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RESEARCH ARTICLE

The dissolution of fluorapatite by phosphate-solubilizing fungi: a balance between enhanced phosphorous supply and fluorine toxicity

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Abstract

Fluorapatite (FAp) is the largest phosphorous (P) reservoir on Earth. However, due to its low solubility, dissolved P is severely deficient in the pedosphere. Fungi play a significant role in P dissolution via excretion of organic acids, and in this regard, it is important to understand their impact on P cycling. The object of this study was to elucidate the balance between P release and F toxicity during FAp dissolution. The bioweathering of FAp was assisted by a typical phosphate-solubilizing fungus, *Aspergillus niger*. The release of elements and microbial activities were monitored during 5-day incubation. We found that the release of fluorine (F) was activated after day 1 (~90 mg/L), which significantly lowered the phosphate-solubilizing process by day 2. Despite P release from FAp being enhanced over the following 3 days, decreases in both the amount of biomass (52% decline) and the respiration rate (81% decline) suggest the strong inhibitory effect of F on the fungus. We thus concluded that F toxicity outweighs P supply, which in turn inhibits fungi growth and prevents further dissolution of FAp. This mechanism might reflect an underappreciated cause for P deficiency in soils.

Keywords Phosphorus dissolution · Fluorine toxicity · *Aspergillus niger* · Bioweathering · RISE · Fluorapatite

Introduction

Phosphorus (P) is an essential element for all life and thus a critical factor in facilitating agricultural productivity (Butler et al. 2018). Available P is always bio-limiting due to its low solubility in the presence of major cations such as calcium (Ca) in soil/aqueous environments (Tiessen et al. 1984; Roberts et al. 1985). Fluorapatite [FAp, $Ca_{10}(PO_4)_6F_2$] is the most common P-bearing mineral phase in igneous, metamorphic, and sedimentary rocks (Pan and Fleet 2002), contributing to over 90% of total P on Earth. However, its low solubility product (*Ksp*, around 10^{-120}) makes P unavailable to the biosphere in most environments (Wang and Nancollas 2008).

Phosphorus deficiency has become a worldwide challenge for agricultural production due to the limited reservoirs of phosphate-bearing rocks over the past 50 years (Natasha 2009). It was predicted that the overall demand for P fertilizers will grow by 2.5–3.0% per year due to the increase in global population (Natasha 2009). Such challenges become more severe when considering the fact that even in regions with abundant FAp, the soils are still insufficient of bioavailable P. For instance, there are ~1.25 billion tons of P ore in Guizhou province, China (Zhang et al. 2014), but the available P in soil surfaces (based on a survey of 770 cultivated soil samples) is lower than 10 mg/L (Yin and Zeng 1993).

Many studies have focused on improving the solubility of FAp (Pan and Darvell 2007; Brahim et al. 2017). Acidic environments can significantly enhance P release from P-bearing mineral phases (Plata et al. 2021), and it has been shown that local acidification by phosphate-solubilizing microorganisms (PSM) can result in the solubilization of Ca-phosphates and mobilization of dissolved phosphate (Jones and Oburger 2011; Konhauser et al. 2011). Specifically, fungi,

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such as the genera *Aspergillus* and *Penicillium*, have been utilized in extracting phosphate from minerals through the secretion of organic acids (Whitelaw 2000). Fungi usually have higher efficiency at enhancing P release compared to bacteria due to their capacity of generating higher acidity (pH around 1–2) than typical phosphate-solubilizing bacteria (pH of ~5) (Li et al. 2016c). *Aspergillus niger* (*A. niger*) has been shown to be one of the most representative PSM because it can secrete multiple and abundant organic acids, e.g., oxalic ($K\alpha_1 = 6.5 \times 10^{-2}$), tartaric ($K\alpha_1 = 9.2 \times 10^{-4}$), and citric acids ($K\alpha_1 = 7.4 \times 10^{-4}$), which enhance the dissolution of P from P-bearing minerals, such as FAp (Li et al. 2016b). Therefore, *A. niger* is considered to have high potential in bioweathering (Song et al. 2019).

