Elemental and isotopic perspectives on the impact of arbuscular mycorrhizal and ectomycorrhizal fungi on mineral weathering across imposed geologic gradients

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5 **Abstract**

Symbiotic mycorrhizal fungi are thought to play a role in weathering by targeting minerals that contain required plant nutrients, such as phosphorus (P), magnesium (Mg) and calcium (Ca). Field experiments coupled with geochemical analyses can provide insights into nutrient cycling in forest landscapes dominated by arbuscular-mycorrhizal (AM) and ectomycorrhizal (EcM) fungi. In-growth bags containing different rock types of varying nutrient content (granite, tonalite) were fabricated to create an in-situ geologic gradient for 100-day deployment in two forest stands dominated by different mycorrhizal symbioses in Hubbard Brook Experimental Forest in New Hampshire, USA. Mineral dissolution within the substrate bags under different biologic conditions was assessed via analysis of major elemental nutrients (Ca, Mg, and P) and isotope ratios of lead (Pb) and strontium (Sr) on leachates representing both the easily exchangeable and future available weatherable mineral stores. We hypothesized that the two types of mycorrhizal fungi would differ in their weathering ability and would show significant variations in tracers of mineral weathering from the same rock type in the two stand but only Ca concentrations in the exchangeable solution of the tonalite and the future weatherable stores solutions of both tonalite and granite varied significantly between the two fungal types. The other measured nutrient concentrations (Mg, P) and Pb and Sr isotopic compositions of the exchangeable and weathering solutions were not significantly different within lithology. Taken together, the results suggest that weathering fluxes in AM- and EcM- dominated forest stands may be more comparable than previously argued.

1. Introduction

Soil biology can influence plant health and productivity, provide access to soil and bedrock nutrients, and consequently can contribute to mineral weathering. Weathering rates and their interactions with biotic demand are among the least constrained parts of ecosystem nutrient budgets intended to advise in recommendations for sustainable forest management practices (Paré and Thiffault, 2016; Futter et al., 2012; Vadeboncoeur et al., 2014). An important component of the soil biology community is symbiotic fungi, which form associations with approximately 80% of plant species and are responsible for major

mineral transformations, particularly the distribution of nutrients such as phosphorus (Hoffland et al., 2004; Gadd, 2007; Berner et al., 2012). Arbuscular (AM) and ectomycorrhizal (EcM) fungi both have the ability to colonize a host plant and form a symbiotic relationship though they are anatomically and phylogenetically distinct (Smith & Read, 2008). EcM fungi form a mutualistic relationship with the roots of plants, including conifers and some temperate angiosperms (particularly the *Fagaceae* and *Betulaceae*), while AM fungi are more common across most families of plants (Taylor et al., 2009). These fungi provide increased access to water and nutrients for the host and in turn receive carbon for survival (Gadd, 2007; Landeweert et al., 2001). This host colonization increases root zone extent, acidification, nutrient uptake, and mineral weathering rates (Hagerberg et al., 2003).

Ectomycorrhizal fungi, largely due to their production of organic acids, are thought to enhance mineral weathering and have been shown to actively seek out nutrients and preferentially colonize areas with higher nutrient content (Hamburg et al., 2003; Hedh et al., 2008; Leake et al., 2008; vanBreemen et al., 2000). Ectomycorrhizal hyphal tips can produce organic anions and protons, thereby promoting the release of essential elements like calcium (Ca) and magnesium (Mg) from minerals and making them available for uptake by the fungi (Hoffland et al., 2004). Ectomycorrhizal fungi have also been observed to create tunneling features in minerals, further supporting the idea of their increased weathering ability (van Breemen et al., 2000; Hoffland et al., 2002; van Schöll et al., 2008).

Ectomycorrhizal fungi have been proposed to be especially important for providing nutrients in soils with low concentrations of available essential elements such as phosphorus (P) or Ca (Blum et al., 2002; Hamburg et al., 2003; Paré & Thiffault et al. 2016; Smits et al., 2012). Chemical signatures (primarily Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$) of a sequential digestion of soil minerals led Blum et al. (2002) to argue that apatite is an important source of Ca in soil at the Hubbard Brook Experimental Forest (HBEF), which is an intensively-studied ecosystem that has undergone many decades of base cation leaching due to elevated acid deposition (Likens et al., 1996). Apatite-derived Ca was found in elevated concentrations in soils supporting tree species known to form symbioses with EcM fungi and, accordingly, Blum et al. (2002) concluded that EcM

dissolution of minerals provided an important pathway for plants to directly access mineral-hosted nutrients. The distribution and cycling of P in older soils is governed primarily by processes such as organic matter recycling and secondary mineral decomposition due to the inaccessibility of P remaining in parent material (Walker and Syers, 1976).

