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NUTRIENT CYCLING ALONG MICROBIAL AND LITHOLOGIC GRADIENTS AND FOSTERING STUDENT SELF-CONFIDENCE IN SCIENCE

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NUTRIENT CYCLING ALONG MICROBIAL AND LITHOLOGIC GRADIENTS AND FOSTERING STUDENT SELF-CONFIDENCE IN SCIENCE

BY

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ABSTRACT

NUTRIENT CYCLING ALONG MICROBILAL AND LITHOLOGIC GRADIENTS AND FOSTERING STUDENT SELF-CONFIDENCE IN SCIENCE

By

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Increased understanding of the impact of biology on weathering rates and its response to environmental factors will lead to more accurate global models and enhanced management practices to optimize productive, healthy forests. Although biological contributions to weathering are established in the literature, more data to translate these observations for implementation in a predictive framework should be obtained (e.g. Taylor et al., 2012). Mycorrhizal fungi have implications for global carbon cycling and increasing carbon storage in soils (Soudzilovskaia et al., 2019) but the extent of their impact is still an area of active research with more studies of local weathering sites still needed (Finlay et al., 2020; Terrer et al., 2016; Norby et al., 2017).

This dissertation examines the role that microbes can have on moderating mineral weathering and nutrient cycling in terrestrial ecosystems. My research combines geochemical data from two field studies and one controlled growth experiment with prokaryotic community composition data to determine how rock type can drive microbial weathering. Results from the two field studies, the latter including microbial community data, suggest that weathering fluxes in forest stands with different dominant mycorrhizal vegetation may be more similar than previously thought and that abiotic factors and rock composition may be responsible for weathering fluxes at the field scale. The growth chamber experiment allowed me to examine two mycorrhizal symbioses across two distinct lithologies in a controlled environment and the

results suggest that mycorrhizal weathering, especially that of AM fungi, may be enhanced when nutrients aren't readily available. Overall this work helps use to constrain the importance of biological weathering.

In the final section of my dissertation I shift my focus to look at how scientists can help engage students in authentic science practice and how this experience might build students' self-confidence in science. I examined an established citizen science program, NASA GLOBE, and focused on how students participation in collecting data using GLOBE protocols, analyzing and reporting it, and communicating this to peers at scientists at the Student Research Symposium (SRS) helped shape students views of themselves and their confidence with science practices. Attending the SRS was seen to have a significant impact on students' confidence in their ability to practice science (ex. "I am able to construct scientific arguments") and their belief that they are "good at science". I hope this work offers an example to other citizen science programs of components that can be used to engage students and improve their confidence in science.

INTRODUCTION

I. Global context

It is important to understand how changing conditions will impact ecosystems in order to improve management strategies, maintain ecosystem health, and accurately model biogeochemical cycling. Soil chemistry and biology can affect plant function, factor into dissolution rates in soil minerals and bedrock (Hoffland et al., 2004), affect nutrient uptake for plants (Gadd, 2004), influence plant distribution (Steidinger et al., 2019) and impact the global carbon cycle (Beerling and Berner, 2005; Soudzilovskaia et al., 2019). Bacteria and fungi in the rhizosphere play a role in weathering, targeting plant necessary nutrients, like phosphorus (P), contained in minerals (Uroz et al., 2009; Berner et al., 2012). Understanding the processes that take place between fungal hyphae, plant roots, and minerals present in the soil will help provide accurate parameters for models that seek to integrate vegetation into carbon and nutrient cycling (Taylor et al., 2012). Mycorrhizal fungi are thought to have implications for carbon cycling dynamics because carbon from the plant is sent to fungal colonizers, accounting for 10-30% of net carbon fixation in grasslands and forests, and a recent global analysis found that ectomycorrhizal (EcM) vegetation is broadly associated with greater soil C stocks in the soil (Leake et al., 2008; Soudzilovskaia et al., 2019). Mycorrhizal fungi may also be subject to varied impacts of climate change, with abundance of both EcM and arbuscular mycorrhizal (AM) trees declining under climate model predictions for 2070 (Steidinger et al., 2019). The different traits of AM and EcM fungi are thought to influence their importance in carbon and nutrient cycling but the differences in the relative contributions of each of these fungal types is still debated (Terrer et al., 2016; Norby et al., 2017). In a recent review of biological weathering Finlay and colleagues highlight the disagreement that still exists regarding the extent that biological weathering contributes to field-scale observations and call for improved representation ways in which biological processes complement abiotic processes that mobilize mineral elements (Finlay et al., 2020).

II. Microbial weathering mechanisms

Mycorrhizal fungi are important components of terrestrial ecosystems, forming symbiotic relationships with host plants and increasing access to nutrients to promote plant growth and survival. Mycorrhizal fungi can create a network of hyphae that are able to penetrate soil pores inaccessible to roots and may also be able to compete with soil-inhabiting microorganisms for recently mineralized nutrients (Gadd, 2007). Phosphorus (P) and other nutrients like calcium (Ca) and magnesium (Mg) can be scavenged from the soil and rapidly transported from the fungi to the host plant, bypassing direct uptake by the plant through root epidermal cells (Smith et al., 2011). AM and EcM fungi both have the ability to colonize a host plant and form a symbiotic relationship providing nutrients in return for carbon to survive (Gadd, 2007; Smith and Read, 2008).

Variations in mycorrhizal colonization and growth habits are proposed to enhance mineral weathering reactions but the degree to which mycorrhizal fungi can impact weathering and the differences that exist between fungal types are still debated. AM fungi are the most ancient mycorrhizal symbionts, with evidence for the presence of AM fungi at the advent of land plants where it is posited that they were key for early plant survival (Sanz-Montero and Aranda, 2012). AM fungi are obligate symbionts that depend on their host plant for sugar. AM fungi colonize the root of a plant, penetrating the cortical cells and forming hyphal features called arbuscules within the cell. These arbuscules provide a large surface area for the exchange of nutrients between fungus and host (Bonfante and Genre, 2010; Smith and Read, 2008).

Ectomycorrhizal fungi arose independently on a number of occasions, as fungal saprotrophs formed symbiotic partnerships with autotrophs, with evidence for reversing behavior from EcM to free-living also taking place (James et al., 2006; Smith & Read, 2008). Ectomycorrhizal fungi may have a dual lifestyle as symbionts with plant roots and facultative saprotrophs in soil, though there is debate regarding the extent of this behavior across the wide spectrum of EcM fungi (Bonfante and Genre, 2010; Plett and Martin, 2011). Some EcM fungi may be able to metabolize fructose, which is a trait shared by pathogenic fungi, while others lack the ability to use carbon sources in the soil and are dependent on the host plant (Plett and Martin, 2011). EcM colonized roots are characterized by a sheath of fungal tissue that encompasses the root, a hartig net of hyphae that grow between epidermal and cortical cells, and extraradical mycelium which grow out from the fungi into the soil (Bonfante and Genre, 2010; Smith & Read, 2008). Ectomycorrhizal fungi are thought to increase mineral weathering more than AM fungi because in addition to increasing surface area and respiration they produce low molecular weight organic acids like oxalate and citrate which can enhance mineral dissolution (Hoffland et al., 2004; Gadd, 2007).