Although fungi have been documented to enhance the solubilization of P from FAp, their growth can be impacted by toxic metals, such as lead (Pb), zinc (Zn), and cadmium (Cd), which are common trace components incorporated in FAp (Chen et al. 1997). These heavy metals can be readily released into soil pore waters as a consequence of mineral dissolution (Wainwright et al. 1993) and inhibit fungal activity via binding to microbial enzymes, degrading proteins, reducing microbial respiration, and reforming microbial morphology (Gadd 2005). Particularly, fluorine (F), which accounts for 3 wt% of FAp, is a toxic by-product that adversely impacts the metabolism of some microorganisms (Ochoa-Herrera et al. 2009; Ghosh et al. 2013; Zuo et al. 2018; Yadav et al. 2019). For example, F can negatively affect the growth of *A. niger* through complexation with Mg^{2+} and Ca^{2+} cations in the cell (Lebioda et al. 1993; Barbier et al. 2010; Mendes et al. 2013), as well as inhibit the activity of phosphoryl transfer enzymes which are essential for energy production and nucleic acid synthesis (Li 2003; Barbier et al. 2010; Ji et al. 2014; Zhou et al. 2015).

Previous studies have documented the potential inhibitory effect of F released during microbial phosphate solubilization (Mendes et al. 2013), but to the best of our knowledge, there have been no studies explaining the balance between toxic F release and nutrient (P) supply during FAp dissolution by PSM. It has previously been demonstrated that the weathering of F-enriched minerals contributed to the increase of F level in aqueous system (Brindha et al. 2016), and F concentrations in wastewater released from P fertilizer manufacturers can reach more than 5000 mg/L (Tew 2018). Thus, it was estimated that 10,400 t of F would be released annually from phosphate fertilizer production (Fuge 2019). Given the magnitude of F release, it is essential to quantify the impact it has on the growth of FAp-solubilizing fungi, i.e., to correlate F release to P biogeochemical cycle.

In this study, we evaluated F toxicity to *A. niger* by quantifying fungal biomass production and respiration during the process of FAp dissolution. We hypothesize that F toxicity will lower FAp dissolution and ultimately lead to a decline in P solubilization in the long term. The objective of our research is to associate the toxicity of F with the biogeochemical cycle of P, both of which originate from the bioweathering of FAp.

Experimental procedures

Sample preparation

Fluorapatite samples were collected from the Kaiyang Phosphate Rock Reserve in Guizhou province, China, which has an estimated 1.25 billion tons of phosphate (Zhang et al. 2014). FAp samples were powdered by a Retsch MM400 mixer and filtered through a 100-μm-sized sieve for the experiments outlined below.

A representative phosphate-solubilizing fungus, *A. niger* (CGMCC No.11544), was isolated from the soybean rhizosphere soil in Nanjing, China. It was previously incubated on potato dextrose agar (PDA) plates at 28°C for 5 days to form sporulation prior to experiments. The formed spores were carefully freed from the culture surface with a fine artist's brush, and the spore concentration was determined by a haemacytometer.

Incubation of *A. niger* with FAp

The liquid PDA medium (50 mL) was transferred into 150-mL conical flasks and was sterilized by autoclaving at 115 °C for 30 min. The experiments were performed with four treatments: (1) culture medium only (Control); (2) FAp + culture medium (Ap); (3) *A. niger* + culture medium (ANG); and (4) *A. niger* + FAp + culture medium (ANG + Ap). The control treatment was designed to investigate the release of P from the medium. In the Ap treatment, FAp was added to the medium with a solid/liquid ratio of 50 mg/50 mL. In the ANG treatment, 0.5 mL spore suspension of *A. niger* (1.05×10^9 spores mL^{-1}) was inoculated in a 50 mL medium. In the ANG + Ap treatment, the medium and FAp were mixed with a solid/liquid ratio of 50 mg:50 mL. Then, a 0.5 mL spore suspension of *A. niger* (1.05×10^9 spores mL^{-1}) was transferred to a 150-mL Erlenmeyer flask. All the treatments were incubated in a rotary shaking incubator at 28°C with an agitation speed of 180 rpm for 5 days. All the treatments were performed in triplicate.

