* plants, using hydraulic lift, can be transferred to associated arbuscular mycorrhizal and ectomycorrhizal fungi to 15 maintain their integrity and activity during drought, even when the fertile upper soil is dry. Carbon allocation in the form of sugars and polyols (Sun et al., 1999) may be important in generating turgor pressure in hyphae and have consequences for weathering of minerals with lattice structure.

While biologically derived molecules such as organic acids and siderophores are strongly implicated in promoting mineral weathering, it is important to note that biologically derived ligands may also inhibit mineral weathering. Among LMW organic 20 acids, only citric and oxalic acids are commonly observed to stimulate mineral weathering (Neaman et al., 2006; Drever and Stillings, 1997), and humic and fulvic acids, which may dominate dissolved organic matter in soil solutions, have been observed to exert an inhibitory effect on mineral dissolution (Ochs, 1996; Drever and Stillings, 1997). However emerging views of soil organic matter based on the 'soil continuum model' (Lehmann and Kleber, 2015), and focusing on the ability of 25 microorganisms to access soil organic matter and its protection from decomposition by soil minerals, may require us to re-evaluate the underlying mechanisms. Exudation of oxalic acid can have a major effect on the desorption of iron-oxide bound organic matter (Keiluweit et al., 2015), promoting carbon loss by liberating organic compounds from protective associations with minerals. Mineral associated organic matter is also thought to be a significant source of N that can be mobilised by organic acids (Jilling et al., 2018).

Different microcosm systems have been used to study interactions between minerals and mycorrhizal fungal mycelia 30 colonizing plant seedlings. Differential allocation of plant-derived C to patches of primary minerals such as quartz and potassium feldspar (Rosling et al., 2004) and to apatite and quartz (Smits et al., 2012) suggest tightly coupled plant-fungal interactions underlying weathering. In the experiment by Smits et al. (2012), when P was limiting, 17 times more ¹⁴C was

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ed to wells containing apatite than to those containing only quartz, and fungal colonization of the substrate increased the release of P by a factor of almost three. Experiments by van Schöll et al. (2006a) demonstrated that limitation of nutrients (P, Mg, K) affected the composition of organic acids exuded by ectomycorrhizal fungi (more oxalate) but not the total amounts. Other experiments by van Schöll et al. (2006b) have demonstrated significant weathering of muscovite by the ectomycorrhizal fungus

5 *Paxillus involutus* when K was in low supply whereas no effect on hornblende was found under Mg deficiency. Selective allocation of biomass to grains of different minerals by *P. involutus* has also been demonstrated (Leake et al., 2008; Smits et al., 2008) suggesting grain scale “biosensing”, however it is also possible that fungal growth may be influenced by topographic structure (Smits and Wallander, 2017). Schmalenberger et al. (2015) demonstrated mineral-specific exudation of oxalate by *P. involutus* using labelled $^{14}\text{CO}_2$ given to the host plant. Oxalate was exuded in response to minerals in the following sequence:

10 Gabbro > limestone, olivine and basalt > granite and quartz. Experiments using flow-through systems (Calvaruso et al., 2013) have also estimated weathering rates of apatite to be 10 times higher when pine seedlings were present, compared with unplanted systems and attributed this to exudation of organic acids by the roots. The plants had been checked for the absence of fungal ‘contaminants’ but inoculation with the mineral weathering bacterial strain *Burkholderia glathei* PML1(12)Rp appeared to have no significant effect on weathering.

15 Fungi, bacteria and plants all produce siderophores, low-molecular-mass, metal-complexing compounds. These bind strongly to Fe^{3+} ~~influencing~~ its release and uptake (Kraemer et al., 2014; Ahmed and Holmström, 2014). The hydroxamate siderophores ferrichrome and ferricocin have been found in soil solution of mor layer podzolic soil overlying granitic rock and intensively colonized by ectomycorrhizal hyphae (Holmström et al., 2004) and should be kinetically and thermodynamically, even more efficient complexing agents for trivalent cations than oxalic and citric acid. Primary minerals

20 containing substantial amounts of Fe, such as hornblende and biotite, show enhanced dissolution rates in the presence of microbial or fungal siderophores (Kalinowski et al., 2000; Sokolova et al., 2010) and attachment of microorganisms to the mineral surfaces appears to lead to greater dissolution of elements from biotite (Bonneville et al., 2009; Ahmed and Holmström, 2015)

Release of potassium from K-feldspar and illite in microcosms by the fungus *Aspergillus fumigatus* was demonstrated by 25 Lian et al. (2008) who showed that release of K was enhanced by a factor of 3-4 by physical contact between the fungus and the mineral surface. Simple types of microcosm are usually used for gene expression studies in order to facilitate extraction of RNA from target organisms. Xiao et al. (2012) used differential expression cDNA libraries of *A. fumigatus* using suppression subtractive hybridization (SSH) technology to investigate the mechanisms by which the fungus weathered K-bearing minerals. K-bearing minerals were found to upregulate the expression of carbonic anhydrase (CA), implying that *A. fumigatus* was 30 capable of converting CO_2 into carbonate to accelerate the weathering of potassium-bearing minerals, which fixed CO_2 . During mineral weathering, the fungus changed its metabolism, produced more metal-binding proteins, and reduced membrane metal transporter expression, which can modulate ion absorption and disposal and promote acid production. Wang et al. (2015) used high-throughput RNA-sequencing (RNA-seq) to study the molecular mechanisms of *Aspergillus niger* involved in weathering of potassium feldspar. The fungus was cultured with soluble K^+ or K-feldspar) demonstrating differential expression of genes

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related to synthesis and transportation of organic acids, polysaccharides and proteins which was closely related to release of K⁺ from the minerals. Regulation of carbonic anhydrase (CA) gene expression in *Bacillus mucilaginosus* and the effects of its expression product in *Escherichia coli* have been examined by Xiao et al. (2014) who found that expression of CA genes was upregulated by the addition of calcite to a Ca²⁺-deficient medium, and that a crude enzyme extract of the expression product 5 in *E. coli* promoted calcite dissolution. Real-time fluorescent, quantitative PCR has been used to explore the correlation between CA gene expression in *B. mucilaginosus* and deficiency/sufficiency of Ca and CO₂ concentration (Xiao et al., 2015) and the results suggest that CA gene expression is negatively correlated with both CO₂ concentration and the ease of obtaining soluble calcium (Xiao et al., 2015). The roles of different CA genes have also been studied in *Aspergillus nidulans* using gene deletion, overexpression and bioinformatics (Sun and Lian, 2019) and the results of this study suggest that the CA gene *canA* 10 is involved in weathering of silicate minerals and carbonate formation, catalysing CO₂ hydration and that *canB* is essential for cellular respiration and biosynthesis in low CO₂ environments. Recent microcosm studies have also used transcriptome analysis to investigate weathering of K-containing feldspar and apatite and demonstrated upregulation of high-affinity ion transporter systems in the ectomycorrhizal fungus *Amanita pantherina* (Sun et al., 2019b).