Nutrients are transferred back and forth between mycorrhizal fungi and their host, though the transport interfaces vary in location and structural complexity based on fungal type (Smith et al., 1994). AM and EcM plant hosts have also been found to have specific traits that help reinforce fungal strategies, supporting a link to the co-evolution of host and symbiont (Averill et al., 2019). These differences in fungal structure, phylogeny, and function support the idea of varying abilities of EcM and AM fungi to enhance nutrient liberation from the soil environment including through mineral weathering. There is debate over the relative effectiveness of AM and EcM fungi in the literature with some proposing EcM fungi will have marked abilities to increase weathering (Hagerberg et al., 2003; Hoffland et al., 2004; Berner et al., 2012) while others argue there is not enough evidence that in the field EcM fungi are more impactful than AM fungi (Quirk et al., 2012; Koele et al., 2014; Remiszewski et al., 2016). EcM hyphae have been shown to interact with apatite minerals, weathering them under fungal colonization

(Hagerberg et al., 2003). The importance of the lithology involved has also been considered, with experiments by Quirk and colleagues showing the preferential colonization of basalt over granite and quartz for both AM and EcM fungi (Quirk et al., 2012). The experiment also indicates the bio-sensing ability of AM fungi and provides evidence that AM fungi actively weather minerals, though the etching on EcM colonized minerals were wider and deeper than those of AM colonized minerals (Quirk et al., 2012). Field-based comparison studies afford a means to evaluate differences in weathering across fungal types. Using buried mesh substrate bags and REE tracers, together with DNA analysis, Koele et al. (2013) found no difference in nutrient uptake between AM and EcM fungal symbioses and that the substrates present in the bags had no effect on the community of mycorrhizal fungi. They conjectured that acidification of the rhizosphere due to decomposition of organic matter was largely responsible for mineral weathering including tunnel features and more passive nutrient uptake by plants and fungi (Koele et al., 2014). The ability of EcM and AM fungi to weather minerals in the subsurface may be more similar than previously argued and this work seeks to elucidate fungal weathering processes and their response to varied lithology in order to contribute to this debate.

III. Citizen science and student engagement

The influence of microbes on nutrient cycling is an example of a complex natural system that is important to understand due to its implications for ecosystem health and global carbon cycling. Ensuring that science is understood and used to make informed decisions is an integral part of everyday life and now, more than ever, it is crucial that citizens are knowledgeable in science. It has been suggested that making science more approachable and accessible to both students and instructors is an important step for encouraging engagement with science and could help improve attitudes toward science (Bandura, 1993; Zimmerman, 2000). There are many ways to approach this goal but both citizen science and experiential education programs have shown themselves to be aligned to support public engagement with science. Citizen science projects engage non-scientists, which could include K-12 students, in the process of research (National Academies of Science, 2018). The goal of the projects may vary but an overarching design to advance scientific knowledge is key, along with active participation by non-scientist parties and communication of the data obtained all contribute to a successful citizen science project (National Academies of Science, 2018).

There is a shortage of studies regarding the attitudes of participants in citizen science programs, in part because of the difficulties surrounding the measurement of attitude (Phillips et al., 2012). Though there is some evidence that supports overall scientific attitudes change positively when participating in inquiry-based science projects, additional research regarding the public's understanding of science suggests the need to focus on the mechanisms that underlie the association between knowledge and attitudes about science (Allum et al., 2008; Price and Lee, 2013). It has been suggested that making science more approachable and accessible to both students and instructors is an important step for encouraging engagement with science and could help improve attitudes toward science (Bandura, 1993; Zimmerman, 2000). There are many ways to approach the goal of increasing student interest in science but both citizen science and experiential education programs have shown themselves to be aligned to support public engagement with science.

IV. Summary

This work seeks to strengthen our understanding of microbially mediated nutrient cycling through the use of geochemical tracers and evaluate the ability of citizen science to provide authentic science experiences that help increase student self-confidence in science. The first three chapters of my graduate work are designed to assess microbial contributions to weathering across ecological, geochemical, and geologic gradients to determine the influence of lithology on microbial communities and the impact that mycorrhizal fungi can have on varied lithology. In my first chapter I conducted a field study at Hubbard Brook Experimental Forest that assessed fungal weathering ability in two forest stands dominated by arbuscular mycorrhizal (AM) and ectomycorrhizal fungi (EcM). In-growth bags with rocks of varying nutrient content were planted in the rhizosphere surrounding AM- and EcM- dominated trees to create and in-situ geologic gradient. Major element (Ca, Mg, and P) concentrations and lead (Pb) and strontium (Sr) isotopes were analyzed for the rock chips retrieved at the end of the study to assess minerals contributing to the weathering solute fluxes. Only calcium (Ca) concentrations varied between the two fungal types and isotopic signatures of the rocks from in-growth bag rocks provided evidence for similar mineral decomposition reactions at both sites. These results suggest that weathering fluxes in AM and EcM dominated forest stands may be more comparable than previously thought and that AM fungi might be underestimated in terms of their weathering ability.

Chapter two examines a controlled greenhouse experiment with both ectomycorrhizal and arbuscular mycorrhizal fungi to obtain geochemical insights into how nutrient availability in underlying lithology impact the weathering potential of these two fungal symbionts. Major and trace element concentrations were obtained for the roots and foliage of *A. saccharum* and *P. sylvestris* seedlings grown with and without mycorrhizal fungi through analysis on the ICP-MS. Magnesium (Mg) isotopes were measured for all samples as well to examine magnesium fractionation under different conditions (mycorrhizal fungi vs. no presence of fungi). Lanthanum concentrations in the roots of mycorrhizal *A. saccharum* sample grown on the P-limited Conway Granite substrate when compared to both non-mycorrhizal *A. saccharum* samples and mycorrhizal and non-mycorrhizal *P. sylvestris* root samples. On the same lithology the mycorrhizal *A. saccharum* root and foliage showed elevated phosphorus concentration when compared to the non-mycorrhizal samples and taken with the lanthanum data could provide evidence for arbuscular mycorrhizal weathering of apatite when grown on a nutrient limited lithology. The variation in seen in Mg isotope signatures across different lithologies and fungal symbionts indicates that there is a multifactorial control on Mg isotope signature. Taken together, major elements, REEs, and Mg isotopes provide insights into the influence rock type has on activating fungal weathering in AM symbionts. The data indicate that rock type, more specifically the presence of plant-necessary nutrients, taken in conjunction with the nutrient status of the growth medium may influence intensity of fungal weathering. This work suggests that biological weathering may be enhanced when nutrients are not readily available to the system and could impact how we think about the importance biological weathering.