Further evidence for EcM contributions to mineral weathering was documented in field and laboratory experiments conducted by Hagerberg et al. (2003). Mesh ingrowth bags containing sand amended with biotite (a source of Mg) or apatite (a source of P) were buried in the organic soil (Hagerberg et al., 2003). Rare earth element (REE) distributions in a *Pinus sylvestris* seedling colonized by EcM fungus showed higher concentrations of REEs in bags amended with apatite, indicating increased apatite weathering. Additionally, bags containing apatite saw a significant increase in fungal biomass, while no difference was observed in bags amended with biotite, suggesting that P and Ca limitation may play an important role in stimulating fungal activity. Overall, Hagerberg et al. (2003) found (1) no clear relationship between the production of EcM mycelium and the nutrient status of the forest field site, (2) bags amended with apatite had more EcM growth than those amended with biotite or the acid-washed sand, and (3) the production of EcM mycelium on apatite amended bags was increased when the forest was experiencing P deficiency.

By contrast, several studies have argued that too much attention has been given to EcM fungi and their ability to contribute substantively to weathering. Some studies have suggested that observed tunneling features could be caused not simply by EcM hyphae but rather by acidification around the mineral area brought on by root respiration, bacteria or other fungi (Sverdrup, 2009; Koele et al., 2013). Smits et al. (2014) argued, by studying a biological gradient across a natural lead contamination gradient, that EcM fungi have negligible effects on apatite dissolution rates. Quirk et al. (2012) indicated the presence of “biosensing” behavior in AM fungi illustrated by the fungal colonization of higher nutrient containing minerals. AM fungi colonized nutrient rich minerals similar to EcM fungi, suggesting active weathering by AM in addition to EcM fungi (Quirk et al., 2012). Using microcosm experiments, Connolly et al. (1999) suggested that the saprotrophic fungi *Resinicium bicolor* may contribute to weathering by entering soils

containing mineral additions and vertically redistributing solubilized ions. A study by Sanz-Montero and Rodriquez-Aranda (2012) suggested that AM fungi may be able to colonize specific materials, based on observed paleontological evidence of AM hyphae preferentially surrounding biotite grains. Results from a study employing paired plots able to host both AM and EcM fungi suggest AM fungi, in addition to bacteria and rhizosphere acidification, can generate tunneling features previously attributed to EcM fungi (Koele et al., 2014). Though they propose AM fungi, bacteria, and increased acidification could contribute substantively to mineral dissolution, the paired plots extended over a large geographic area, thereby introducing the possibility that microclimates may also contribute to the results (Koele et al., 2014).

Here we present results of a new field-based approach employing planted sets of mesh bags containing two lithologies with compositional differences in three nutrients (Ca, Mg, and P). Our experimental design enabled us to address the hypotheses that *in-situ* weathering is enhanced due to differing mineral contents of the rock, and weathering is enhanced in forest plots dominated by EcM symbioses versus forest plots dominated by AM symbioses. Our experiment is advantageous over earlier studies in that our bedrock-supplemented bags contain mineral abundances appropriate for typical continental bedrock and the proximity of the two sites mitigates the influence of variations in temperature and precipitation on weathering. We assessed relative abundances of major elements from samples deployed in the field to explore nutrient availability and used isotopic techniques to identify the minerals undergoing decomposition reactions. If EcM fungi do have a greater ability to weather minerals the ingrowth bags deployed in the EcM dominated plot should have higher nutrient fluxes from the nitric leach, which represents future available nutrient stores, due to EcM fungal tunneling and weathering of mineral boundaries. Additionally Sr and Pb isotopic ratios should indicate increased mineral dissolution at the EcM dominated plot.