15 **Summary:**

Earlier microcosm demonstrations of selective allocation of carbon to different minerals by ectomycorrhizal mycelium have now been complemented by newer studies demonstrating that selective C allocation to nutrient containing minerals through intact ectomycorrhizal mycelium results in significant increases in nutrient uptake by the host plants (Smits et al. 2012). There is still disagreement about the relative importance of different molecules as weathering agents and better information is 20 required about their chemical identity, concentration and rates of turnover at weathering interfaces. Advances in DNA based techniques have enabled a range of microcosm experiments in which the regulation of weathering interactions between fungi and minerals has been examined in microcosms and further studies based on transcriptomics will provide a more detailed understanding of how weathering of different minerals is regulated in individual species. However, DNA-based community profiling methods should also be used to improve understanding of more complex weathering consortia involving both bacteria 25 and fungi.

5 Systemic consequences of microorganism-mineral interactions in an ecological and evolutionary context

There is strong support for the idea that microorganism-mineral interactions have important consequences at global spatial scales and evolutionary time scales and some of these are illustrated in Fig. 3. Indeed, the concept of “mineral evolution” (Hazen et al., 2008) suggests that over two thirds of the number of minerals that exist today (>5300) are the result of chemical 30 changes mediated by living organisms (Fig 3. a). The best known of these is the Great Oxidation Event about 2.3 billion years ago (2.3 Ga) (Kump, 2008; Luo et al., 2016) during which the Earth’s atmosphere changed from one that was almost devoid

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of oxygen to one that is one-fifth oxygen. Inclusions of potentially biogenic carbon within Hadean zircons as old as 4.1 Ga (Bell et al., 2015) suggest that biological processes could have been operating during the Hadean Eon. Early microbial communities would have developed within sub-surface mineral environments to avoid high levels of ionizing radiation at the interface between the atmosphere and lithosphere. The sub-aerial biofilms at this interface today remain stressful environments (Gorbushina, 2007) but ionizing radiation levels are now much lower due to thickening of the Earth's atmosphere. Biomarker evidence (Brocks et al., 1999) in rocks formed 200 million years (Ma), before the increase in atmospheric oxygen, suggests that oxygen was already being produced before 2.5 Ga. Oxygenic photosynthesis by cyanobacteria is a likely source of this oxygen but there is evidence that stromatolites were abundant between 3.4 and 2.4 Ga, prior to the advent of cyanobacteria and oxygenic photosynthesis (Allen, 2016) and that Archaean microbial mats of protocyanobacteria switched between photolithoautotrophic and photoorganoheterotrophic metabolism prior to the evolution of cyanobacteria with simultaneous, constitutive expression of genes allowing both types of metabolism. It is also likely that phototrophy based on purple retinal pigments similar to the chromoprotein bacteriorhodopsin, discovered in halophilic Archaea, may have dominated prior to the development of photosynthesis (DasSarma and Schweitzerman, 2018). The activity of these early microorganisms and subsequent accumulation of oxygen in the atmosphere paved the way for the evolution of plants and there is a large and diverse body of evidence that the plastids of algae and higher plants evolved from free-living bacteria by endosymbiosis involving endosymbiotic gene transfer (Zimorski et al., 2014) as well as horizontal gene transfer (Archibald, 2015) (Fig 3 b).

Evolution of higher plants and development of vegetation has had a substantial effect on mineral weathering. The first well differentiated forests appeared in the Devonian, and increases in the volume of roots from the Silurian to the Devonian are associated with increases in clay enrichment and chemical weathering in subsurface horizons and drawdown of atmospheric CO₂ (Retallack, 1997). Dissolution of bedrock, accelerated by growth of plants and enhanced weathering of silicates, resulting in HCO₃⁻ carried to the sea and precipitated as carbonates, would have led to removal of CO₂ from the atmosphere and the large drop in CO₂ during the Devonian 400-360 Ma ago is thought to be associated with the rise of land plants and spread and development of forests (Berner, 1997).

The ubiquitous distribution of microorganisms today suggests that plants are not standalone entities, but should be considered from a holistic perspective, as *holobionts*, including the full diversity of the many different microorganisms associated with them (Vandenkoornhuyse et al., 2015). Almost all plant roots are colonized by microbial symbionts, making it difficult to quantify the separate contributions of plants and associated microorganisms to mineral weathering. There is broad agreement that fungi are important biotic agents of geochemical change (see Gadd, 2010, 2013 a, b, 2017) and that coevolution of fungi and plants has enabled them to have increasing influence as biogeochemical engineers (Fig 3 c-g). Fungi exert significant influence on biogeochemical processes, especially in soil, rock and mineral surfaces and the plant root-soil interface, where mycorrhizal fungi are responsible for major mineral transformations, redistribution of inorganic nutrients and flow of C. They are important components in rock inhabiting communities with roles in mineral dissolution

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and secondary mineral formation. The ubiquity and significance of lichens as pioneer organisms in the early stages of mineral soil formation, and as a model for understanding weathering in a wider context, has been discussed by Banfield et al. (1999) and Chizhikova et al. (2016). In lichens, photosynthetically fixed C is transferred from the photobionts (green algae and cyanobacteria) to a fungal thallus in contact with the mineral surfaces. Non-photosynthetic prokaryote assemblages are 5 also present in a zone of microbially-mediated weathering where mineral surfaces are covered in complex mixtures of high molecular weight polymers, clays and oxyhydroxides, and mineral weathering is accelerated via polymer-mediated dissolution/transport/recrystallization. Increasing evidence suggests that these bacteria are integral components of lichen thalli, contributing to the overall fitness of the lichen in functionally diverse ways (Grube et al., 2015) and that the structure 10 of the bacterial microbiome is influenced by the identity of the photoautotrophic symbionts (Hodkinson et al., 2012). Whilst the functional roles of these bacteria are still poorly understood, some have been demonstrated to solubilize phosphate 15 (Sigurbjörnsdóttir et al., 2015). There are similarities in the carbon compounds produced by fungi forming lichens and other fungi, but in later successional stages other types of symbiosis occur, involving mycorrhizal plants, and throughout evolution successive increases in the size of plants (Quirk et al. 2015) have allowed larger amounts of carbon to be allocated to larger root systems and greater amounts of mycorrhizal mycelium and exudates – increasing their potential for interacting with 20 mineral substrates. Although the genetic potential for hydrolytic decomposition of cellulose and other plant cell wall components has contracted in comparison with their saprotrophic ancestors (Kohler et al., 2015; Martin et al., 2016), saprotrophic fungi also exude the same types of carbon compounds as ectomycorrhizal fungi, including organic acids. *Paxillus involutus*, an ectomycorrhizal species, derived from a clade of brown-rot fungi, appears to have retained the non- 25 enzymatic Fenton chemistry used by brown-rot fungi to extract N from organic matter (Nicolás et al., 2019). *P. involutus* produces oxalate and weathers minerals and it is possible that different organic acids have multiple effects beyond weathering but, as far as we are aware, differences in organic acid production have not yet been studied comprehensively from an evolutionary perspective. Fahad et al. (2016) compared mobilization of base cations and P from granite particles by saprotrophic and ectomycorrhizal fungi *in vitro* and found statistically higher levels of accumulation of Mg, K and P by the ectomycorrhizal fungi, but only a few species were examined and further systematic comparisons of larger numbers of 30 species need to be conducted to establish the generality of this result. Symbiotic ectomycorrhizal fungi are thought to have evolved repeatedly and independently from saprotrophic precursors, so there should have been selection for ectomycorrhizal fungi that can efficiently mobilize nutrients and transfer them to the large sinks created by their host trees. However there have also been multiple reversals from the symbiotic habit to the free-living saprotrophic habit (Hibbett et al., 2000) so caution should be exercised in generalizations based on lab experiments. *In-vitro* experiments, in which fungi are cultured without their host plants, also introduce artifacts since the host plants act as important sinks for weathering products, preventing feedback inhibition of weathering processes due to accumulation of reaction products.