My third chapter returns to maple and beech/birch dominated plots in Hubbard brook and incorporated an additional field site dominated willows to assess if and how the prokaryotic community composition responds to different lithologies and if nutrient mobilization and weathering reactions are altered by these microbes. Lead isotopes and Mg, Sr, and Rb concentrations were used to assess microbial impacts on nutrient mobilization and element cycling. In addition to geochemical data, 16s data were sequenced from soils at each site as well as from the soil surrounding in-growth bags, and the crushed rocks within the bags. Isotopes revealed mineral weathering signatures driven by lithology, not biology. The prokaryotic community compositions were seen to be distinct between sites, even for the two Hubbard Brook sites. There were some differences between the community found on nutrient poor and nutrient rich lithologies within the same site, but this was harder to tease apart. This work helps to illuminate the role of lithology in microbial colonization and may also support the idea that abiotic factors and rock composition may drive weathering at a broad scale.

My final chapter takes a step back to look at how the experience of participating in authentic science practice can help increase student engagement with the field. Recognizing the importance of a science literate population and finding ways to reach students who make feel disconnected from the field of science is important to me both as a scientist and as a high school educator. My final chapter focuses on how participation in the NASA GLOBE (Global Learning and Observations to Benefit the Environment) Student Research Symposium has the capacity to positively impact students' attitude towards science and confidence with science practices. I found that students who participated in the GLOBE Student Research Symposium reported a significant ($p < .05$) increase in agreement with statements that indicate confidence in science practices. They also took more pride in their accomplishments in science and identified themselves as "good at science". I hope this study can offer a model of how citizen science programs can be used to support experiential education within the formal structure of K-12 public education with the goal of improving student attitudes toward science and fostering science literacy.

My dissertation chapters have been formatted for submission to peer-reviewed journals. As of August 2020, the first chapter of this dissertation has been published in *Chemical Geology*. The citation for the first chapter in this dissertation is as follows:

Remiszewski, K.A., Bryce, J.G., Fahnestock, M.F., Pettitt, E.A., Blichert-Toft, J., Vadeboncoeur, M.A., Bailey, S.W., 2016. Elemental and isotopic perspectives on the impact of arbuscular mycorrhizal and ectomycorrhizal fungi on mineral weathering across imposed geologic gradients. Chem. Geol. 445, 164–171. doi:10.1016/j.chemgeo.2016.05.005

CHAPTER 1: ELEMENTAL AND ISOTOPIC PERSPECTIVES ON THE IMPACT OF ARBUSCULAR-MYCORRHIZAL AND EXTOMYCORRHIZAL FUNGI ON MINERAL WEATHERING ACROSS IMPOSED GEOLOGIC GRADIENTS[1]

1.1 Abstract

Symbiotic mycorrhizal fungi are thought to play a role in weathering by targeting required plant nutrients, such as phosphorus (P), magnesium (Mg) and calcium (Ca) contained in minerals. Field experiments coupled with geochemical analyses 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 sites under two different mycorrhizal symbioses in Hubbard Brook Experimental Forest in New Hampshire, USA. Mineral decomposition within the substrate bags under different biologic conditions was assessed via analysis of major elemental nutrients (Ca, Mg and P) and lead (Pb) and strontium (Sr) isotopic signatures on solutions representing both the easily exchangeable and weathered mineral stores. Only Ca concentrations in the exchangeable solutions produced by the tonalite and weathered stores of both tonalite and granite varied significantly between the two fungal types. The other measured nutrient concentrations (Mg, P) and isotopic compositions of the exchangeable and weathering solutions were indistinguishable for individual rock types. Taken together, our results suggest that weathering

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[1] This chapter has been published in *Chemical Geology* and the citation is as follows: Remiszewski, K.A., Bryce, J.G., Fahnestock, M.F., Pettitt, E.A., Blichert-Toft, J., Vadeboncoeur, M.A., Bailey, S.W., 2016. Elemental and isotopic perspectives on the impact of arbuscular mycorrhizal and ectomycorrhizal fungi on mineral weathering across imposed geologic gradients. Chem. Geol. 445, 164-171. doi:10.1016/j.chemgeo.2016.05.005

fluxes in AM and EcM forests may be more comparable than previously argued and support the idea that weathering contributions of other sources in AM forests may be underestimated.

1.2 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 (Hamburg et al. 2003, Futter et al. 2012, Vadeboncoeur et al., 2014). An important component of the soil biology community are symbiotic fungi, which form associations with approximately 80% of plant species and are responsible for major mineral transformations, particularly the distribution of nutrients like phosphate (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.

Ectomycorrhizal (EcM) fungi form a mutualistic relationship with the roots of plants, including conifers and some temperate angiosperms (particularly the Fagacae 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 (Hedh et al., 2008; Leake et al., 2008; vanBreemen et al., 2000). Quirk et al. (2012) showed that AM fungi can also sense areas of higher nutrient content and that the subsequent colonization resulted in mineral weathering, though to a lesser extent than caused by EcM fungi. Hyphae tips produced by EcM are known to produce organic anions and protons, thereby promoting the release of essential elements like calcium (Ca) and magnesium (Mg) from minerals and make them available for uptake by the hyphae (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 (vanBreemen et al., 2000; Hoffland et al., 2002; van Schöll et al., 2008).

Ectomycorrhizal fungi have been proposed to be especially important for providing nutrients from soil minerals lacking essential elements like Ca or P (Blum et al. 2002, Smits et al. 2012). Chemical signatures (primarily Sr/Ca and 87Sr/86Sr) of a sequential digestion of soil minerals led Blum et al. (2002) to argue for apatite as an important source of Ca in soil in the Hubbard Brook Experimental Forest (HBEF) ecosystem with an established history of soil leaching from 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 direct access to bedrock-hosted nutrients in thin, glacial soils. 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 protected nature of any primary P remaining in the system, which makes apatite contributions a very important part of P dynamics (Walker and Syers, 1976).

Further evidence for EcM contributions to mineral pools was documented in field and laboratory experiments conducted by Hagerberg et al. (2003) in Skåne, Sweden, employing ingrowth mesh bags containing sand amended with Mg-rich biotite or P-rich apatite buried in the organic soil horizon or in trenched plots to control for fungal mycelium growth (Hagerberg et al. 2003). Rare earth element (REE) distributions in a Pinus sylvestris seedling colonized by EcM fungus showed that bags amended with apatite saw a significant increase in fungal biomass, while no difference was seen in bags amended with biotite, suggesting that P and Ca limitation may play an important role in stimulating fungal activity. Rare earth element contents of EcM roots in apatite-amended bags were significantly higher than those of EcM in contact with non-amended sand bags. 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) apatite-amended bags stimulated the production of EcM mycelium more 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. 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 New Zealand 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 study employing implanted sets of mesh bags containing two distinctive lithologies with a compositional gradient in three key nutrients (Ca, Mg, and P). Our experimental design enabled us to address if in situ weathering is enhanced due to differing mineral contents of the rock and if weathering is enhanced in forest plots dominated by EcM symbioses versus a forest plot 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 precludes 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.

1.3 Methods

1.3.1 Experimental Design and Field Deployment

Field experiments were conducted in Hubbard Brook Experimental Forests (HBEF; 43.9ºN, 71.8ºW), a mixed hardwood/coniferous forest in the White Mountains of New Hampshire a site in the Long-Term Ecological Research (LTER) Program (Figure 1.1). Hubbard Brook receives an average of 1395 mm of precipitation per year with a mean annual temperature of 5.5ºC, ranging from a mean of -8.5ºC in January to a mean of 18.8ºC 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 3.5-4.5 (Bourgault et al. 2015). Soils are thin on upper slopes with bedrock exposed in stream channels and along ridgelines (Bailey et al., 2014).