2. Approach

2.1 Experimental design and field deployment Field experiments were conducted in Hubbard Brook Experimental Forest (HBEF; 43.95°N, 71.78°W). HBEF is a mixed hardwood/coniferous forest in the White Mountains of New Hampshire, USA and a site

in the Long-Term Ecological Research (LTER) Program (Figure 1a). HBEF receives an average of 1395 mm of precipitation per year with a mean annual temperature of 5.5°C, ranging from a mean of -8.5°C in January to a mean of 18.8°C in July (A. Bailey et al., 2003). Soils at HBEF are Spodosols (Bailey et al., 2014) developed in glacial drift of primarily granitic origin (S. Bailey et al., 2003) with a pH ranging between 3.5 and 4.5 (Bourgault et al., 2015). Soils are thin on upper slopes with bedrock exposed in stream channels and along ridgelines (Bailey et al., 2014). This is an ideal site to test if *in-situ* weathering is enhanced in forest plots dominated by EcM versus AM symbioses due to the presence of well-documented sites dominated by vegetation known to associate with these fungi (Schwarz et al., 2003; vanDoorn et al., 2011). The experiment was conducted across two forested stands selected from over 400 forest plots (Schwarz et al., 2003) for the greatest prevalence of AM- and EcM-host tree species. Site 206 is a mixed beech/birch plot dominated by beech (*Fagus grandifolia*) and yellow birch (*Betula alleghaniensis*), which are known to associate with EcM fungi. Site 237 is dominated by sugar maple (*Acer saccharum*), which associates with AM fungi. Trees were selected in both plots based on their size and their proximity to non-dominant vegetation to control for fungal type. Soil pH was assessed from samples obtained from each site at the time of in-growth bag collection. 20 mL of DI water was added to 10g of the homogenized soil sample and repeatedly agitated and allowed to rest. The pH was then measured with a Corning 430 pH meter. Average pH measurements for sites 237 and 206 were 4.24 ± 0.13 and 4.33 ± 0.13 (n=6 samples), respectively (Table 1).

To test the weatherability of different rocks and to assess the fungal affinity for different rock types, nylon mesh bags containing two types of crystalline rocks were planted in the field following procedures adapted from Wallander et al. (2001). The mesh bags were designed in two layers to allow for plant roots to penetrate the outer layer of 250µm mesh, while the second layer of 50µm mesh excludes roots but will allow soil solution, microbes, and fungal hyphae to enter. Rocks of two lithologies with differing P₂O₅, MgO, and CaO contents were used (Table 2).

Conway granite with low MgO, CaO, and P₂O₅ contents (0.47, 0.20, and 0.03 wt. %, respectively) collected from Grafton County was selected to represent a low-nutrient substrate (Barker, 2013). Biotite tonalite with high MgO, CaO, and P₂O₅ contents (2.3,

3.03, and 0.91 wt. %, respectively) collected from Strafford County was used as a nutrient-rich substrate (Barker, 2013). The Conway granite has been dated to 181 Ma and the tonalite is associated with the Barrington pluton, which has an age of 364 Ma (Eusden and Barreiro, 1989; Eby et al., 1992). Petrographic analysis indicates that apatite is the main carrier of P_2O_5 in these rocks. Samples of both rocks were chipped, crushed, and sieved to 250-500 μ m and acid washed (24 hours in 1M nitric acid (HNO_3)) and rinsed repeatedly with 18M Ω •cm DI water. The acid washing of crushed rocks was completed prior to burial to remove any mineral grains that were exposed during the crushing process, which is not representative of how AM or EcM fungi would encounter such mineral grains in the soil environment. Aliquots (~ 10 g) of acid-washed rock chips were then sealed into double-layered mesh bags and buried (Figure 1b). A Conway granite and tonalite bag were withheld from field installation and instead stored at 20⁰C in a dark dry environment. These bags were sub-sampled in the same manner as those subjected to field treatments to serve as controls for isotopic and elemental analyses.

Mesh bags were buried in June 2014 at the base of birch/beech trees on site 206 and at the base of maple trees on site 237 (Supplemental Figure 1). Bags were buried within the organic horizon at 10 cm depth or at the interface of the organic horizon and mineral A or E Horizon where the organic horizon was thin. O horizons in typical Hubbard Brook Spodosols have a mean depth of 6.3 cm and a range of 0-18 cm (Bailey, 2014). After 100 days bags were retrieved with a 16% recovery loss experienced across the two sites when bags could not be found due to loss of flagging tape and possible disturbance by animals (Figure 1c, Supplemental Figure 1).