A parallel incubation experiment was conducted to measure microbial respiration. Fifty milliliter of the liquid PDA medium (containing 50 mg of FAp) was added into a 100-mL serum bottle (in triplicate). Then, 0.5 mL of the spore suspension was added. All the bottles were covered with parafilm and incubated for 60 h at 28°C in dark. The respiration rate of the fungus was measured by calculating CO_2 fluxes to evaluate their bioactivity. Gas samples were collected by sealing the

bottles 1 h prior to sampling (unsealed at all other times) for the purpose of CO_2 measurement. The gas samples (8 mL) were collected every day during incubation, by using a polyethylene syringe with three-way stopcocks.

For all of the above treatments, pH and the concentrations of dissolved Ca, F, and organic acids in the medium were analyzed after filtration through 0.22 μm membranes. After 5 days incubation, the fungal pellets were filtered from the medium. All the fungal pellets were washed and air dried at 65°C for 3 h before weighting.

To investigate the morphology of bio-weathered FAp by *A. niger*, a FAp thin section (3 cm × 2 cm × 2 mm) was inserted into the PDA agar plates. We used a sterile loop to inoculate spores to solid PDA medium. Additionally, the FAp surface was investigated by Raman imaging and scanning electron microscopy (RISE) after 5-day incubation. After surface wiped by anhydrous ethanol, the FAp thin section was investigated by electron microprobe (EMP). Experimental sketch and microscopy images were provided in Fig. S1 (Supplementary Material).

Instruments

The pH was measured with a SG98 InLab pH meter (Mettler-Toledo Int. Inc.) with an Expert Pro-ISM-IP67 probe. The P and Ca concentrations of the medium were analyzed by inductively coupled plasma optic emission spectrometry (ICP-OES, Agilent 710). The F concentrations were analyzed by ion chromatograph (ICS, Metrohm 940). The CO_2 concentrations were analyzed using a GC equipped with flame ionization detector (GC-7890B, Agilent Technology Inc.). The concentrations of oxalic and citric acids were analyzed by HPLC (Agilent 1200). The column temperature of the HPLC was set at 30°C. The standard solutions of oxalic acid were diluted into 50, 40, 30, 20, 10, 5, and 0 mg/L, respectively. The *R* square value of the internal standard curve was 0.999.

The RISE system consists of a WITec (Wissenschaftliche Instrumente und Technologie GmbH, Germany) Alpha 300 confocal Raman microscope combined with SEM (TESCAN-VEGA3). Both SEM mode and LM (light microscopy) modes were applied under RISE. The spectral region of 0–4500 cm^{-1} was recorded using 488-nm laser (3 mW with 30 × 4-s scans). To investigate the homogeneity of stoichiometry after fungal dissolution, Ca and P concentrations of the FAp section were collected by EMP (JXA-8230, JEOL) after 5-day incubation. The Ca and P were calibrated by using Durango apatite.

Statistical analysis

All the treatments were conducted in triplicate. Average values and standard deviations were calculated for each experiment. One-way ANOVA, with Turkey's test, was performed on the data. If groups did not contain the same lowercase letter, it means the groups were significantly different (P <0.05). The R 3.6.2 software was used for statistical analyses.

Results and discussion

The biomass and respiration influenced by FAp

The weight of biomass in the ANG + Ap treatment (*A. niger* + FAp + culture medium) was lower than that in the ANG treatment (*A. niger* + culture medium) (see Fig. 1A). After 5-day incubation, the weight of biomass for the ANG treatment increased from 402.23 to 1928.57 mg (Fig. 1A). By contrast, the weight of biomass increased from 58.64 to only 930.47 mg for the ANG +Ap treatment over the same time period (Fig. 1A). This difference in biomass between the two treatments could possibly be due to the F release during FAp weathering, which was toxic to microorganisms. Previous studies have also shown that a decrease of about 75% in fungal growth was found when F concentrations were elevated to levels of 22.9 mg/L (Mendes et al. 2013).