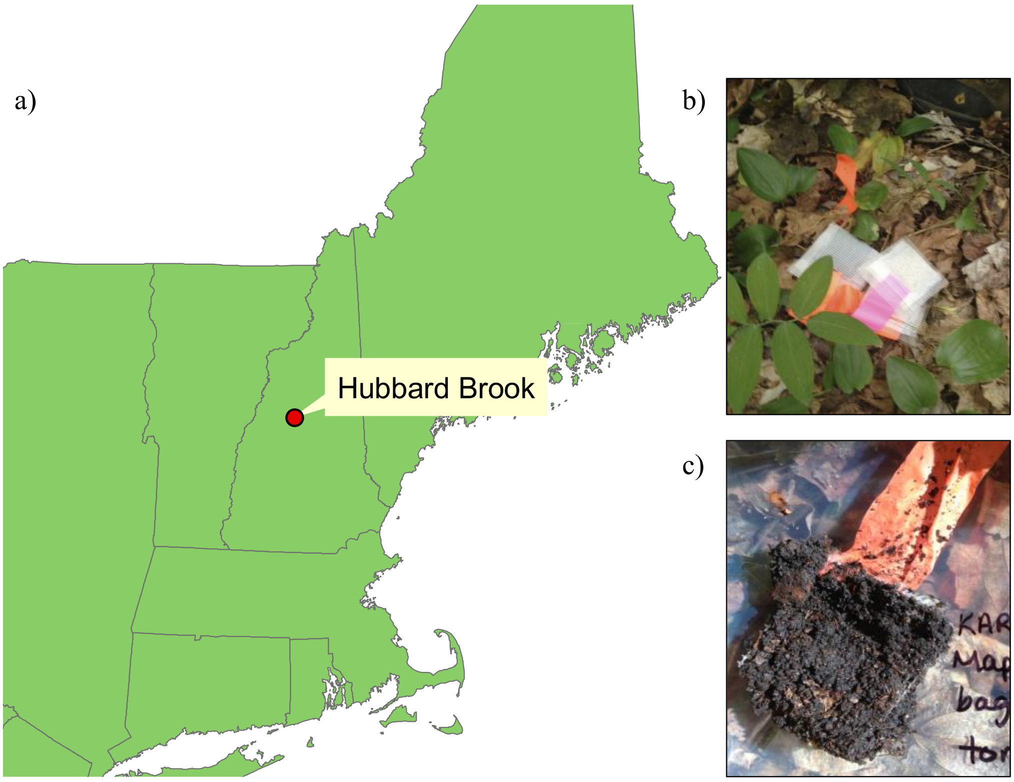

Figure 1.1: (a) Map of New England including sketched location of Hubbard Brook LTER (b) mesh in-growth bags before deployment (c) tonalite in-growth bag from maple-dominated site after retrieval at day 100.

This is an ideal site to test if in situ weathering is enhanced in forest plots dominated by EcM vs. AM symbioses due to this shallow depth to bedrock and 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 deployed across two forested stands selected for their prevalence of AM- and EcM-dominated plots. Site 206 is a mixed beech/birch plot dominated by beech (Fagus grandifolia) and birch (Betula sp.), which are known to associate with ectomycorrhizal 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 to avoid seedlings, and their proximity to non-dominant vegetation to control for fungal type.

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 double 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 and microbes, including fungal hyphae, to enter. Rocks of two lithologies with distinctive P_2O_5, MgO and CaO contents were used (Table 1.1).

Table 1.1. 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	**Bar 3 - Tonalite**
SiO_2	74.70	57.79
TiO_2	0.14	1.84
Al_2O_3	13.12	17.25
Fe_2O_3	1.92	9.27
MnO	0.02	0.24
MgO	0.47	2.3
CaO	0.20	3.03
Na_2O	3.91	2.67
K_2O	4.6	4.15
P_2O_5	0.02	0.91
Total	99.12	99.45

Conway Granite with low MgO, CaO, and P_2O_5 content (0.47, 0.20, and 0.03 wt. % respectively) collected from Grafton County was selected to represent low-nutrient substrate (Barker NHGS, 2013). Biotite tonalite with high MgO, CaO, and P_2O_5 content (2.3, 3.03, and 0.91 wt. % respectively) collected from Strafford County was used as a nutrient-rich substrate (Barker NHGS, 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 250-500µm and acid washed (24 h in 1N nitric acid) and rinsed iteratively with 18MΩ DI water. Aliquots (~ 10g) of acid-washed rock chips were then sealed into double-layered mesh bags and buried (Figure 1.1b). A Conway Granite and tonalite bag were withheld from field installation and instead stored at 20$_{o}$C 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 in site 206 and at the base of maple trees in site 237 (Supplemental Figure A.1). Bags were buried in the organic horizon at 10 cm depth or where the Organic Horizon met the mineral A Horizon, whichever occurred first. 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 1.1, Supplemental Figure A.1).

1.3.2 Analytical Techniques

After removal from the ground, bags were stored at -20°C 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) 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 (NH4Cl) at pH=7 in the UNH Geochemistry Clean laboratory. An additional 24-hour 1.0 N nitric acid leach allowed for assessment of the fraction that may weather over longer time scales. Leachate volumes (~10 mL) collected after both steps were subsampled and analyzed for elemental contents and isotopic compositions.

Abundances of Mg, P and Ca were assessed for both sites and rock types on an AttoM High Resolution (HR)- ICP-MS at the University of New Hampshire. Accuracy and precision for Mg, P and Ca were assessed at ≤ 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 and Blum, 2007). Aliquots (~3 g) of leachate samples were taken from the original NH4Cl and HNO3 leaches and dried down to concentrate the elements prior to isotopic analyses. 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). Procedural blanks were < 400 ng and < 200 ng for Sr and Pb, respectively, which was negligible for the abundances of Sr and Pb measured. Collected solutions were dried down and redissolved in 2% HNO3 for analysis on the Nu plasma II ES multi-collector inductively coupled plasma mass spectrometer (MC-IPC-MS). Lead instrumental mass fractionation was corrected externally via Tl normalization (White et al. 2000), and isotope ratios were additionally adjusted for instrumental drift using sample-standard bracketing (Albarède et al. 2004) and the values for NIST SRM reported by Eisele et al. (2003). Ten NIST SRM 981 analyzed as “samples” in addition to the bracketing standards produced averages (and 2σexternal) of $_{208}$Pb/$_{204}$Pb = 36.727 (0.005), $_{207}$Pb/$_{204}$Pb = 15.498 (0.002) and $_{206}$Pb/$_{204}$Pb = 16.941 (0.002). Strontium isotopes were corrected internally for instrumental mass bias relative to 86Sr/88Sr = 0.1194 and additionally adjusted relative to NIST SRM 987 bracketing standards. The NIST SRM 987 bracketing standards gave 0.710248 (2σexternal = 0.000016). We interpret our data in the context of forest floor Pb isotope compositions represented by HBEF sporocarps that reflect the soil solution (Supplemental Table A.3). Sporocarp Pb isotope data were analyzed on the Nu Plasma 500 HR MC-ICP-MS at ENS Lyon after separation of Pb and using the same MC-ICP-MS techniques as described above with a NIST SRM 981 average for n=7 of $_{208}$Pb/$_{204}$Pb = 36.726 (0.007), $_{207}$Pb/$_{204}$Pb = 15.498 (0.003) and $_{206}$Pb/$_{204}$Pb = 16.941 (0.002).