Samples of EcM sporocarps (fungal fruiting bodies) of *Cortinarius violaceus*, *Lactarius camphoratus*, and *Leccinum* spp. were collected from a nearby stand at HBEF and the nearby Bartlett Experimental Forest, 35km to the northeast of HBEF, to assess the background soil solution Pb isotopic composition (Vadeboncoeur, 2013).

2.2 Analytical techniques After removal from the soil, mesh ingrowth bags were stored at -20⁰C to stop any ongoing biological activity. Aliquots (~ 1 g) of rock chips were subsampled from mesh bags. Sequential extraction techniques (Blum et al., 2002; Nezat et al., 2007) were used to identify the abundances of major and trace elements in the exchangeable fraction (i.e. the most readily exchanged ions) using a 24-hour leach of 1 M

ammonium chloride (NH_4Cl) at $\text{pH} = 7$ in the UNH Geochemistry Clean laboratory. An additional 24-hour 1.0 M HNO_3 leach allowed for assessment of the fraction that may weather over longer time scales. Leachate volumes (~ 10 mL) were collected after both steps and were subsampled and analyzed for elemental contents and isotopic compositions.

Abundances of Mg, P, and Ca were measured for both sites and rock types on an AttoM High Resolution inductively coupled plasma mass spectrometer (HR)- ICP-MS at the University of New Hampshire. Accuracy and precision for Mg, P, and Ca were assessed at $\leq 2\%$ by replicate analyses of NIST 1643e and NRC SLRS-4, and SLRS-5.

Lead (Pb) and strontium (Sr) isotope ratios were analyzed in order to identify minerals contributing to the weathering solute fluxes (e.g., Erel et al. 2004). Aliquots (~ 3 g) of leachate samples were taken from the original NH_4Cl and HNO_3 leaches and dried down to concentrate the elements prior to isotopic analyses. Sporocarps were brought to the lab and 50-100 mg of clean tissue subsampled and digested in concentrated HNO_3 for Pb isotopic analysis (Vadeboncoeur, 2013).

Lead purification was carried out using standard separation procedures on AG1-X8 anion-exchange columns (e.g., Bryce and DePaolo, 2004). Eichrom Sr Spec resin (50-100 μm mesh) was used to separate Sr from each sample following procedures adapted from Bryce et al. (2005). Total procedural blanks were < 400 ng and < 200 ng for Sr and Pb, respectively, which is negligible for the amounts of Sr and Pb measured. Collected solutions were dried down and redissolved in 2% HNO_3 for analysis on the Nu plasma II ES multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Lead instrumental mass fractionation was corrected externally via Tl normalization (White et al., 2000), and Pb isotope ratios were additionally adjusted for instrumental drift using sample-standard bracketing (Albarède et al., 2004) and the values for NIST SRM 981 reported by Eisele et al. (2003). Ten NIST SRM 981 analyzed as “samples” in addition to the bracketing standards produced averages (and $2\sigma_{\text{external}}$) of $^{208}\text{Pb}/^{204}\text{Pb} = 36.727$ (0.005), $^{207}\text{Pb}/^{204}\text{Pb} = 15.498$ (0.002) and $^{206}\text{Pb}/^{204}\text{Pb} = 16.941$ (0.002). Measured strontium isotope compositions were corrected internally for instrumental mass bias relative to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and additionally adjusted relative to NIST SRM 987

bracketing standards. The NIST SRM 987 bracketing standards gave 0.710248 ($2\sigma_{\text{external}} = 0.000016$).

We interpret the data in the context of Pb isotope compositions represented by HBEF sporocarps, which reflect the soil solution (Supplemental Table 4). The sporocarp data were part of a pilot study aimed at investigating whether sporocarp Pb isotope compositions could display specific weathering signatures, but the resulting Pb isotope compositions were uniform spatially and across sporocarp species. Lead was abundant and we used it to serve as a background Pb isotopic composition for the soil system that includes atmospheric deposition and weathering contributions. Sporocarp Pb isotope data were analyzed on the Nu Plasma 500 HR MC-ICP-MS at ENS Lyon after prior separation of Pb and using the same MC-ICP-MS techniques as described above (except that Pb was dissolved in a 0.05 M HNO₃ solution) with a NIST SRM 981 average for n=7 of $^{208}\text{Pb}/^{204}\text{Pb} = 36.726$ (0.007), $^{207}\text{Pb}/^{204}\text{Pb} = 15.498$ (0.003) and $^{206}\text{Pb}/^{204}\text{Pb} = 16.941$ (0.002).

