Review of « Influences of CO2 and Fungus-Assisted Bioweathering on Fluoridated Apatite » by Su et al.

Overall, while the manuscript addresses an interesting topic on the combined effects of CO_2 and fungal bioweathering on fluoridated apatite, the study is not fit for publication. It requires quite substantial clarifications and strengthening in many aspects of the discussion – I have strong reservations on the main claim pushed by the authors. The introduction relies heavily on reviews rather than primary studies, this limits precision and depth in describing fungal weathering processes and CO_2 effects and leaves a feeling of being a bit swallow. Key mechanisms, such as fungal strategies, hyphal acidification, and microbial community alterations, apatite weathering kinetics need more precise and quantitative context. The methods section is sometimes opaque, lacking sufficient detail on experimental procedures, and analytical parameters. Several claims in the results and discussion are either not supported by the data presented or lack sufficient quantitative evidence, particularly regarding Ca/P alterations. As it stands, I am not supportive of publication in Biogeosciences.

1 – Reference list is too heavy on the reviews/synthesis, more or less 1/3 of the total reference falls in this category – and are repeatedly cited for many different processes (e.g., Rawat et al., 2021 – 4 times ; Hoffland et al., 4 times etc.) In my opinion, this indicates a lack of precision and shows superficiality in the introduction.

Lines 61 : There are different types of fungi. Bonneville et al. use ectomycorrhiza (fungi in symbiosis with tree roots), which is an important distinction to make here, as the demand for P is not the same as in saprophytic fungi.

Lines 62 : What complementary process ?

Lines 67 : The use of Filipelli et al. (2008) is not appropriate here as this work does not show direct apatite dissolution kinetics, especially in relation to pCO2. At least give some reference that measure apatite dissolution kinetic as a function of pH. There are plenty.

Lines 69 : The same issue with the use of Drever et al., 1994. Again a review – please cite some actual study that measured or calculated pCO2 in rhizosphere or bulk soil instead of relying on reviews.

Lines 71 : The acidification near hyphae at the microscale was actually measured in Bonneville et al. 2011 and again Schmalenberger et al. 2015. Please cite primary studies.

Lines 72 and 73 : In what ways CO2 alters the structure of microbial communities ?

The introduction is not very exhaustive with respect to primary studies (i.e., no reviews!) of fungal bioweathering. Some papers that could be cited include Rosling et al. (2007) in Geobiology or Smits et al. (2014 see below for references), which provide field evidence questioning the efficiency of fungal weathering of apatite. Including such studies would give the introduction more breadth, which currently feels quite shallow. For example, the manuscript discusses the effect of CO2 on apatite weathering, but rates and kinetics—a quantitative aspect—are completely left out. The introduction needs to be more precise and detailed; there are too many shortcomings at the moment for the manuscript to be acceptable for Biogeosciences.

Line 104 : « Sterile water » ? OK, but what type of water ?? MilliQ ? Be precise

Line 103-106 : This protocol is quite opaque to readers who are not familiar with growing fungus. It should be rewritten more clearly.

Line 110 : Appetite ? This must be an error.

Line 110-111 : Please provide the Miller indices of the apatite face exposed to weathering

Line 131 : What is the P content of the PDA medium used in section 2.4 ? Are those P-limited conditions ?

Line 150-151 : I wonder about the effect of applying sterile water at the end of each weathering experiment ? Why is this treatment applied? In my experience with fungal weathering experiments, fungi can fragment rock substrate into very fine particles that are likely lost during this treatment, not to mention the potential dissolution of those colloidal/nanoparticle. The addition of water and its subsequent drying can also be induce the precipitation of secondary phases indepedently of fungal colonization. Was any control trial performed on non-exposed apatite slices to see the effect ? Overall I think this is not a good idea and the potential effect of this treatment should be discussed.

Line 156-158 : For EDS analysis, the count rate (counts·s^{-1}) is important—please indicate this. .

Line 166-169 : Concerning TEM-EDS measurements, what is the spot size of the beam, the step size along the profile, and the accelerating voltage used. What X-ray lines were analyzed and importantly the count s-1. There is a lack of explanation on how the Ca and P peak are quantitatively measured from EDS (e.g., background substraction). There is some ambiguity as the measurement are said to be semi-quantitative and yet Fig. 3 presents quantification of Ca and P and of their ratio.