1.4 Results and Discussion

1.4.1 Nutrient Mobilization

Exchangeable nutrients, which are those liberated by 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-leach (Figure 1.2, Table 1.2, Supplementary Table A.1). In interpreting the results, we must take into account the relatively low number of exchange sites afforded by rock chips in comparison to soils on which the NH4Cl leaching is more typically conducted to assess the nutrient availability in the soil solution (e.g., Nezat et al. 2007). Accordingly, the solute concentrations in the exchangeable fraction at pH 7 must be considered to include a minimal amount of mineral dissolution, especially after acid washing prior to deployment and incubation in soils for 100 days. We therefore interpret exchangeable concentrations of macro- and micro-nutrients cautiously as much of what was liberated by weathering would be 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.

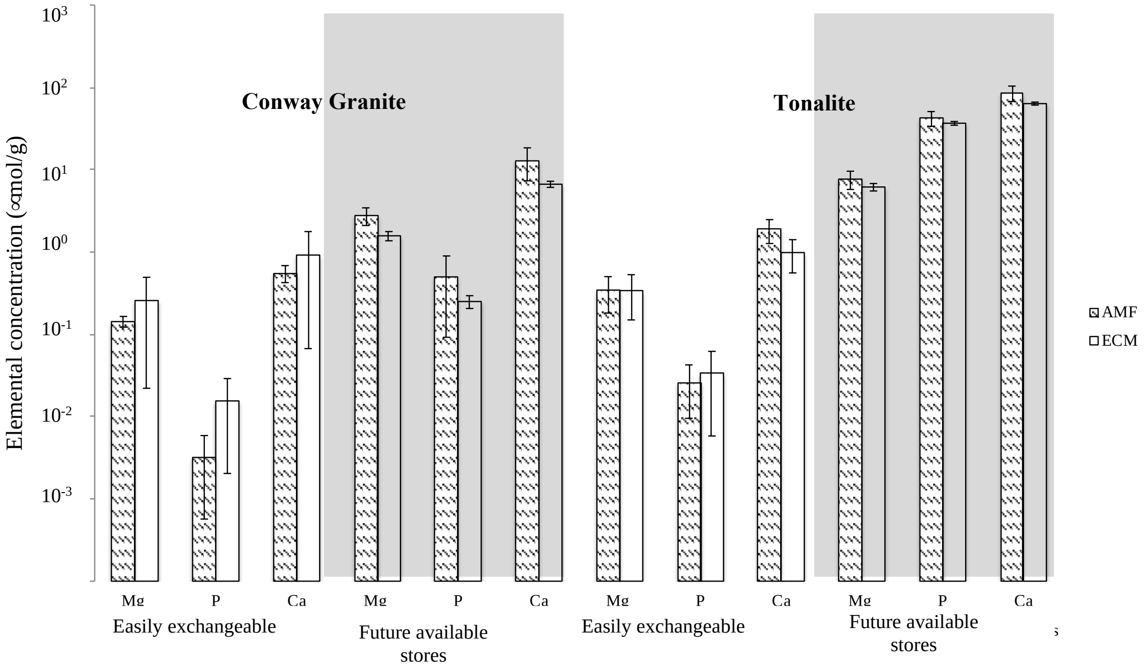

Figure 1.2: Average elemental concentrations of Mg, P and Ca of Conway Granite and tonalite samples from both AM- and EcM-dominated sites (represented by hash marks and solid bars, respectively). 1σ standard deviation between the various in-growth bags planted at both sites (AM site n=8, EcM site n=7) represented by error bars

Analyses of the exchangeable fraction in the retrieved mesh bags confirm that there were not significantly different average elemental fluxes between the AM- and EcM-dominated sites (Figure 1.2, Table 1.2). Exceptions to this generalization include the significant Ca fluxes from tonalite ammonium chloride leaches ($p < 0.01$) (Table 1.2). 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, supporting the argument that the exchangeable fraction measured on retrieved deployed mesh bags must be considered a minimum. Of the three nutrient elements studied in the easily exchangeable fraction, P from the field bags had the lowest concentrations when compared to that of the control bag.

Table 1.2. Average concentrations for Mg, P and Ca in easily exchangeable and future available stores leachates in both AM- and EcM-dominated sites.

		Control (μmol/g)	**AMF Average (μmol/g)**	**AMF Std. dev[1]**	**EcM Average (μmol/g)**	**EcM Std. dev[1]**	**p-value[2]**
Conway Granite	Mg	0.863	0.143	0.021	0.257	0.235	0.249
Ammonium chloride	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	0.991
Nitric	P	0.242	0.492	0.400	0.250	0.044	0.529
	Ca	7.272	12.85	5.542	6.641	0.561	0.006
Tonalite	Mg	0.527	0.340	0.160	0.339	0.190	0.001
Ammonium chloride	P	0.096	0.026	0.016	0.034	0.028	0.131
	Ca	2.406	1.866	0.600	0.982	0.428	0.016
Tonalite	Mg	4.849	7.642	1.917	6.142	0.641	0.067
Nitric	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

[1] Standard 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.

There were also only few significant differences in the average elemental concentrations between AM- and EcM-dominated sites recorded in the nitric acid leaches, which are generally interpreted to represent future readily available nutrient stores. Exceptions to this generalization include significant Mg flux from the Conway Granite nitric leachate ($p < 0.01$)

and significant Ca fluxes from the nitric leach of both Conway Granite and tonalite ($p < 0.1$) (Table 1.2). The control, unburied rock chips subjected to the same laboratory leaching treatment, had comparable or lower elemental solute concentrations in the nitric 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 nitric leach process.

Interestingly, in no case were the average elemental fluxes from the EcM-dominated site higher than those of the AM-dominated site. The higher average Ca concentrations observed in the maple AM-dominated site support the importance of Ca for sugar maple health and therefore AM fungal survival (Schaberg et al., 2006; Vadeboncoeur, 2010). The fact that AM fungi appear to be more adept at making Ca more mobile from both rock types in the future (as represented by the application of nitric leach) could reflect that the effectiveness of the AM fungi to liberate nutrients from soil and rock may be strongly element specific.

When bags were removed from the ground in many cases roots were seen entering the first layer of mesh and hyphae were visible in 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 that root or hyphae from tree and fungal species not contained within the plot or from small saplings and shrubs in the plot colonized the mineral mesh bags as they were planted around the sites. Additionally, saprotrophic fungi in the area and the community of soil bacteria could have acted upon the ingrowth bags impacting nutrient fluxes (Connolly et al. 1999; Koele et al. 2009; Uroz et al. 2009; Christophe et al., 2013). Though abiotic field conditions (e.g., precipitation, soil pH, temperature and soil organic matter chemistry) 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 design allowed for employment in sites where most of the variability in these field conditions is minimized.