3. Results and Discussion

3.1 Nutrient mobilization The NH₄Cl leach, for both the AM- and EcM-dominated plots, produced on average lower solute concentrations of major elements (Mg, P, and Ca) from the Conway granite and tonalite samples when compared to the HNO₃ leachate (Figure 2, Table 3, Supplementary Table 1). This was to be expected based on the relatively low number of exchange sites afforded by relatively coarse rock chips in comparison with soils on which the NH₄Cl leaching is more typically conducted to assess the nutrient availability from cations stored on clay mineral and organic matter exchange sites (e.g., Nezat et al., 2007). Accordingly, the solute concentrations from the NH₄Cl pH 7 leach should reflect a minimal amount of mineral dissolution due to the acid wash prior to bag deployment and the incubation time of 100 days. We therefore interpret exchangeable concentrations of macro- and micronutrients cautiously as much of what was liberated by weathering was likely lost to the soil solution or taken up by surrounding hyphae or roots. Yet, it is reasonable to assume that this loss occurred over all experiments and was not responsible for fractionating the isotopic signature of the exchangeable solution (cf. Section 3.2).

Analyses of the exchangeable fraction assessed via NH_4Cl leaches confirm that there were not significantly different average elemental fluxes between the AM- and EcM-dominated forest stands (Figure 2, Table 3). An exception to this generalization can be found in the highly significant difference in Ca fluxes from tonalite NH_4Cl leaches from bags planted at AM- and EcM- dominated sites ($p < 0.01$) (Table 3). For both rock types, the exchangeable fraction assessed from the control, a sample that was not buried, had higher solute concentrations than the easily exchangeable fraction represented by the ammonium chloride leach in the buried experiments. This finding supports the argument that the exchangeable fraction measured on retrieved deployed mesh bags must be considered a minimum.

There were few significant differences in the average elemental concentrations between AM- and EcM-dominated sites recorded in the HNO_3 acid leaches, which are generally interpreted to represent future readily available nutrient stores. A highly significant difference ($p < 0.01$) was seen in the Mg concentrations for the Conway granite, with higher Mg concentrations present in the AM- dominated site. There was also a significant increase in Ca concentrations ($p < 0.05$) in the AM- dominated forest plots in both the tonalite and Conway granite HNO_3 leachates ($p < 0.05$) (Table 3). The control, unburied rock chips subjected to the same laboratory leaching treatment, had similar or lower elemental solute concentrations in the HNO_3 leaches than the average solute concentrations of the nitric leaches of the deployed samples. We interpret this finding as a manifestation of biotic or abiotic field conditions that promoted mineral weathering, allowing those nutrients to become more easily removed by the HNO_3 leach process. Differences in mineralogy of the two rock types selected for this experiment are also important for interpreting the major element fluxes, especially calcium. Ca/P ratios in both leachates were higher for the Conway granite than for the tonalite, which suggests that mineral dissolution reactions in addition to apatite may be at play (Supplemental Table 1). The increased presence of anorthite-rich plagioclase in the tonalite when compared to the Conway granite helps explain the higher flux of Ca from the tonalite bags due to the enhanced weatherability of anorthite-rich plagioclase as documented in numerous experiments (e.g., Stillings and Brantley, 1995).

Interestingly, in no case were the average elemental concentrations from the EcM-dominated site significantly higher than those of the AM-dominated site. The average percentage of elements liberated in the nitric leach compared to the whole rock
285 (determined by XRF analyses) show no significant difference between the two sites with p values for tonalite and Conway granite being 0.159 and 0.224, respectively (Table 4). The higher average Ca concentrations observed in leachates from the maple AM-dominated site (Table 3) are consistent with higher demand for Ca by sugar maple compared to other tree species (Long et al., 2009; Vadeboncoeur, 2010) and therefore
290 fungal survival. The fact that AM fungi appear to be more adept at making Ca mobile from both rock types for the future (as represented by the HNO_3 leach treatments) suggests that the effectiveness of the AM fungi to liberate nutrients from soil and rock may be strongly element specific.