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Many studies of ectomycorrhizal influence on weathering rates have been performed over short periods and do not always provide clear evidence that processes observed at the laboratory-scale play a significant role in “soil-scale” mineral dissolution

rates. Smits et al. (2014) used a vegetation gradient from bare soil, via sparse grass to Norway spruce forest in a natural lead contaminated area in Norway, to study long-term effects of vegetation on apatite weathering in moraine deposited at the end of the last glaciation. Vegetation had a strong stimulatory effect on apatite weathering, and 75% of the variation in apatite weathering could be explained by soil pH, but the effect of plant roots and mycorrhizal symbionts on this process could not be separated. In the top 20 cm of the mineral soil an additional mechanism, not mediated by pH, enhanced dissolution of apatite. The authors suggested this might be caused by deprotonated LMW organic acids, leading to higher concentrations of the organic-metal complexes on the mineral surfaces but that the origin of these acids was probably not ectomycorrhizal fungi, since these fungi were absent in the grass vegetation at the highest pH area of the vegetation gradient. Under these conditions, the biomechanical and chemical effects of ectomycorrhizal fungi on apatite weathering seemed to be minor, but these effects are probably dependent on the nutrient status of the forest. Enhanced colonization of apatite by ectomycorrhizal hyphae in laboratory systems (Rosling et al., 2004; Smits et al., 2012) is also commonly found under field conditions, but only when P availability is low (Rosenstock et al., 2016; Bahr et al., 2015; Almeida et al., 2018). The potential for weathering by ectomycorrhizal fungi is probably much higher under these conditions and the nutrient status of the forest should be considered when biological weathering rates are quantified, at least for apatite weathering, where P status has a strong effect on fungal colonization of apatite. In contrast, no enhanced colonization of biotite and hornblende by ectomycorrhizal hyphae was found in Norway spruce forests in the Czech Republic under low K or Mg availability (Rosenstock et al., 2016). This suggests that ectomycorrhizal fungi have a smaller potential to enhance weathering of these minerals compared to apatite. However, these results should be treated with caution since no quantitative/chemical estimates of the mineral weathering were made and use of ergosterol-based estimates of fungal biomass as a proxy for 'weathering' can be misrepresentative, since some ectomycorrhizal fungi that actively release LMW organic acids may not invest much carbon in their own biomass. Further investigations using RNA-based analysis of active microbial communities, combined with temporal assessment of weathering kinetics, should reveal the true potential of microorganisms in biogeochemical weathering in forest ecosystems. Effects of N-fixing microorganisms on weathering activity have not been studied in detail but the resulting inputs of N might be expected to drive growth and increase demand for rock-derived nutrients. Recent studies by Perakis and Pett-Ridge (2019) based on uptake of strontium (Sr) isotopes, suggest that nitrogen fixing red alder (*Alnus rubra*) trees can take up significantly more rock-derived Sr than five other co-occurring tree species, although the mycorrhizal fungi colonising these trees were not identified.

Fungal weathering of rocks and minerals through biomechanical and biochemical attack has been studied extensively. Proton-promoted dissolution is supplemented by ligand-promoted dissolution of minerals by strong chelators such as oxalic and citric acid that may act synergistically with siderophores. Secondary minerals may be deposited as carbonates, oxalates or other mycogenic minerals and mineraloids and the role of "rock-eating fungi" has been discussed in addition to the role of "rock-eating fungi" (Fomina et al., 2010). Fungi are prolific producers of oxalate, and oxalotrophic bacteria are capable of oxidizing calcium oxalate to calcium carbonate. Since the oxalate is organic in origin, and half its C is transformed into mineral

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C with a much longer residence time, this process represents a potential major sink for sequestration of atmospheric C (Verrecchia et al., 2006). Precipitation of carbonate minerals by microorganisms during silicate weathering has also been discussed by Ferris et al. (1994) in relation to its potential role as a sink for atmospheric CO₂. The oxalate-carbonate pathway may not be important in boreal forest soils, however the African oxalogenic iroko tree *Milicia excelsa*, together with associated saprotrophic fungi and bacteria, enhances carbonate precipitation in tropical oxisols, where such accumulations are not expected due to the acidic nature of the soil (Cailleau et al., 2011), and the same phenomenon has been demonstrated in acidic soils of a Bolivian tropical forest (Cailleau et al., 2014). Studies of bacterial assemblages in soil associated with ectomycorrhizal roots of *Pinus massoniana* and *Quercus serrata* have revealed enrichment of oxalotrophic bacteria using the oxalate-carbonate pathway, representing a potential long-term sink for photosynthetically fixed carbon derived from the atmosphere (Sun et al., 2019a). The role of microorganisms in dissolution and modification of karst stones such as limestone and dolomite has also been studied (Lian et al., 2010, 2011). Microbially mediated chemical corrosion and precipitation in surface and underground water can play a role in pedogenesis and provide a sink for atmospheric CO₂ and the role of carbonic anhydrase in hydrating atmospheric CO₂ to HCO₃⁻ has been investigated in relation to changes in CO₂ concentration and availability of Ca²⁺ (Xiao et al., 2014, 2015). The results of the latter study suggest that the importance of microbial carbonic anhydrase on silicate weathering and carbonate formation may be higher at current CO₂ levels than under primordial conditions 2 Ma ago when CO₂ levels were much higher.

Rapid decreases in soil respiration following the girdling of forest trees (Högberg et al., 2001), suggest that the flux of current assimilates to mycorrhizal roots is directly connected to the supply and respiration of C in soil. In another study (Högberg and Högberg, 2002), extractable DOC in a 50-year-old boreal forest, was 45% lower in girdled plots than in control plots, suggesting a large contribution by roots and associated fungi to soluble C pools, although the contribution of these two components could not be determined separately. Biogeochemical weathering of silicate rocks is a key process in the carbon cycle (Pagini et al., 2009) and, although consumption of CO₂ by weathering is small compared with transfers associated with photosynthesis and respiration, it is the dominant sink in global carbon balance and controls atmospheric CO₂ and climate patterns at scales of millennia or longer (Goudie and Viles, 2012). Catchment-scale field studies consistently indicate that vegetation increases silicate rock weathering and incorporating the effects of trees and fungal symbionts into geochemical carbon cycle models has relied upon simple empirical scaling functions. Taylor et al. (2012) used a process-based approach to derive quantitative estimates of weathering by plant roots, associated symbiotic mycorrhizal fungi and climate, concluding that vegetation and mycorrhizal fungi enhance climate-driven weathering by a factor of up to two.