The microbial respiration results were consistent with the above biomass analysis. The maximal CO_2 emission rate was reached on day 1 for both the ANG and ANG + Ap treatments

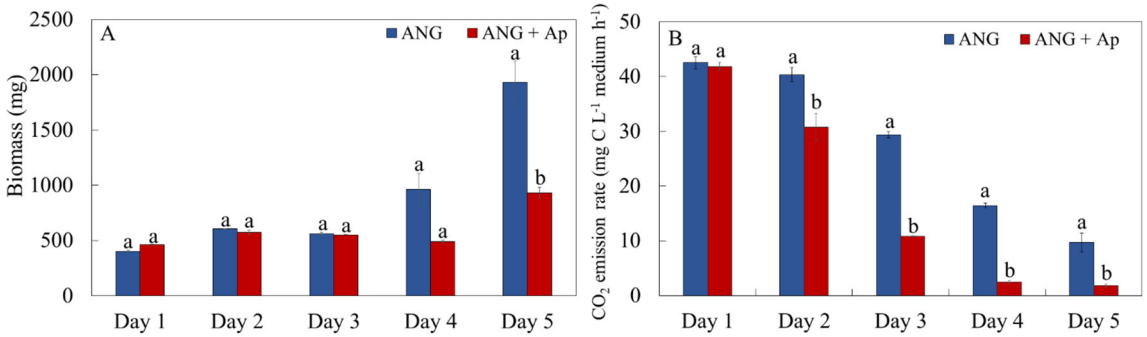

Figure 1. The biomass (**A**) and rate of respiration based on CO_2 emission (**B**) for ANG and ANG + Ap treatments during 5-day incubation. "a" and "b" are labels for one-way ANOVA test, where different letters represent different groups. Columns with the same letter are not significantly different by the Tukey's test (P < 0.05). Data presented is mean + standard error *(N=3)*

with similar hourly respiration intensity, i.e., 42.51 and 41.77 mg C L^{-1} medium. The respiration rate of the ANG + Ap treatment was consistently lower than that of the ANG treatment, suggesting the possibility of F toxicity in the ANG + Ap medium (Fig. 1B).

P, Ca, and F release from FAp

The P released from FAp (with or without *A. niger* addition) was measured after 5 days of incubation. In the Ap treatment, the P concentration was stable at 55.96 mg/L, which is close to the value (57.56 mg/L) of the control treatment (Fig. 2A), indicating the low P solubility of FAp. In the ANG treatment, the concentration of P increased slightly from 5.45 to 6.35 mg/L during the first 2 days of incubation. The concentration of P then declined to below the detection limit by day 3 (Fig. 2A). By contrast, in the ANG + Ap treatment, the concentration of P increased from 3.19 (day 1) to 261.95 mg/L (day 5) (Fig. 2A). Compared with other cultural media, the P concentration in the ANG + Ap treatment was the lowest on day 1 but was the highest among all the treatments after 2 days of incubation (Fig. 2A).

The concentrations of Ca in the medium were stable at the level of 5 mg/L throughout the experimental period for the control treatment (Fig. 2B). In the Ap treatment, the Ca concentration was stable at 21.76 mg/L over the experimental period (Fig. 2B). By contrast, Ca concentration increased from 1.27 to 2.75 mg/L for the ANG treatment during the first 2 days and then decreased to 0 mg/L by day 4 (Fig. 2B). The Ca concentration in the ANG + Ap treatment increased dramatically from 32.42 to 132.84 mg/L during the first 2 days, but then fluctuated within 110–120 mg/L during the rest of experimental period (Fig. 2B).

With regards to F concentrations in the culture media, the Ap treatment had relatively consistent F concentrations of around 2.48 mg/L. In the ANG + Ap treatment, the F concentration increased from 88.99 to 213.73 mg/L during the first 4 days. It then slightly decreased to 204.37 mg/L by day 5 (Fig. 3). The F toxicity experiments demonstrated that F concentration of 40 mg/L can lead to a decrease in *A. niger* bio-reactivity (see Fig. S5 in Supplementary Material). The F concentration in ANG + Ap treatment were ~90 mg/L after 1-day incubation, which is higher than the previously reported value (22.9 mg/L) (Mendes et al. 2013). Variations in fungal strains and incubation conditions would possibly cause such differences, but all the evidences suggested that a considerable amount of F was accumulated during fungal weathering of FAp. This confirmed our previous results of the decline in the activity of *A. niger* (e.g., the low biomass and respiration rates in ANG + Ap compared to ANG) (see Fig. 1).