Line 207-208 : How can those numbers be quantified if the TEM_EDS is said to be semi-quantitative (see line 168).

Line 220 : « -9-9 nm » ? Must be a mistake.

Line 238 : what is a « screw dislocation » ? This term must be defined.

Line 243-244 : « *A. niger induced more P depletion zones on the CFAP (Figs. 3a, c), suggesting that CFAP is more vulnerable to fungal weathering than LFAP*. »
This statement is not supported by the data shown in Figure 3. The data do not show a convincing Ca/P increase, synonymous of P depletion. At best, the topmost data point in CFAP show some P depletion but the rest of the Ca/P profile in CFAP (and LFAP) is within the bulk average meaning that there is no P alteration. The constant of Ca and P decrease at depth (in % atomic) are indicative of a thickness effect (i.e., the FIB foil is thinning out toward the top). In TEM-EDS, % atomic percent is not a concentration per unit volume, this is a normalized ratio of detected X-Ray intensities. Thickness variations affect the signals of elements differently. P (and O) emits lower energy X-rays than Ca, so its signal is absorbed more strongly as thickness increase. In addition, O (which contributes a large portion of the total signal) is strongly affected by thickness, which can bias normalized ratios. As a result, the relative percentages of Ca and P can change with depth even when their true concentrations do not.
My advice : work with smaller depth profile – say 500 nm within FAP or even smaller to minimize thickness change effect and detect some feintier chemical alteration. Use

STEM-EDS (instead of TEM-EDS) that focused beam down to a few nm and allow much finer characterization. After all, 45 days of alteration is not much, in order to gain time, you need to look small.

Line 255-257 : « *The results that more calcium oxalate were formed near the mycelium on the CFAP than LFAP (Figs. 2c, d), further confirmed that the bioweathering of CFAP is stronger than that of LFAP* »
This claim is only vaguely supported by the data presented. In figure 2, there is only a small portion of the mycelium network shown (is that representative ?) Using a collection of SEM images, it would have been easy to count Ca-oxalate crystals on the two treatments and make a stronger case for that there is indeed a difference between to two treatment.

Line 257- 263 : *« A. niger can also accelerate the physical destruction of FAP through the biomechanical forces of mycelium growth. Fungal appressoria can produce osmotic pressures of up to 10–20 μN/μm2 during hyphal growth, which would substantially accelerate the physical weathering (Hoffland et al., 2004; Howard et al. 1991). Screw dislocations in crystal cross-sections destabilize CFAP structure, enhancing its susceptibility to biomechanical destruction. Moreover, the released fluorine from FAP did not cause evident toxicity on the mineral surface. »*

Again, this whole paragraph is not supported by the data shown. Do the authors observe appressoria (those are recognizable structure)? To my knowledge, *Aspergillus niger* do not form appressoria. As for the biomechanical forcing, this could have been shown as in Bonneville et al., 2009 (https://doi.org/10.1130/G25699A.1) looking at crystal orientation by SAED using SAED (electron difftraction in TEM), but no such data presented.

Lines 264 -294 : This section is not very convincing. OK there might be a rougher surface developping on apatite crystal due to soil and fungal respiration but this discussion lacks nuance. First, acidification near hypha due to respiration was shown before on a number of rock substrate (see Schmalenberger et al, 2015 -https://doi.org/10.1038/srep12187), then Smits et al. (2014) -https://doi.org/10.1007/s11104-014-2222-6 presented field evidence questionning the acceleration of apatite weathering by fungi, in fact this study showed a retarding effect of fungal colonization on apatite weathering under field conditions.

This section is not very convincing. OK, there might be a rougher surface developing on apatite crystal due to soil and fungal respiration, but this discussion lacks nuance. First, acidification near hyphae due to respiration was shown before on a number of rock substrates (see Schmalenberger et al., 2015). Then Smits et al., 2014 presented field evidence questioning the acceleration of apatite weathering by fungi; in fact, this study showed a retarding effect of fungal colonization under field conditions likely due to complex interactions with soil chemistry, microbial communities, and organic matter. The manuscript would benefit from acknowledging these contrasting observations, discussing the limitations of laboratory-based microcosm experiments, and providing a more balanced interpretation of how fungal respiration and CO_2 may affect apatite weathering in both controlled and field-relevant contexts.