The geoengineering potential of artificially enhanced silicate weathering is now increasingly well established (Köhler et al., 2010) and addition of pulverised silicate rocks to different croplands has been advocated as an effective strategy for global carbon dioxide removal (CDR) and ameliorating ocean acidification by 2100 (Taylor et al., 2016; Beerling et al., 2018). Large scale field trials are now in progress <http://lc3m.org/> but basic information about the way in which different microorganisms drive the sequestration processes in different soil types is still missing. Recent studies on carbonate weathering by ectomycorrhizal fungi colonizing tree roots (Thorley et al., 2015) suggest that ectomycorrhizal tree species weather calcite

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containing rock grains more rapidly than arbuscular mycorrhizal (AM) trees because of greater acidification by the ectomycorrhizal trees. Weathering and corresponding alkalinity export to oceans may increase with rising atmospheric CO₂ (Andrews and Schlesinger, 2001) and associated climate change, slowing rates of ocean acidification.

Transfer of increasing amounts of photosynthetically derived carbon to ectomycorrhizal fungi and improved colonization of mineral substrates during evolution of plants (Quirk et al., 2012, 2014) are consistent with the idea that weathering of silicate minerals and sequestration of C into ocean carbonates has led to drawdown of global CO₂ levels during the rise of ectomycorrhizal trees over the past 120 Ma (Taylor et al., 2011; Morris et al., 2015). However, the relative constancy of atmospheric CO₂ levels and absence of even further reductions over the final 24 Ma of the Cenozoic has been attributed to a negative feedback mechanism caused by CO₂ starvation (Beerling et al., 2012) that is predicted, by numerical simulations, to 10 reduce the capacity of the terrestrial biosphere to weather silicate rocks by a factor of four. Differences in the magnitude of carbon transfer from plants to different types of mycorrhizal fungal symbionts, and the physiological mechanisms regulating this transfer are influenced by the biotic and abiotic environment, as well as the life history and evolutionary origins of the symbiosis. Common-garden experiments (Koelle et al., 2012), using sister clades of plants (with different types of mycorrhiza), might provide a suitable way of comparing functional groups but broad generalisations should be made with extreme care 15 since there is a high degree of context dependency (Field et al., 2017). Ericoid mycorrhizal fungi can produce copious amounts of LMW organic acids that solubilize inorganic zinc compounds (Martino et al., 2003) but there are so far no systematic studies of their role in different weathering interactions in comparison to other fungi. Further comparative studies of the role of different types of mycorrhizal symbioses in mineral weathering may shed light on the different physiological mechanisms involved. Soil microorganisms can have strong effects on plant resource partitioning and it has been shown (Ryan 20 et al., 2012) that *Kennedia* species inoculated with arbuscular mycorrhizal fungi allocated lower amounts of carboxylates to the rhizosphere but had higher concentrations of P than non-inoculated plants, presumably using less strongly sorbed forms of P.

Inferences about evolutionary development of weathering have been drawn using vertical scanning interferometry to study 25 "trenching" of silicate mineral surfaces (basalt) buried under different tree species growing in an arboretum (Quirk et al., 2012) and suggest that trenching and hyphal colonization increase with evolutionary progression from AM fungi to ectomycorrhizal fungi, and with progression from gymnosperm to angiosperm host plants. It is suggested that this evolutionary progression resulted in release of calcium from basalt by ectomycorrhizal gymnosperms and angiosperms at twice the rate achieved by AM gymnosperms, and that forested ecosystems have become major engines of continental silicate weathering, regulating global CO₂ concentrations by driving calcium export into ocean carbonates (Quirk et al., 2012) (Fig. 4). Additional laboratory 30 studies of the same tree species using different CO₂ environments suggest that weathering intensified during evolutionary progression from AM fungal symbionts to ectomycorrhizal symbionts and that calcium dissolution rates were related to photosynthate energy fluxes and higher during simulated past CO₂ atmosphere (1500 ppm) under which ectomycorrhizal fungi evolved (Quirk et al., 2014).

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Summary:

Microorganisms have interacted with minerals for billions of years, enriching the atmosphere with oxygen and shaping the evolution of minerals long before the evolution of land plants. There is strong evidence that the plastids of algae and higher plants ~~evolved from free-living bacteria through endosymbiosis and plants have continued to evolve in conjunction with~~

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5 microorganisms through symbiotic alliances (mycorrhiza, actinorhiza, rhizobia, plant growth-promoting rhizobacteria (PGPR) etc.) such that they are really holobionts – assemblages of organisms. This ~~enabled the holobionts to become successively~~ more efficient biogeochemical engineers. Hypotheses have been advanced concerning the evolutionary development of weathering and ~~differing contributions of different types of mycorrhizal symbiosis. Further advances in understanding will~~ require more studies of different combinations of plant and fungal species, accompanied by rigorous, DNA-based, *in-situ*

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10 identification of the different fungal symbionts. However, the magnitude of carbon transfer to different types of mycorrhizal fungal symbionts, and the physiological mechanisms regulating this transfer are highly context dependent and advances in ~~knowledge~~ will require sound ecological understanding, based on integration of a diverse array of biotic and abiotic factors.

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Better information is still required on the identity of bacteria and fungi colonizing bedrock outcrops and other mineral substrates in forests. The diversity of these communities is high and it is important to identify the particular taxa that are most

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15 active in competing for plant derived C and to identify the amounts and chemical forms in which it is delivered to mineral surfaces. Use of ¹³C-based stable isotope probing is likely to be helpful in identifying the most active taxa delivering plant-derived C to mineral surfaces. Analysis of the chemical composition of compounds involved will necessitate further studies using nanoSIMS, NMR and FTIR spectroscopy. Improved understanding of weathering at an ecological level requires better knowledge about the processes involved in sequestration of atmospheric CO₂ and further investigation of the forms in which 20 C is sequestered during weathering in forests is necessary. Weathering processes are impacted by different environmental conditions and types of forest management and further studies are required to investigate how ~~these are impacted by changes~~ in atmospheric CO₂ concentration and effects of N deposition and fertilization.

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6 Methods using stable isotopes

25 Stable isotopes, especially of Ca and Sr, have been used extensively to source the origin of Ca in drainage water; when applied to plant tissues, they can be used to trace plant nutrients back to their primary source. Isotope tracing has been mostly used to study apatite weathering. Apatite is a calcium–phosphate mineral, and because P has no stable isotopes, the uptake dynamics can only be studied via the Ca ion (or potentially the ¹⁸O/¹⁶O in the phosphate group). In most rocks and soils, apatite is the sole primary P source. However, its contribution to the soil solution Ca pool is minor compared with other minerals. If the Ca 30 isotope ratio in the plant is more similar to the signature in apatite than to the signature in the soil solution, then it indicates that the plant directly acquires Ca from apatite. Blum et al. (2002) applied this technique to a temperate mixed forest using

Ca:Sr ratios in soil water, minerals in the soil and different mycorrhizal and non-mycorrhizal trees. The authors concluded that direct calcium uptake by ectomycorrhizal fungi weathering apatite in the parental material could compensate for calcium loss in base-poor ecosystems. Data on element ratios should, however, be interpreted with care, because of high variation of Ca:Sr ratios in different plant tissues and limited understanding of the cycling of these elements in plants (Watmough and Dillon, 2003), as well as contradictory data of Dijkstra and Smits (2002) (see below) that suggest the conclusion of Blum et al. (2002) is overstated. Field studies using mesh bags containing microcline and biotite, buried in Swedish *Picea abies* forests (Wallander et al., 2006) used the ^{87}Sr : ^{86}Sr ratio to calculate the fraction of Sr in the mycorrhizal root tips that had originated from the minerals. Although the total amounts of Sr released from the minerals could not be calculated since the total plant biomass enriched with ^{87}Sr was unknown, the study clearly demonstrates the potential of ectomycorrhizal fungi to mobilize and take up nutrients such as Ca and K from microcline and biotite under field conditions.