In the short term (at the time scale of several days), *A. niger* secretes organic acids to enhance P release (Figs. 4 and 5). However, when the F concentration reaches toxic levels, the growth of fungi becomes inhibited which leads to no further increase of P concentration in the experimental cultures (Fig 2A). Meanwhile, the suppression of microbial growth will also reduce P consumption in the system. Therefore, a relatively high P concentration was observed in our experiments (see the treatment ANG+Ap in Fig. 2). It should also be pointed out that laboratory incubation usually provides the ideal environment for *A. niger* growth, whereas the natural environments could have additional environmental stress/limitations (Moody et al. 2019). Hence, we propose that in natural environment, phosphate solubilization triggered by *A. niger* will be lower than our experimental results.

Organic acid secretion

Oxalic acid is the primary organic acid secreted by *A. niger*. In the ANG treatment, the concentration of oxalic acid averaged 626.56 mg/L during the 5 days of culture (Fig. 4A). The concentrations of oxalic acid increased from 514.27 to 708.97 mg/L during the first 3 days and then experienced a slight decline at day 4 (671.26 mg/L) (Fig. 4A). At day 5, the concentration of oxalic acid further declined to 626.56 mg/L. By comparison, the ANG + Ap treatment had oxalic acid concentrations significantly lower than that of the ANG treatment, which fluctuated in a range of 30 mg/L during the 5 days of

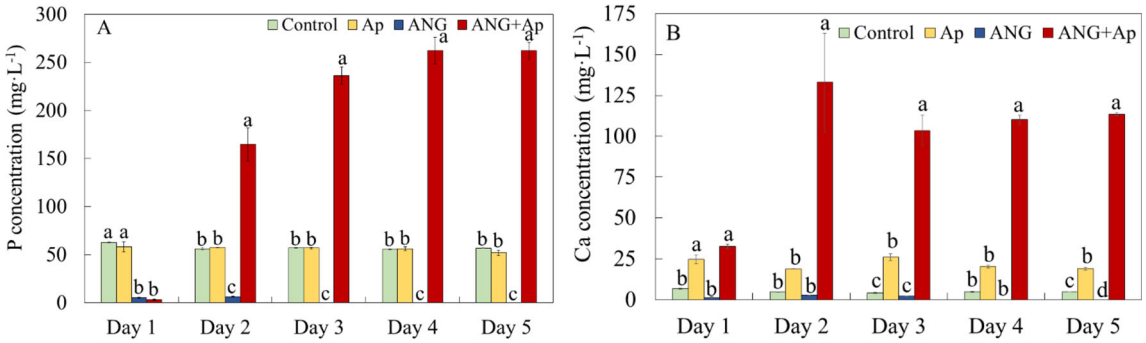

Figure 2. The concentrations of P (**A**) and Ca (**B**) in the liquid PDA medium. "a," "b," "c," and "d" are labels for one-way ANOVA test, where different letters represent different groups. Columns with the same letter are not significantly different by the Tukey's test ($P < 0.05$). Data presented is mean + standard error ($N=3$)

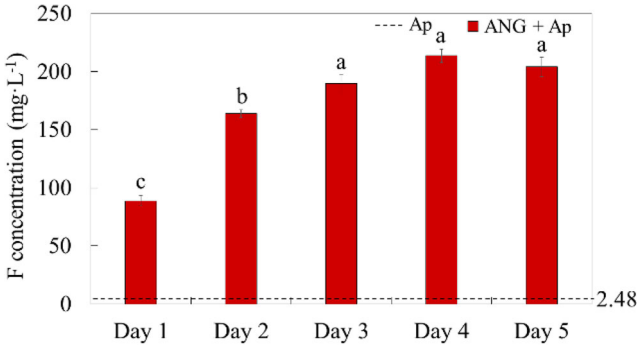

Figure 3. The concentrations of F in the ANG + Ap treatment. "a," "b," and "c" are labels for one-way ANOVA test, where different letters represent different groups. Columns with the same letter are not significantly different by the Tukey's test ($P < 0.05$). Data presented is mean + standard error ($N=3$)

incubation and declined to 19.23 mg/L at the last day of the treatment (Fig. 4A). We attribute the difference in oxalic acid concentration between ANG + Ap and ANG to the fact that the release of F in ANG + Ap treatment leads to the decline of oxalic acid secretion. There is also another possibility that oxalate acid could bind with the released calcium and form calcium oxalate crystals.