In many cases when bags were removed from the ground roots were seen entering the
295 first layer of mesh, and hyphae were visible in the second layer, within the rock substrate. Although steps were taken to isolate for AM and EcM fungi in the choice of field sites we cannot rule out the possibility that root or hyphae from tree and fungal species outside the plot or from other herbaceous shrub species in the plot colonized the mineral mesh bags as they were planted around the sites. Additionally, saprotrophic fungi and soil
300 bacteria could have acted upon the in-growth bags, impacting nutrient fluxes (Connolly et al., 1999; Koele et al., 2009; Uroz et al., 2009; Christophe et al., 2013). Abiotic field characteristics (e.g., precipitation, soil $p\text{H}$, and temperature) will also impact the nutrient fluxes, especially from the easily exchangeable fraction, and are recognized as an important factor in the reactions occurring within the ingrowth bags. Our experimental
305 design allowed for deployment in sites spatially close with the same climate and similar soil $p\text{H}$ (Table 1) implying that much of the variability in these field conditions is minimized. The results are interpreted through the lens of AM- and EcM- dominated ecosystems, fully recognizing that many factors in the ecosystem contribute to mineral dissolution.

310 *3.2 Isotopic assessment of mineral decomposition reactions*

Lead and strontium isotopes have proven useful for identifying mineral dissolution reactions during weathering (e.g., Nezat, 2007). Generally, old plutonic rocks, typical in many continental environments, have distinctive weathering profiles of Sr and Pb as radiogenic, easily weatherable minerals such as biotite and apatite are depleted and the weathering solution becomes dominated by the modally predominant minerals (e.g., feldspars) (Erel et al., 2004). These easily weatherable minerals bear distinctive isotopic signatures with biotite dissolution liberating radiogenic Sr and apatite dissolution liberating radiogenic Pb. Lead isotopes for all samples show little variation between the two fungal types on the same lithology (Figure 3) but display a marked contrast from the soil solution Pb isotopic compositions. We interpret the Pb isotopic composition from the soil solution relative to fungal sporocarp data from HBEF and nearby Bartlett Experimental Forest. These compositions are similar despite a difference in lithology as HBEF soils are dominantly derived from the Devonian Kinsman granodiorite (S. Bailey et al., 2003), while Bartlett soils are formed from Conway granite (Vadeboncoeur, 2013). Radiogenic $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ indicate the importance of apatite dissolution in Conway granite samples subjected to nitric leaching (Figure 3)(Erel et al., 2004). Control bags for both granite and tonalite also fall within the range of the bags subjected to the 100-day field treatment and indicate that mineral breakdown reactions in the field treatment are comparable to abiotic mineral decomposition (Figure 3). Elevated solute fluxes of key nutrients (Ca, Mg, P) in the nitric solutions (Figure 2, Table 3), however, are consistent with enhanced mineral decomposition. The $^{206}\text{Pb}/^{204}\text{Pb}$ isotopes plotted as a function of P concentrations for both leachates shows elevated $^{206}\text{Pb}/^{204}\text{Pb}$ values in the nitric leachate of the Conway granite and suggests the importance of apatite as a source of P (Figure 4).

Radiogenic Sr isotope signatures in the exchangeable fractions suggest the contribution of biotite dissolution to the solute fluxes across both sites (Figure 5) (Bailey et al., 1996). Increasing feldspar and apatite contributions are apparent with decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ in the HNO_3 leachates (Figure 5). $^{87}\text{Sr}/^{86}\text{Sr}$ isotope values plotted as a function of Mg concentrations in the leachates help to indicate the early importance of biotite contributions in both rock types, with more radiogenic Sr seen in the NH_4Cl leachates (Figure 6). This radiogenic signature is less visible in the HNO_3 leachates though

magnesium concentrations increase, indicating the contribution of Mg from other minerals within the rocks (e.g., hornblende) as well as the contribution of less radiogenic Sr from other phases (e.g., plagioclase feldspar). The increasingly radiogenic Pb isotopic compositions are also consistent with increasing apatite contributions (Erel et al., 2004). The resulting Pb isotope signatures for these mineral dissolution reactions are not substantially different based on the dominant fungal symbioses of the sites. Additionally solutes generated from the control aliquot of chips not subjected to 100 days of field exposure was also found to plot within the range of the field-deployed samples. It is possible that an *in-situ* experiment of 100 days may not be appropriate for all locations and may instead depend on the biotic activity in the area with slower growing ecosystems like a mature cool climate forest needing an *in-situ* time of multiple growing seasons for mycorrhizal fungi to provide measurable differences.