In many forest ecosystems, plant-available pools of Mg, Ca, and K are assumed to be stored in the soil as exchangeable cations adsorbed on the cation exchange complex (exchangeable pools). However, other storage forms of Mg, Ca, and K that have not been fully characterized may play an important role in plant nutrition and biogeochemical cycles and be plant-available on very short time scales (<1 day). Isotopic dilution techniques using the stable isotopes ^{26}Mg , ^{44}Ca , and ^{41}K have been developed (van der Heijden et al., 2018) to trace and quantify the pools of Mg, Ca, and K (isotopically exchangeable pools) in the soil of a hardwood forest that contribute directly to equilibrium processes between the soil water and the soil. These show that isotopically exchangeable pools of Mg, Ca, and K are greater than traditionally measured exchangeable pools. Storage forms of Mg, Ca, and K in the isotopically exchangeable pool could include chelation with soil organic matter, retention on soil aluminum and iron oxides and hydroxides through phosphate and/or organic acid bridges and site-specific adsorption. The isotopic dilution method is a relevant tool to quantify the plant-available pools of Mg, Ca, and K on short time scales (source and sink pools) and is a very promising approach to characterize and quantify the processes responsible for the depletion and/or replenishment of these pools over longer time scales.

Field studies of small rock fragments isolated from a Finnish *P. sylvestris* forest with *Tricholoma matsutake* fruiting bodies (Vaario et al., 2015) revealed the presence of *T. matsutake* on 97% of the rock fragments and laboratory assays using X-ray diffraction confirmed the ability of the fungus to absorb some trace elements directly from the rock fragments, but uptake of Mg and K did not appear to be significant. In contrast, laboratory studies of the capacity of different fungi to mobilize P and base cations from granite particles (conducted within QWARTS) (Fahad et al., 2016) suggest that some ectomycorrhizal fungi can mobilize and accumulate significantly higher concentrations of Mg, K and P than non-mycorrhizal fungi. The mycorrhizal fungi can fractionate Mg isotopes, discriminating against heavier isotopes and we found a highly significant inverse relationship between $\delta^{26}\text{Mg}$ tissue signatures and mycelial concentration of Mg (Fig. 5).
This provides a theoretical framework for testing hypotheses about fungal weathering of minerals in future experiments. If active mobilization and uptake of lighter ^{24}Mg isotopes results in relative enrichment of heavy Mg isotopes left in soil solution and soil, this should be evident in areas of active weathering. Mesocosm experiments, conducted within the QWARTS project (Mahmood et al., in preparation), employing a gradient of increasing organic matter depletion to simulate progressively more intense forest biomass harvesting,

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revealed significant and successive enrichment of ^{26}Mg signatures in the soil solution in the B horizon, associated with increased availability of organic matter and resultant increases in plant and fungal biomass (Fig. 6). No such enrichment was found in other horizons or in systems without plants (and therefore without mycorrhizal fungi). This suggests that significant biological weathering of Mg takes place in the B horizon, driven by higher plant biomass that enables improved carbon allocation to the fungal mycelium and also constitutes a larger sink for uptake of mobilized base cations. Although the experiments provide strong support for the idea of biologically driven mobilization of Mg from B horizon mineral soil, the process was not sufficient to maintain optimal tree growth in systems with a severely reduced organic matter pool. In addition, studies carried out under both field and laboratory conditions show that Mg isotope fractionations are controlled by the same biological factors in the critical zone, defined as the outer layer of earth from vegetation to the soil. Silicate rocks show a relatively small range of variation in Mg isotopic ratios (denoted as $\delta^{26}\text{Mg}$) (Bolou-Bi et al., 2009; Shen et al., 2009; Uhlig, et al., 2017). During the weathering of these rocks at watershed level, it was revealed that isotopic fractionation of Mg isotopes was in favour of light isotopes in soil solution, while the soils were enriched in heavy isotopes (Pogge von Strandmann et al., 2008; Tipper et al., 2010). Studies conducted in forest ecosystems, (Bolou-Bi et al., 2012; Mavromatis et al., 2014; Uhlig et al., 2017) indicate variation in soil solution signatures of surface soil layers, suggesting a role of vegetation through the Mg isotope cycle (uptake and litterfall), soil exchangeable fraction and rainwater, in addition to light Mg isotope return via litterfall. In deeper soil horizons, however, the soil solution signatures may be the result of two additional processes (a) the mineral dissolution leaching the light isotope into solution and subsequently weathered minerals are systematically enriched in heavy Mg isotopes relative to fresh rock, and (b) clay formation and/or Mg adsorption removing the heavy Mg isotope from soil solution (Huang et al., 2012; Opfergelt et al., 2014). Mg isotope fractionation has also been observed under laboratory conditions during the dissolution of primary minerals (Wimpenny et al., 2010).

In studies of Ca isotope cycling in forest ecosystem, it appears that the soil solution and exchangeable fraction generally display enrichment in the heavy isotope compared to soil particles, bedrock and rainwater (Holmden and Bélanger, 2010; Hindshaw et al., 2011). However, the soil solution isotope signatures are not the simple result of weathering processes in soils because the congruent dissolution of rock or mineral observed in lab and field conditions did not cause any measurable Ca isotope fractionation (Hindshaw et al., 2011; Ryu et al., 2011; Cobert et al., 2011). This suggests that another process, such as the preferential uptake of the light Ca isotope (^{40}Ca) by vegetation, decreases the soil solution Ca isotope ratio in the upper horizon in addition to light Ca isotope return via litterfall (Page et al., 2008; Holmden and Bélanger, 2010). In deeper soil horizons, soil solution $\delta^{44/40}\text{Ca}$ may result from the dissolution of minerals such as apatite. Interestingly, experiments by Dijkstra and Smits (2002) indicate that most of the Ca taken up by trees comes from litter recycling. In a comparable mixed forest, also in the north-eastern United States, the annual Ca import from weathering in the rooting zone is less than 0.3% of the annual Ca uptake, which was a four-fold smaller flux than the annual atmospheric deposition (Dijkstra and Smits, 2002). Inputs of nutrients such as P, from atmospheric deposition, may also be significant in coastal Fynbos systems (Brown et al., 1984) and the Florida everglades (Redfield et al., 2002). However, the data from our QWARTS experiments suggest that

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mobilization of Mg may function differently in boreal coniferous forests, with higher amounts being mobilized from inorganic substrates in the B horizon.

Mycorrhizal fungi play a central role in mobilizing N and P from organic substrates and when these are depleted, N and P limit tree growth, resulting in reduced C supply to the mycorrhizal mycelium and reduced capacity for mobilization of base cations from the mineral horizons. Although mobilization of Mg from the B horizon was sufficient to support increased biomass production in systems supplied with extra organic material (Fig. 6), it was not sufficient to compensate for losses of base cations when organic material was most depleted. The results of these experiments are therefore consistent with the predictions of modelling that, under intensive forestry with removal of organic residues, base cation supply will not be sustainable in the long term. Intensive, sustained harvesting of biomass may lead to N limitation before base cations become limiting. Applications of different fertilizers (Xiao et al., 2017) or inadvertent N deposition (Averill et al., 2018) may have negative effects on both weathering and C sequestration.