1.5 Isotopic assessment of mineral decomposition reactions

Lead and strontium isotopes have proven useful for identifying mineral breakdown 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 dominant minerals (e.g., feldspars) (Erel et al. 2002). Lead isotopes for all samples show little variation between the two fungal types on the same rock type (Figure 1.3) but display a marked contrast from the soil solution Pb isotopic compositions which we interpret from fungal sporocarp data from HBEF and neighboring Bartlett Experimental Forest where soils are formed on local Conway Granite. Radiogenic $_{208}$Pb/$_{204}$Pb and $_{207}$Pb/$_{204}$Pb indicate the importance of apatite dissolution in Conway Granite samples subjected to nitric leaching (Figure 1.3). 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 1.3). Elevated solute fluxes of key nutrients (Ca, Mg, P) in the nitric solutions (Figure 1.2, Table 1.2), however, are consistent with enhanced mineral decomposition.

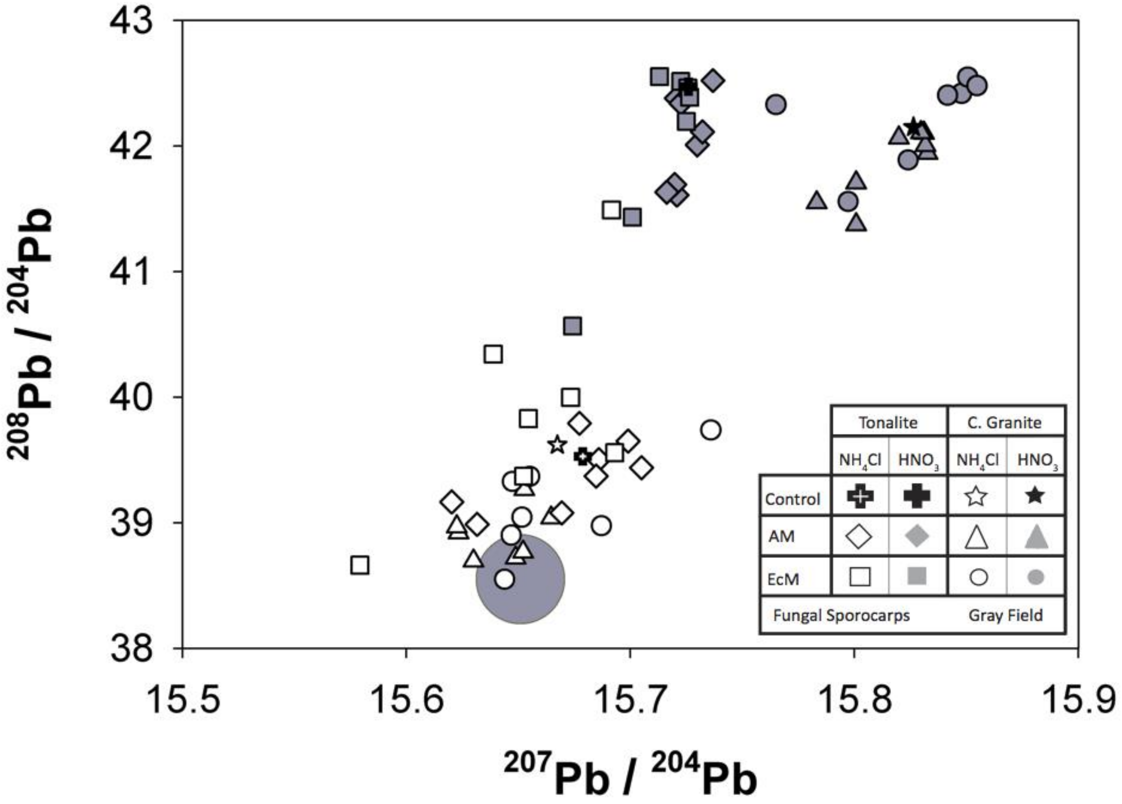

Figure 1.3: ^{208}Pb/^{204}Pb vs. ^{207}Pb/^{204}Pb for granite and tonalite samples from both AM- and EcM-dominated sites. Lead isotopic data for sporocarps harvested from Bartlett and Hubbard Brook Experimental Forests shown as a field and are used to approximate bulk soil composition (Pb isotopic data from the sporocarps are provided in Appendix Table A.3).

Radiogenic Sr isotope signatures in the exchangeable fractions indicate the strong leveraging of biotite dissolution on the solute fluxes across both sites (Figure 1.4). Increasing feldspar and apatite contributions are apparent with decreased ^{87}Sr/^{86}Sr in the nitric leaches (Figure 1.4). The increasingly radiogenic Pb isotopic values are consistent with increasing apatite contributions. In both cases the signals for these mineral dissolution reactions are not significantly different based on the dominant fungal symbioses of the sites. As with exchangeable solutions, solute generated from a 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, though similar time scale experiments have shown increased fungal colonization and others over longer periods have observed similar findings as well (Wallander et al., 2001; Koele et al. 2013).