Compared to the decrease in oxalic acid production in our experiments, previous work has shown that the production of citric acid was usually enhanced under environmental stress (Li et al. 2016a). In the ANG treatment, the concentration of citric acid increased from 958.24 to 1187.48 mg/L after the first 2 days of incubation. Afterwards, it dropped to 409.60 mg/L at day 3 (Fig. 4B) and then decreased to 35.68 mg/L and 31.88 mg/L at days 4 and 5, respectively. For the ANG + Ap treatment, the concentration of citric acid was 556.20 mg/L at day 1 and then increased to 999.15 mg/L and 921.31 mg/L at days 4 and 5 (Fig. 4B). Despite higher citric acid secretion, the acid constant of citric acid ($K\alpha_1 = 7.4 \times 10^{-4}$) is two orders of magnitude lower than that of oxalic acid ($K\alpha_1 = 6.5 \times 10^{-2}$); thus, citric acid shows relatively low impact to the dissolution of FAp and release of P. Meanwhile, the elevated citric acid concentration in ANG + Ap treatment provides further evidence for F toxicity. Such toxic effects can be even higher when considering the fact that F content in FAp can reach to 3wt% and *A. niger* may have experienced greater F stress on FAp surfaces.

The pH values of the culture media fluctuated between 2 and 5 for both the ANG and the ANG + Ap culture. In the ANG treatment, the pH value dropped from 3.42 to 2.03 after the first 2 days, and then increased to 4.38 at day 5 (Fig. 5). By comparison, the pH value of the ANG + Ap treatment started initially high (4.76 at day 1) and then decreased to 3.40 with fluctuations of 0.06 during the following 4 days. The pH value of the ANG treatment followed a general increasing trend (except for day 1) compared to the ANG + Ap treatment that decreased during the 5 days of treatment (Fig. 5).

Observation of FAp surface using RISE and SEM

Clusters of spores were observed on the surface of the FAp thin section (Fig. 6A), and the observation of spores on the thin section was confirmed by Raman spectra based on the RISE technique (Fig. 6B). The peak at ~984 cm^{-1} was due to the stretching of carbon atoms bonded with other nitrogen or carbon atoms, which was usually attributed to the presence of proteins (Moradi et al. 2017). The intense peak at ~1558 cm^{-1} was assigned to δ(NH) and ν(CH) of the amide group in the fungus (Edwards et al. 1995) (Fig. 6B). Notably, there were no evident hyphae accumulating on the FAp surface. The observation of only spores and scarce hyphae at the surface of FAp is likely attributed to the toxicity of F to fungi during FAp dissolution, because previous studies have shown that spore germination is more stable than hyphae extension when fungi were under environmental stress (Bartolomeesteban and Schenck 1994; Mcmillen et al. 1998; Palma-Guerrero et al. 2008). Other possibilities, such as the higher affinity of spores to FAp surfaces than hyphae, could also explain this phenomenon.

Observation of FAp surface using EMP

The average weight percentage of P_2O_5 (42.55 wt%) and CaO (55.01 wt%) were measured based on EMP analyses on the

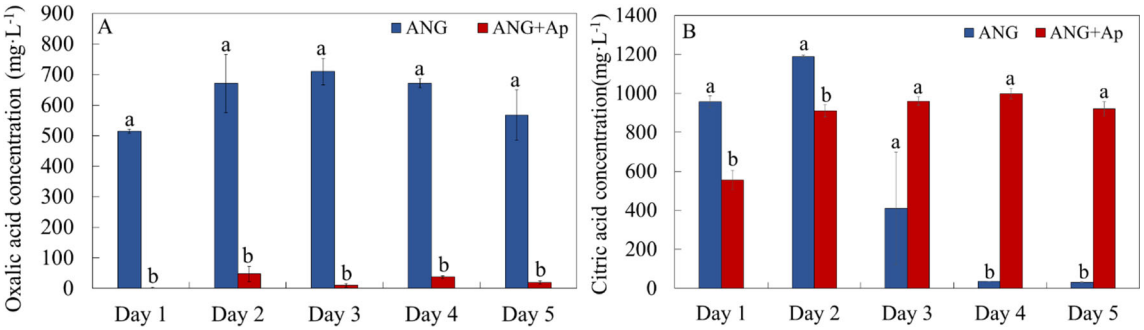

Figure 4. The concentrations of oxalic acid (**A**) and citric acid (**B**) secreted by *A. niger*. Columns with the same letter are not significantly different by the Tukey's test ($P < 0.05$). Data presented is mean + standard error *($N=3$)*