Smits and Wallander (2017) advocate detailed studies of the liquid chemistry of local weathering sites at the micrometre scale, together with up-scaling to soil-scale dissolution rates, and the authors suggest that future research should focus on whole ecosystem dynamics, including the behaviour of soil organic matter, and that early-stage primary succession ecosystems on low reactive surfaces, such as fresh granites, should be included. Smits and Wallander (2017) also recommend the use of stable isotopes by choosing minerals and soils with distinct isotope ratios.

Summary:

Experiments using stable isotopes have potential to improve understanding of the roles played by different groups of micro-organisms in biological weathering. *In-vitro* studies of base cation mobilization from granite particles so far suggest that symbiotic mycorrhizal fungi may be more efficient at mobilizing Mg, K and P than saprotrophic fungi but it is necessary to test a wider range of species before such broad conclusions can be drawn. Care should also be exercised in interpreting experiments conducted *in vitro* in the absence of host plants, since these provide important sinks for mobilized nutrients that could otherwise retard weathering reactions should they accumulate. Fractionation of stable Mg isotopes by mycorrhizal fungi, with preferential uptake of lighter isotopes, results in enriched levels of ^{26}Mg in soil solution and laboratory experiments with reconstructed podzol profiles have demonstrated that this enrichment occurs primarily in the B horizon. The data suggest that this pathway may be of significance in the field but reductions in (N-containing) organic matter resulted in reduced tree growth and reduced Mg uptake, suggesting that increased biological weathering of Mg is unlikely to compensate for losses of Mg through organic matter removal if N is also limiting. However, K and P were also deficient in this experiment so conclusions should be drawn with care. Similar experiments with isotopes of other elements may reveal wider information about patterns of nutrient uptake. In addition to their possible weathering effects, mycorrhizal fungi play important roles in N acquisition from organic substrates, illustrating how decomposition and weathering are intercoupled.

7 Modelling of biological weathering in forest soils

Sustainable resource use necessitates balancing removals from ecosystems with inputs. Designing forest biomass harvest plans and calculating critical loads of acid deposition to ensure the health of headwater streams necessitates a quantitative understanding of mineral weathering rates, which, in turn, necessitates a quantitative understanding of the magnitude and character of biological weathering. Furthermore, the dependence of global patterns of ecosystem productivity on inputs of nutrients from mineral weathering requires a quantitative understanding of biological weathering to model the carbon cycle in the context of climate change. Direct and indirect quantification of weathering have proven to be very challenging, necessitating models that can aid us in understanding and projecting long-term effects of biological weathering.

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7.1 Information needs and possible improvements

10 Based on the preceding sections, we have identified five biological processes that can be incorporated into models quantifying soil mineral weathering rates, to make them more mechanistic and useful as predictive tools:

- Exudation of LMW ligands promoting weathering
- Nutrient uptake rates as a driver of weathering reactions
- The concentration effect of biofilms on weathering-promoting ligands and protons
- 15 ·The dependence of the above process on particular microbial and plant assemblages, including mycorrhizal type.
- The dependence of the above processes on carbon flux from autotrophs, and the sensitivity of this to water and nutrient availability.

The stimulatory effect of particular LMW organic acids and siderophores on soil mineral weathering rates is a function of 20 both exudation rate as well as biological degradation rates of the same compounds. The chemical composition of soil water DOC and exudates exerts considerable control on the degree of stimulation, or, potentially, inhibition of weathering rates. Modelling ligand-promoted dissolution as a function of total DOC without consideration of DOC character may lead to inaccurate interpretations of mineral dissolution rates derived from experiments with specific organic species. Geochemical 25 weathering models require the incorporation of mechanisms, either through equilibrium equations or inhibitory factors that allow the build-up of weathering products to slow weathering rates, as discussed below. The treatment of soil solution fluxes should allow for accumulation of weathering products in soil microenvironments (such as around mineral surfaces and mycelia), as bulk soil solution data may not capture the concentration gradients found around mineral surfaces. The stimulatory effects of exudates are highly concentration dependent, and many studies fail to find sufficiently high concentrations of 30 weathering promoting ligands in bulk solution, while other studies indicate that biofilms may allow these compounds to concentrate by orders of magnitude near mineral surfaces, increasing their effectiveness as weathering agents. Similarly, precipitation accelerating dissolution, bio-acidification and CO₂ respiration effects are likely to be magnified under biofilms.

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The dependence of the above processes on particular microbial and plant assemblages has not yet been determined and requires further detailed studies of the specificity of ectomycorrhiza-bacteria interactions and the physiological differences between different bacteria and fungi in their ability to promote dissolution of different minerals. Further information is also required on the variation in carbon flux from autotrophs to different fungal and bacterial components of biofilms in contact with different minerals and the sensitivity of this carbon flux to differences in water and nutrient availability.

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7.2 Developments and improvements in modelling biological weathering

Akselsson et al. (2019) present an extensive review of methods for estimating weathering rates in forest soils. These range from mass balance budget calculations (e.g. Simonsson et al., 2015) and gravimetric approaches (Turpault et al., 2009), to the depletion method based on the elemental concentration differences between weatherable and unweatherable minerals (such as zirconium bound in zircon or titanium in rutile), to dynamic models based on the transition state theory (e.g. Stendhal et al., 2013; Erlandsson et al., 2016). Approaches to modelling mineral weathering by fungi were discussed by Rosling et al. (2009). Biological weathering processes have, more or less mechanistically, been integrated into the process descriptions of a diversity of ecosystem models. Here we attempt to describe the major approaches to implementing important biological processes into weathering rate estimates over the last decade.

Catchment and ecosystem mass balance approaches have been widely employed to estimate mineral weathering rates. The simplest assume that the soil and standing biomass nutrient pools are at steady state, and more complex approaches have attempted to account for changes in soil and biomass pools. A general feature of all mass-balance approaches though, is that weathering rates are derived from the sum of inputs and outputs into other pools in the system. Models have been developed to describe increasingly complex sets of processes, as well as to apportion calculated weathering fluxes into individual contributing mineral species (Price et al., 2013). Meta-analysis across large numbers of studies (Hartmann and Moosdorf, 2011) and the application of machine learning approaches (Povak et al., 2014) can further increase the utility of mass-balance approaches for evaluating the potential importance of different processes to weathering rates. Biomass accumulation emerges in many simulations (Wilcke et al., 2017; Zetterberg et al., 2016) as a key flux controlling the dissolution and retention rates of mineral weathering products and a major source of uncertainty (Simonsson et al., 2015; Zetterberg et al., 2016). While mass-balance approaches, given careful scrutiny of inherent assumptions, are valuable for estimating weathering rates, the derivative nature of these weathering estimates reduces their value for assessing the mechanisms that control weathering rates.

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They may thus not be suitable for use in predicting future weathering rates under conditions for which they have not been calibrated or validated.