The isotopic ratios of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ suggest nominally similar minerals contribute to the solute flux, with the weathered fraction dominated by apatite and feldspar dissolution in both cases (as suggested by the Pb isotopes). Elevated major element fluxes, in deployed samples vs. those not deployed, indicate larger amounts of weathering occurred in the field-deployed samples.

4. Summary and implications

Elemental fluxes from both sites were very similar for P and Mg in both NH_4Cl and HNO_3 leachates. Calcium fluxes were significantly higher on average in the AM-dominated sites for tonalite in the easily exchangeable fractions and for both rock types in the HNO_3 leachates that represent future available stores. These findings from field experiments conducted in close proximity with similar climate conditions support earlier findings employing paired distal sites (Koele et al., 2014) that the soil microbial communities in forests dominated by AM-associated tree species may be just as effective as those in EcM-dominated forests.

Isotopic signatures of leachates extracted from in-growth bags provide evidence for similar mineral dissolution reactions at both sites in each lithology that are distinct from the soil isotopic contributions. Radiogenic $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ at both sites support the idea that apatite dissolution is the dominant reaction in the Conway granite in

the long term at both sites and does not appear dependent after 100 days *in-situ* on the
375 varying biology present on the site. Isotopic signatures of leached solutions ($^{87}\text{Sr}/^{86}\text{Sr}$
along with $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$) suggest biotite dissolution in the earlier stages of
weathering is followed by feldspar and apatite decomposition as weathering progresses.
The most important factors controlling the chemical and isotopic signatures of the solute
were rock type and leachate reagent (NH_4Cl to model the exchangeable nutrients versus 1
380 M HNO_3 to model future nutrient stores), with no impact of AM versus EcM fungi noted
over the 100-day treatment. Our findings may indicate that both EcM and AM fungi, or
the soil microbial communities in sites where they dominate, are equally efficient at
obtaining the nutrients that their host plants need from minerals within the soil or that
sparse EcM species within AM-dominated plots may serve to enhance weathering. Our
385 findings further suggest that future studies seeking to quantify microbial contributions to
weathering should combine geochemical techniques to identify solute fluxes and mineral
decomposition reactions with biological techniques to isolate and quantify the biological
community active in the weathering process.

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Figure Captions

590 Figure 1: (a) Map of New England including sketched location of Hubbard Brook LTER
(b) mesh in-growth bags before deployment (c) tonalite in-growth bag from maple-
dominated site after retrieval at day 100.

595 Figure 2: Average elemental concentrations of Mg, P and Ca of Conway granite and
tonalite samples from both AM- and EcM-dominated sites (represented by hash marks
and solid bars, respectively). Tonalite average elemental concentrations are depicted in
the shaded half of the figure and future available stores for both rock types are outlined
with a dashed line. 1σ standard deviation between the various in-growth bags planted at
both sites (AM site n=8, EcM site n=7) represented by error bars.

600 Figure 3: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ for granite and tonalite samples from both AM- and
EcM-dominated sites. Lead isotopic data for sporocarps harvested from Bartlett and
Hubbard Brook Experimental Forests shown as a field and are used to approximate bulk
soil composition (Pb isotopic data from the sporocarps are provided in Supplemental
605 Table 3).

Figure 4: $^{206}\text{Pb}/^{204}\text{Pb}$ vs. P concentration in ppm for Conway granite and tonalite samples
from both AM- and EcM- dominated sites. Tonalite samples are depicted by diamonds
for the AM- dominated site and squares for the EcM- dominated site. Conway granite
610 samples are depicted by triangles for the AM- dominated site and circles for the EcM-
dominated site. In both cases open symbols represent the NH_4Cl leach and shaded
symbols represent the HNO_3 leach.