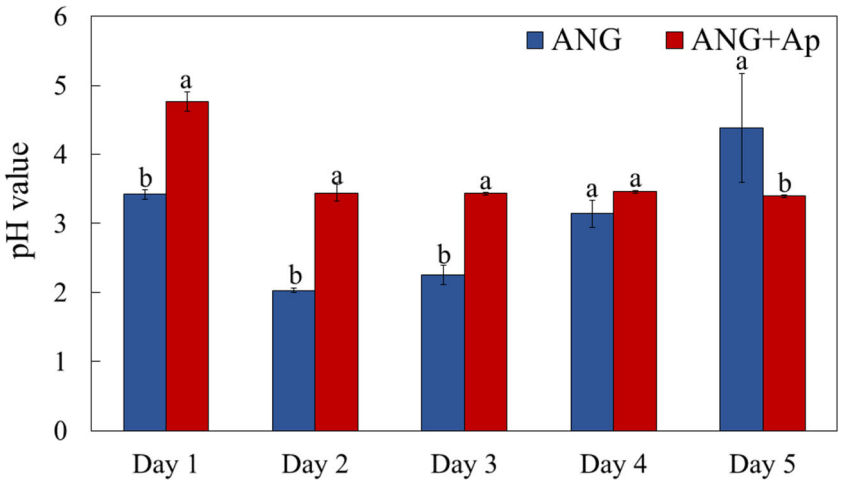

Figure 5. The medium pH values of ANG and ANG + Ap treatments. Columns with the same letter are not significantly different by the Tukey's test ($P < 0.05$). Data presented is mean + standard error *(N=3)*

FAp section (after removal of fungus and spores) (Fig. S2). The Ca/P molar ratio of the 21 spots (randomly selected) on the FAp surface showed an average value of 1.64 (Fig. S3). The values have a low standard error of 0.0041, indicating the homogeneity of Ca/P ratios after incubation with fungus (Fig. 7 and Fig. S2 &S3). A previous study demonstrated that surface compositional variation could cause chemical heterogeneity on mineral surface (Li et al. 2016b). For example, in an experiment studying lizardite dissolution by fungi, the chemical heterogeneity was reflected by the depletion of Fe. Our results, however, showed that FAp surfaces were relatively homogeneous, which could possibly be due to the fact that there were no obvious hyphae accumulating on the FAp surface because of the F stress. Therefore, the results in present study confirmed that *A. niger* did not dissolve FAp effectively, based on both the limited biochemical and biomechanical weathering on FAp surface.

FAp has a F/P molar ratio of 1/3, while our experimental results show that the concentration of F is always higher than P in the ANG + Ap treatment, i.e., F/P >1 (Fig. S4A). Moreover, in the ANG + Ap treatment, we observed a linear correlation between the released P and F, with a slope of ~1.3 (Fig. S4B). The relatively low P might be due to the consumption of P by the fungus during incubation. We hence conclude that F concentration will be relatively higher than P in the FAp dissolution environment, which would prove highly toxic to the microorganisms.

Many areas in the world experience challenges of P deficiency, even though they have abundant phosphate reserves. For example, apart from Guizhou province in China, Morocco has around 77–85% of the world's remaining P reserves (Kauwenbergh 2006), yet arable lands in Morocco still have the problem of P insufficiency (Walan et al. 2014). Our study shows that F toxicity should be considered in terms of the effectiveness of FAp bioweathering. In addition, there is also a potential threat that F can penetrate through soil profile and contaminate groundwater. For example, in Guizhou province, it has been reported that F content in groundwater reaches levels of 1.5 mg/L, which is higher than drinking standard (1.0 mg/L) (Pickering 1985; Zhu et al. 2000). Widespread F toxicity can cause low phosphate solubilizing by microorganisms at a large