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Taylor et al. (2011) built on a geochemical model developed by Banwart et al. (2009) which attempts to quantify the contribution of biologically derived protons and ligands to mineral weathering rates, and distinguishes between vegetation which forms arbuscular mycorrhizal associations and vegetation that forms ectomycorrhizal associations. Their model, based on the GEOCARBSULF model, assumes that AM fungi do not exude significant amounts of organic acids while ectomycorrhizal fungi do, and models the activity of that exudation as that of oxalic acid. They also divide the soil volume

into an area of immediate proximity to mycorrhizal hyphae, the mycorrhizosphere, and the bulk soil. When they applied their model over the last 200 Ma they observed that the draw-down of global atmospheric CO₂ levels over the last 120 Ma could largely be attributed to the emergence and diversification of angiosperms and the spread of ectomycorrhizal fungi. However, in addition to organic acid exudation, hyphal length density, which defined the volume of the mycorrhizosphere, was 5 parameterized to be 25-fold greater in ectomycorrhizal fungal dominated ecosystems than AM dominated systems. Modelled soil chemistry and the resulting terrestrial carbon sink, were also highly sensitive to hyphal length density. Taylor et al. (2012) further developed this weathering model based on mycorrhizal association type and coupled it to a dynamic global vegetation model and validated it against a global dataset of watershed flux data. The resulting model, when applied over the last 200 Ma indicated that biological weathering was stronger in the distant past than today, and estimated that vegetation and mycorrhizal 10 fungi have increased terrestrial weathering rates by a factor of 2. While their model performed reasonably well in the validation across a global series of catchment data, their findings did not support a distinct dichotomy in weathering behaviour between AM-dominated and EM-dominated ecosystems. Quirk et al. (2014) build on the model developments of Taylor et al. (2011, 2012) to illustrate the potential for a feedback between atmospheric CO₂ levels and biological weathering rates, such that, as 15 CO₂ levels increase, global plant productivity and autotrophic soil inputs of protons and organic acids do so as well, stimulating biological weathering and serving as a negative feedback to increasing CO₂ levels. As CO₂ levels decrease, so does biological weathering. This sequence of models develops hypotheses concerning the role of land-plants in the geology of earth and the global biogeochemical carbon cycle, with a framework to account for differential biological weathering activity by distinct 20 vegetation types. While considerable evidence exists pointing to the potential for ectomycorrhizal fungi to be more potent weathering agents, than AM fungi, field studies comparing weathering rates in paired AM- and ectomycorrhiza- dominated forests have failed to find significant differences in mineral weathering rates (Koele et al., 2014; Remiszewski et al., 2016). Future applications utilising rhizosphere or mycorrhizosphere vs bulk soil volumes should place more emphasis on the choice 25 of hyphal length densities, and should likely use functions, as opposed to fixed parameters, that depend on plant type as well as plant productivity and nutrient status to describe fine root and mycorrhizal hyphal root lengths.

Roelandt et al. (2010) coupled a reactive transport model to the Lund-Potsdam-Jena global dynamic vegetation model, 25 which they termed Biosphere-Weathering at the Catchment Scale (B-WITCH), and were able to model base cation efflux accurately from the Orinoco watershed. They concluded that vegetation exerts a major role on mineral weathering rates, but that this role is primarily hydrological, via evapotranspiration fluxes. However, while their model did feature organic ligand-promoted dissolution, the source of those ligands was decomposition only, they treat the entire rooting zone as a single 30 interconnected solution, and while they do feature plant functional types, those functional types do not correspond to belowground physiology or mycorrhizal association. The B-WITCH model appears to reflect the most mechanistic approach amongst global dynamic vegetation models to estimating mineral weathering rates, but additional processes may need to be implemented to capture the influence of biology on mineral weathering rates.

Maher et al. (2010) applied the reactive transport geochemical model CrunchFlow, which estimates weathering rates based on experimentally-derived dissolution equations for individual minerals, to examine the effect of fluid residence time (which

in turn controls the transport of weathering products away from mineral surfaces) on mineral weathering rates. They observed a strong inverse relationship between fluid residence time and weathering rates and interpreted this as clear evidence for transport control of weathering rates in natural ecosystems. Lawrence et al. (2014) coupled an organic acid module to the CrunchFlow model to examine the potential role of organic acids, modelled as oxalic acid, on mineral weathering rates, and 5 observed that the primary effect of oxalic acid was to increase soluble Al but decrease free Al^{3+} concentrations in solution; mineral weathering was enhanced near the zone of oxalic acid production (the topsoil) but decreased further down the profile. The description of organic acid levels as the product of production and decomposition processes and the geochemical description of ligand-promoted chelation, dissolution, and transport may be useful process descriptions to model the effects of 10 biological exudates on mineral weathering rates and adaptable across a range of models. Winnick and Maher (2018) developed CrunchFlow to examine the dependence of mineral weathering rates on gaseous and dissolved CO_2 concentrations, and observed a very strong relationship between weathering rates and soil CO_2 , and suggested that this may be an important mechanism by which soil respiration of vegetation (and mycorrhizal fungi) may stimulate mineral weathering.

Mineral weathering is currently fully dynamically simulated in the PROFILE and ForSAFE models, which have been 15 widely used for unsaturated soils (for recent examples see Akselsson et al., 2016; Erlandsson et al., 2016; Belyazid et al., 2019; Phelan et al., 2014). In ForSAFE, tree cover, soil microbes and related biological processes are also integrally simulated. All processes described here refer to how they are simulated in the model based on best available empirical and theoretical knowledge. Trees are assumed to affect weathering through a number of causal pathways: Firstly, trees have a direct negative 20 influence on soil moisture through transpiration. The consequent reduction in soil moisture limits weathering directly, as the latter is directly dependent on water wetted mineral surface area. Water uptake also leads to an increase in element concentrations, which in turn activates the so-called weathering brakes that slow down the weathering rates as solute concentrations increase according to the principles of the transition state theory governing the weathering equations (Erlandsson et al., 2016). Secondly, nutrient uptake reduces the concentration of base cation weathering products, releasing 25 these brakes, thereby promoting weathering rates. Thirdly, plants are responsible for the production of organic matter, which, through below ground allocation and litter fall, feeds soil organic carbon, dissolved organic carbon and CO_2 concentrations. Both organic radicals and higher soil CO_2 pressure have positive influences on weathering rates. At the same time, the 30 decomposition of litter also releases the base cations contained in the former, thus increasing element concentrations and thereby slowing down weathering rates. The role of organic radicals and CO_2 pressure overrides the inhibition from the release of base cations. Fourthly, plants have a direct effect on soil solution proton concentration which promotes higher mineral dissolution, i.e. weathering. Plants can lower pH through the production of organic matter, but most importantly through the uptake of positively charged cations and release of protons to counterbalance charge. Lower pH in turn promotes higher weathering rates, but also the solubility of aluminium ions whose higher concentrations act as weathering brakes. The net effect on weathering, i.e. the balance between the positive effect from lower pH and the negative from higher aluminium concentrations, may differ depending on soil properties. ForSAFE does not treat the belowground physiology of trees as a

function of mycorrhizal type, but, as each tree species has a discrete parameter set, including root distribution and activity, mycorrhizal weathering promoting activities can be implemented largely within existing process descriptions. The contribution of biological weathering may be improved by division of the soil volume into rhizosphere or mycorrhizosphere and bulk soil portions. Process descriptions of root and hyphal influence on the solution and surface chemistry within the 5 rhizosphere/mycorrhizosphere could also be improved. Division of DOC into discrete chemical functional classes (promoting vs inhibitory, actively exuded vs. incomplete decomposition products) could increase our understanding of the influence of ligand promotion or inhibition of weathering rates.