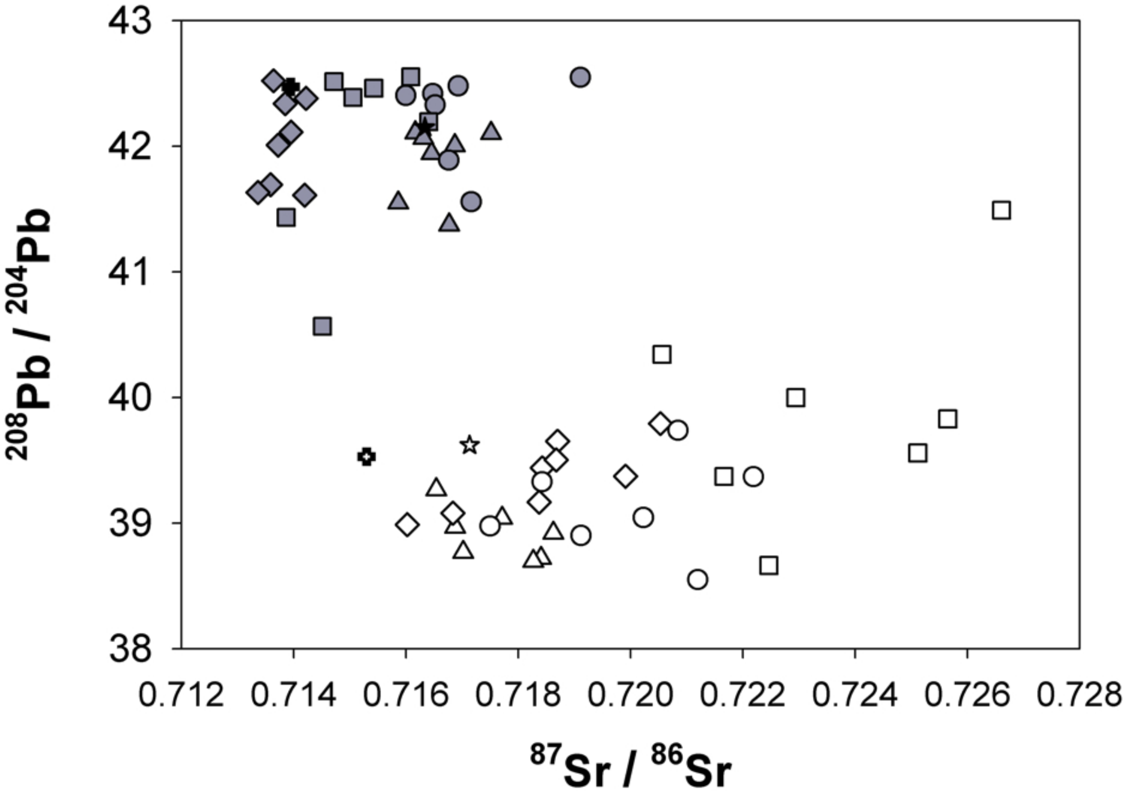

Figure 1.4: ^{208}Pb/^{204}Pb vs. ^{87}Sr/^{86}Sr for granite and tonalite samples from both AM- and EcM-dominated sites. Symbols as described in Figure 1.3

The isotopic balance of ^{208}Pb/^{204}Pb, ^{207}Pb/^{204} Pb and ^{87}Sr/^{86}Sr suggests nominally similar modes of mineral contributions to the solute flux with the weathered fraction dominated by apatite and feldspar dissolution in both cases (as suggested by the Pb isotopes), while the elevated major element fluxes indicate that larger amounts of weathering has happened in the field-deployed samples.

1.6 Summary and Implications

Elemental fluxes from both sites were very similar for phosphorus and magnesium in both 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 nitric leaching solutions 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 AM fungi could be equally effective at accessing nutrients stored in rock and soil minerals.

Isotopic signatures of the in-growth bag rocks provide evidence for similar mineral decomposition reactions at both sites that are distinct from the soils. Radiogenic ^{208}Pb/^{204}Pb and ^{207}Pb/^{204}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 varying biology present on the site. ^{87}Sr/^{86}Sr taken together with ^{208}Pb/^{204}Pb and ^{207}Pb/^{204}Pb indicate the dissolution of biotite in the earlier stages of weathering followed by feldspar playing a stronger role in the nitric leachate to simulate future nutrient availability. 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 versus 1 N HNO_3 to model future nutrient stores), with no impact of AM vs. EcM fungi noted over the 100-day treatment. Our findings may suggest that both EcM and AM fungi 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. We 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 biologic community active in the weathering process.

1.7 Acknowledgements

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Undergraduate Research Fund and Hamel Center for the support of her work. Hubbard Brook Experimental Forest is operated and maintained by the US Forest Service, Northern Research Station, Newtown Square, PA.

CHAPTER 2: IMPACT OF LITHOLOGY ON MYCORRHIZAL MINERAL WEATHERING REACTIONS

2.1 Highlights

- We investigated the influence of arbuscular mycorrhizal (AM) and ectomycorrhizal (EcM) fungi on weathering across two rock types.
- We examined elemental fungal enrichment factors to assess how lithology influenced mineral nutrient release.
- *A. saccharum* seedlings grown with AM fungi on nutrient-poor substrate show increased ability to obtain elements from the rock compared to those grown without a fungal symbiont.
- There was no isotopic fractionation of Mg from roots to foliage in samples grown with AM fungi compared to those grown without fungi.

2.2 Abstract

Mycorrhizal fungi, both ectomycorrhizal (EcM) and arbuscular mycorrhizal (AM), influence mineral weathering and nutrient cycling in ecosystems. The relative effectiveness of AM and EcM fungi at weathering is uncertain, with some field studies arguing that AM and EcM fungi both contribute to weathering processes while others argued EcM fungi may inhibit weathering. Here, we tested weathering patterns in a controlled growth chamber setting with AM and EcM symbioses across two lithologies. The results of this study address the hypotheses that a) fungal weathering is enhanced in minerals containing plant-necessary nutrients when plants are in a nutrient-poor environment, b) fungal weathering is higher in microcosms that contain EcM symbioses than in those with AM symbioses, and c) seedlings grown with AM fungi would align with field measurements made by Kimmig et al. (2018) and have less magnesium isotope fractionation in host plants relative to the non-mycorrhizal seedlings. Elemental concentrations were measured, and fungal enrichment factors were calculated for AM and EcM samples grown on a nutrient-rich (marl) and nutrient-poor (granite) lithologies. Magnesium (Mg) isotopes were measured in roots and foliage across lithologies and fungal type. The data suggest that AM fungi can increase access to important nutrients in minerals when grown in a nutrient-poor environment. Rare earth elements (REE) were also measured as markers of mineral weathering. Low levels of europium (Eu) when compared to other REE like lanthanum indicate apatite weathering and this signal was seen in AM but not EcM symbioses. Magnesium isotopes fractionated in maple samples that were grown without fungal inoculum but not in those grown with AM fungi. Together with elemental enrichment data, our finding supports the idea that rock type influences mycorrhizal weathering, with nutrient-poor lithologies requiring active weathering by mycorrhizal fungi, and that AM fungi may influence Mg isotope signatures during transport between fungi and host maple trees.

2.3 Introduction

Mycorrhizal fungi, important components of nutrient cycling in terrestrial ecosystems, are symbiotic fungi that form associations with a variety of land plants in diverse ecosystems (Smith & Read, 2008). Both ectomycorrhizal (EcM) and arbuscular mycorrhizal (AM) symbioses receive carbon from the host plant and in turn increase the absorptive surface area of their host's root system via the production of fungal mycelium and can provide increased access to essential water and nutrients (Gadd, 2007). These fungi can contribute to a combination of physical and chemical weathering processes, aiding in the creation of physical inroads into a rock's surface via tunneling or by producing chelating compounds that raise the pH of the soil solution surrounding the rock (Drever, 1997; Banfield et al., 1999). EcM fungi are thought to increase mineral weathering more than AM fungi due to their production of low molecular weight organic acids like oxalate and citrate which can enhance mineral dissolution (Landeweert et al., 2001; Hoffland et al., 2004; Gadd, 2007). EcM fungi can also generate tunneling features in minerals and can seek out and preferentially colonize high nutrient minerals and enhance mineral weathering (Blum et al., 2002; Hamburg et al., 2003; Leake et al., 2008, Smits et al., 2012). Conversely the ability of AM fungi to weather minerals in the soil is less clear. AM fungi have not been shown to produce oxalic acid or other chelating compounds and instead it is thought localized alterations in pH due to increased respiration may lead to minor increases ion mobilization in small scale around the hyphae (Gadd, 2007).

There is debate over the relative abilities of AM fungi to influence weathering and nutrient cycling due to their different traits (Terrer et al., 2016; Norby et al., 2017). Some studies have observed bio-sensing behavior and tunneling features in AM colonized minerals (Sverdrup, 2009; Quirk et al., 2012; Koele et al., 2013). Sanz-Montero and Rodriguez-Aranda (2012) argue that AM fungi may have played an important role both in the past with paleo evidence of arbuscular mycorrhizae and their role in mineral weathering from Miocene paleosols. Experiments conducted by Quirk et al. (2012) support the hypothesis that plants associated with both AM and EcM fungi can dynamically allocate C to the mycorrhizae that are able to provide access to plant-limited nutrients, leading to degraded mineral surfaces and intensified weathering.