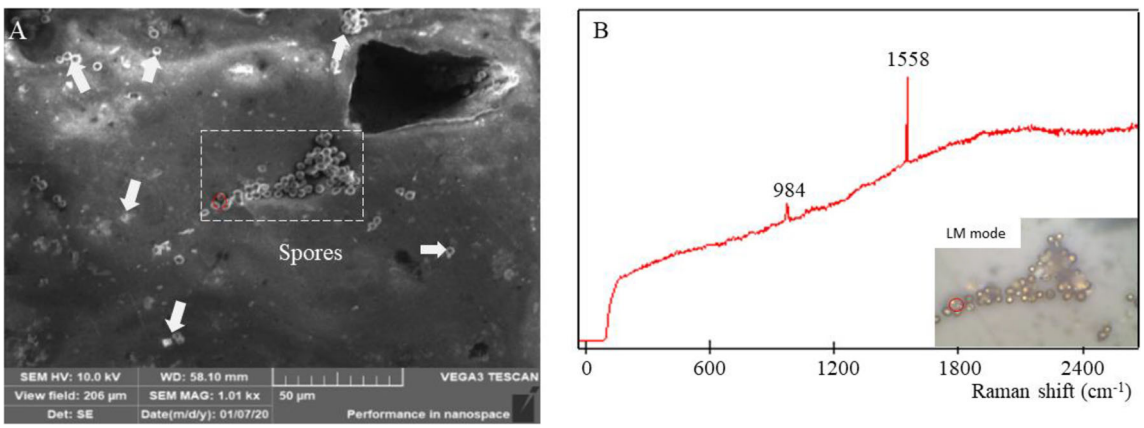

Figure 6. RISE analysis on the surface of FAp (with SEM and Raman spectroscopy). **A** SEM imaging on the FAp surface after 5-day incubation with *A. niger*. The arrows and rectangle denote clusters of spores. The red circle is the Raman spot site. **B** RISE spot analysis (0–2700 cm^{-1}) on the FAp surface

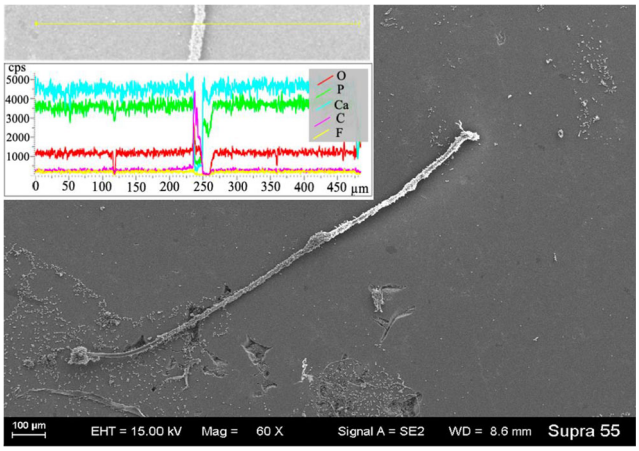

Figure 7. SEM imaging and EDS analysis on the FAp surface. SEM imaging on the FAp surface after 5-day incubation. EDS was performed as line scanning on the FAp surface. The intensity of different element are shown in different color. (red, oxygen; green, phosphorus; blue, calcium; pink, carbon; and yellow, fluorine)

geographical scale, which in turn can lead to P deficiency in terrestrial systems.

Conclusions

In this study, we elucidated the processes of FAp dissolution by *A. niger* by analyzing the concentrations of released P, Ca, and F from FAp. In addition, microbial biomass and respiration were measured to assess the toxicity of F and the nutrient supply. Our results demonstrated that PSM could secrete organic acids to enhance P release from FAp, which led to the increased microbial growth. However, F was also released to the aqueous environment and significantly inhibited PSM growth (on a timescale of days). The outcome of both mechanisms resulted in the decrease in biomass and rate of respiration compared to blank PSM culture (ANG culture). Significantly, we conclude that the toxicity of F exceeds the benefits of P for PSM growth. Further studies of F levels in the nature environments are required to explain its toxicity towards PSM and correlation with P cycling.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11356-021-15551-5.

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Availability of data and materials All data generated or analyzed during this study are included in this published article (and its supplementary information files).

Author contribution The manuscript was written by X.S., W.H., and K.K., with assistance of Y.G., M.S., and L.T; Ms. Y.G. contributed to the graphical abstract; X.S., L.T., and M.S. participated in the experiment design; X.S., W.H., and Y.G. analyzed and interpreted the data; the project was supervised by Z.L.

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Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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