7.3 Research priorities for modelling biological weathering

10 For models to be useful as predictive and instructive tools, to reproduce past and understand future responses to land management or climate change, they must be mechanistic, and describe explicitly processes that significantly impact the desired model outputs. At the same time, each additional layer of complexity, additional parameter and equation, and value that needs to be calibrated makes a model more difficult to apply across a range of settings, and may reduce the usefulness of 15 the model and hamper proper validation. In the above mentioned models we see those trade-offs in the treatment of DOC as single chemical species, in the division of AMF and EMF fungi into two hyphal length density classes, or angiosperms and gymnosperms, and in the treatment of all soil solution as a uniformly mixed pool as opposed to bound and mobile water. The appropriate level of complexity and the right set of processes and parameters for models that seek to quantify soil mineral weathering rates will ultimately depend on the particular time and spatial scale of the enquiry, as well as the quality of data 20 available.

There is evidence that, today, we lack models that are sufficiently mechanistic with regard to biological weathering to allow us to determine, with sufficient certainty, what levels of extraction from forests are sustainable, sustainable (acidic) deposition levels on catchments, or how patterns of global primary productivity may change over the next century in response 25 to global change. Despite this, modelling developments over the last decade have established clear paths for future developments. In the previous section we highlighted potential improvements to specific models. In general, attempts to model the effects of ligand promoted dissolution as a function of total DOC or oxalic acid as a marker for LMW compounds open the door for more complex descriptions of soil solutions and their effects on mineral weathering rates. The observation, across a variety of both empirical studies and modelling approaches, that nutrient uptake into vegetation is a major driver of 30 weathering rates should continue to drive research into the effects of soil solution concentrations near mineral surfaces, and their deviation from bulk soil solution, as a factor controlling dissolution rates. Ongoing research into the extent and chemistry of microbial biofilms in soils, aided by technological developments in microprobes and spectroscopy, is giving an increased understanding of their importance and extent in the soil for controlling the solution chemistry at mineral surfaces, which may

lead to incorporation into models. Spectroscopic techniques have given evidence of secondary layer formation and selective cation leaching that may limit mineral dissolution and cation supply on long time scales. These processes are so far not implemented in existing models. Similarly, a growing consensus on the importance of root length density and hyphal length density as important explanatory factors governing biological process rates, should provide both process descriptions and data 5 to incorporate them, potentially with the effects of biofilms, into models. Greater appreciation of the influence of species identity (bacterial, fungal, or plant) on weathering promotion will increase the granularity of biosphere descriptions, increasing the mechanistic nature of weathering rate models as predictive tools, particularly as environmental and management changes have the potential to alter species composition. A major area of model development has been in global plant productivity, not least because of the central role in the carbon cycle. Advances in describing belowground allocation (as opposed to 10 aboveground) have lagged far behind, but now, as appreciation of the longer residence time of below ground carbon increases, our understanding of how different factors control relative belowground allocation as a function of total productivity is increasing rapidly, and this should provide valuable data to improve model descriptions of biological weathering processes. Potentially, the increased use of forced experiments like drought induction, flooding, plantation, ditching, fire intervention at 15 different scales and using different weathering models can instruct us on the level of understanding that these different models achieve and where their weaknesses lie.

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8 Conclusions

In this paper we attempt to outline the consequences of interactions between minerals, microorganisms and plants at different spatial scales and to review the influence of biological processes on mineral weathering within an evolutionary context. The 20 interaction of microorganisms with rocks and minerals took place for 3.5 billion years before the appearance of the first land plants and there is documented evidence that early microorganisms had wide-ranging effects on both chemical and biological processes (Fig. 3), including (a) the accumulation of oxygen in the atmosphere, and the evolution of over two thirds of the minerals that exist today and (b) the evolution of plastids through serial endosymbiosis. The subsequent evolution of higher plants made possible by efficient photosynthesis and successive increases in their size, nutrient acquisition and ability to 25 colonize and allocate photosynthetically-derived carbon to mineral (and organic) substrates, has enabled them to have increasing influence as biogeochemical engineers (Fig 3c-g). Microbial symbionts have played an integral part in the evolution of plants and their ability to capture growth limiting nutrients such as N (Moreau et al., 2019). The influence of vegetation on mineral substrates is almost axiomatic but quantification of the contribution of plant-associated microorganisms to mineral weathering is problematical for two reasons. *Firstly*, the ubiquitous distribution of microorganisms, the fact that plants devoid 30 of microorganisms do not exist under natural conditions, means that plants need to be considered from a more holistic perspective, as holobionts, together with the many different microorganisms associated with them. *Secondly*, processes occurring at small spatial scales are difficult to quantify and upscale to the catchment, ecosystem or global scale. Although the

combined effects of plants and their microbial symbionts have quantifiable effects on mineral dissolution and capture of nutrients, continued effort must be directed at elucidating the identity, distribution and functional characteristics of these many different microbial taxa. Sverdrup et al. (2009) acknowledged the importance of “biologically induced systemic effects” on weathering and concluded that “the growth of the trees and forest growth represents the largest single biological process that 5 can affect weathering, followed closely by decomposition of organic matter”. Boreal and temperate forest ecosystems are characterised by ubiquitous symbiotic associations with ectomycorrhizal fungi and the central axiom of the current paradigm of ectomycorrhizal functioning is that these systems have evolved to promote tree growth through efficient uptake of nutrients, in particular through mobilisation of N via decomposition of organic substrates (Lindahl & Tunlid, 2015; Nicolás et al, 2019). Ectomycorrhizal fungi are therefore very likely to influence mineral weathering directly or indirectly and additional 10 information about their direct interactions with mineral substrates and likely responses to different types of environmental stresses, including those induced by forest management practices, is an important research priority. Weathering of minerals is important not just with respect to the sustainability of forestry. It is evident that the global weathering engine has had long-term effects on atmospheric CO₂ levels. Long term stabilization of C, derived from the atmosphere, in organic and mineral substrates, may take place through interactions involving glycoproteins, melanin, extracellular polymeric substances and 15 formation of secondary minerals and mineraloids. Better understanding of these processes may facilitate improved forestry management practices that not only ensure sustainable production of biomass but can also be integrated into new carbon dioxide reduction technologies.

Author contributions

20 R.D. Finlay wrote most parts of the paper but with suggestions and inputs from all co-authors. N. Rosenstock, S. Belyazid and S. Köhler, in particular, wrote most of the section on modelling and E. Bolou-Bi and H. Wallander provided substantial input to the section on stable isotopes. S. Mahmood provided substantial input ~~to~~ Figures 5 and 6. The work described in Figures 5 and 6 was carried out by S. Mahmood and Z. Fahad with advice from S. Köhler. E. Bolou-Bi carried out the stable isotope analyses in these experiments.

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25 Competing interests

The authors declare that they have no conflict of interest.

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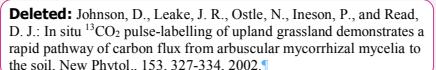
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