Figure 5: $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ for granite and tonalite samples from both AM- and
615 EcM-dominated sites. Symbols as described in Figure 4.

Figure 6: $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Mg concentrations in ppm for Conway granite and tonalite samples
from both AM- and EcM- dominated sites. Symbols as described in Figure 4.

Figure1

b)

c)

Figure2

Figure3

Figure4

Figure5

Figure6

Table 1. *pH* measurements for soil samples collected at time of bag harvest from maple dominated site #237 and beech/birch dominated site #206.

Bag code	Rock type	Dominant tree at site	pH
CG1	Conway Granite	Maple	4.30
CG5	Conway Granite	Maple	4.08
CG11	Conway Granite	Maple	4.11
T10	Tonalite	Maple	4.33
T14	Tonalite	Maple	4.20
T5	Tonalite	Maple	4.40
CG17	Conway Granite	Beech/birch	4.30
CG20	Conway Granite	Beech/birch	4.45
CG26	Conway Granite	Beech/birch	4.17
T29	Tonalite	Beech/birch	4.24
T18	Tonalite	Beech/birch	4.30

Table 2. XRF analyses for Conway granite (Lin-1) and tonalite (Bar-3) rock samples provided by the New Hampshire Geological Survey and used in mesh in-growth bags.

	Lin-1 Conway Granite (wt %)	Bar 3 – Tonalite (wt %)
SiO₂	74.70	57.79
TiO₂	0.14	1.84
Al₂O₃	13.12	17.25
Fe₂O₃	1.92	9.27
MnO	0.02	0.24
MgO	0.47	2.3
CaO	0.20	3.03
Na₂O	3.91	2.67
K₂O	4.6	4.15
P₂O₅	0.03	0.91
Total	99.12	99.45

Table 3. Average concentrations for Mg, P and Ca in easily exchangeable and future available stores leachates from mesh ingrowth bags containing Conway granite and tonalite in both AM- and EcM-dominated sites.

¹Standard deviation represents variations between the various mesh in-growth bags planted at the AM and EcM sites (n=7 and n=8 respectively).

²*p* values were determined from a two-tailed heteroscedastic t-test, values of *p* < .01 indicate highly significant within the 99th percentile while *p* < .05 indicate significant values in the 95th percentile

		Control ($\mu\text{mol/g}$)	AMF Average ($\mu\text{mol/g}$)	AMF Std. dev ¹	EcM Average ($\mu\text{mol/g}$)	EcM Std. dev ¹	<i>p</i> - value ²
Conway granite	Mg	0.863	0.143	0.021	0.257	0.235	0.249
<i>Ammonium chloride</i>	P	0.004	0.003	0.003	0.015	0.013	0.053
	Ca	0.829	0.553	0.129	0.916	0.849	0.304
Conway granite	Mg	1.848	2.763	0.668	1.566	0.199	0.001
<i>Nitric</i>	P	0.242	0.492	0.400	0.250	0.044	0.131
	Ca	7.272	12.85	5.542	6.641	0.561	0.016
Tonalite	Mg	0.527	0.340	0.160	0.339	0.190	0.991
<i>Ammonium chloride</i>	P	0.096	0.026	0.016	0.034	0.028	0.529
	Ca	2.406	1.866	0.600	0.982	0.428	0.006
Tonalite	Mg	4.849	7.642	1.917	6.142	0.641	0.067
<i>Nitric</i>	P	36.566	42.043	8.532	36.488	1.903	0.112
	Ca	59.694	85.264	18.028	63.333	2.570	0.011

Table 4: Ratio of major elements from in-growth bag leaches to whole rock composition (determined via XRF), expressed as a percent. *p* values of 0.159 and 0.224 were calculated for tonalite and Conway granite samples respectively and were determined from a two-tailed heteroscedastic t-test. Values of *p* < .01 indicate highly significant within the 99th percentile while *p* < .05 indicate significant values in the 95th percentile.

AM Site	Mg %	P %	Ca %
Ratios av. Nitric/WR			
Conway	2.37	13.53	36.02
Tonalite	1.34	25.40	15.78
EcM Site	Mg %	P %	Ca %
Ratios av. Nitric/WR			
Conway	1.34	6.86	18.62
Tonalite	1.08	22.05	11.72