A field-based comparison study in New Zealand by Koele et al. (2014) evaluated differences in weathering based on fungal type and found tunneling features and rare earth element (REE) uptake, indicative of apatite weathering, in both AM and EcM plots (Koele et al., 2014). Remiszewski et al. (2016) conducted field experiments fabricating an *in-situ* geologic gradient in the mixed hardwood/coniferous experimental forest at Hubbard Brook. Major elemental nutrients coupled with strontium (Sr) and lead (Pb) isotopic values for both high and low nutrient rock types buried in AM and EcM dominated forest stands indicated that weathering fluxes in these forest stands may be very similar (Remiszewski et al., 2016). By contrast, a field study conducted by Smits and colleagues (2014) found a retarding effect of EcM fungi on mineral weathering in an area with galena-rich quartzite and natural lead contamination (Smits et al., 2014). The lack of EcM impact on weathering highlights the need to study the influence of bedrock type on fungal weathering activity. The idea of a "bottom up" control of geologic substrate on plant growth has been suggested based on field data (Castle and Neff, 2009), but this is explored further in this controlled growth chamber experiment. Rock nutrient content has been shown to impact arbuscular mycorrhizal nutrient mobilization in a microcosm experiment and supports the idea of ground up control (Burghelea et al., 2015).

Magnesium (Mg) is a critical plant nutrient needed for RNA generation and is crucial for photosynthesis, as chlorophyll has Mg as a central atom. It is also known to be fractionated by plants as it is transported throughout the plant and from older to newer growth (Bolou-Bi et al., 2010, 2012; Tipper et al., 2010, 2012). Fungi have impacts on Mg isotope signatures that can impact interpretation of Mg isotopes at the soil, ecosystem, and river catchment scale but the signatures of individual fungi and the underlying mechanisms that drive them are an active area of research (Fahad et al. 2016, Pokharel et al., 2017, Kimmig et al., 2018). The substrate the fungi are grown on and interact with will also determine Mg isotope signals. In a study by Fahad and colleagues (2016), ectomycorrhizal fungi grown on granite substrate are enriched in lighter isotopes when compared to non-mycorrhizal fungi. They suggested that this depletion in δ_{26}Mg in ectomycorrhizal fungi may be explained by a higher capacity to mobilize Mg from the mineral substrate when compared to the growth medium (Fahad et al. 2016). In a study by Kimmig and colleagues (2018) maple trees, known arbuscular mycorrhizal fungi hosts, in the field did not show signs of uptake-related Mg isotope fractionation. They coupled these data showing a lack of fractionation in the field with nonmycorrhizal maple laboratory specimens showing enrichment in heavy Mg isotopes and pointed to the role of arbuscular mycorrhizal fungi in determining the Mg isotopic signature (Kimmig et al. 2018). As Mg isotope signals are critical for estimating global scale continental weathering, having a better constraint on Mg isotope signatures and fractionation effects across mycorrhizal fungal types is critical.

Constraining the influence of mycorrhizal fungi on mineral weathering and differences in weathering ability between AM and EcM fungi can help improve models of nutrient cycling that work to incorporate biotic factors and help improve understanding of critical zone processes (Taylor et al., 2009; Brantley et al., 2011; Taylor et al., 2012). Recent meta-analysis by Terrer et al. (2016) suggested the importance of mycorrhizal fungi in modeling carbon and CO_2 impacts on vegetation. The results predicted an enhanced ability of plants with established EcM symbioses to see continued growth under increased CO_2 levels while AM-colonized plant growth was limited by N availability, leading Terrer et al. (2016) to call for the implementation of mycorrhizal symbionts in future models to enhance accuracy in predicted carbon dynamics under future climate change. In response, Norby et al. (2017) asserted a proper assessment of the impact of mycorrhizal fungi on carbon cycling must include ecosystem age and physiological differences in the plants included in the models. The poorly quantified role of fungal components to weathering fluxes make it challenging to translate these observations for implementation in a predictive framework (e.g., Taylor et al., 2012).

Studies of fungal symbioses under controlled conditions afford a means to isolate the fungal symbioses from environmental or other biotic factors in the ecosystem environment. Here we present work conducted in a controlled greenhouse setting with AM and EcM symbioses across two lithologies that addresses the hypotheses that a) *fungal weathering is enhanced in minerals containing plant-necessary nutrients when plants are in a nutrient-poor environment*, b) *fungal weathering is enhanced in microcosms that contain EcM symbioses versus those with AM symbioses* and *c) AM fungi can inhibit Mg isotope fractionation in their* *host plants.* The design of this experiment allows for bedrock-supplemented bags which contain mineral abundances appropriate for typical continental bedrock to be implanted in the controlled greenhouse environment coupled with a watering regime which mitigates the influence of variations in temperature and precipitation on weathering. Relative abundances of elements and Mg isotopic ratios were determined for microcosm samples in order to gain insight in mineral decomposition linked with nutrient distributions across the two different lithologies.

2.4 Methods

2.4.1 Experimental design

Pinus sylvestris, an EcM-associated tree, and *Acer saccharum*, an AM-associated tree, were grown as seedlings in a sterile environment. These seedlings were then inoculated with *Suillus bovinus* (EcM) and *Glomus intraradices* (AM), fungal symbionts, with a subset of seedlings reserved to act as a non-mycorrhizal control. Cold-stratified *Acer saccharu*m seeds were collected from the ground beneath a stand of large sugar maples at East Foss Farm Cemetery in Durham, NH, USA. Surface-sterilized *Pinus sylvestris* and *Acer saccharum* seeds were sown in a perlite/vermiculite mixture moistened with a balanced nutrient solution (Ingestad and Kahr, 1985). The experiment was carried out in a growth chamber with 300μmol m_{-2} s_{-1} controlled photosynthetically active radiation (PAR), at least 70% relative air humidity, day/night rhythm of 18hr/6hr, and temperature ranging from 22_{o}C in the day to 15_{o}C at night (Hoff, 2009). One month after sowing, a number of uniform seedlings were selected for the experiment. *A. saccharum* seedlings were inoculated by dipping the root systems into a suspension of *Glomus intraradices* spores and replanting in the perlite/vermiculite mix. Non-mycorrhizal *A. saccharum* seedlings followed the same procedure but were not inoculated with the fungal spores and were planted in a separate tray of perlite/vermiculite mix. A sandwich technique was used to inoculate *P. sylvestris* seedlings with *Suillus bovinus* (van Tichelen & Colpaert 2000). Non-mycorrhizal seedlings of *P. sylvestris* followed the same procedure in the absence of fungal inoculum.

Seedlings were then transferred to 150-cm containers filled with sized (2-4 mm) perlite previously acid-washed with 0.5% H_2SO_4. Perlite was selected due to its low nutrient buffering. To simulate nutrient-poor and nutrient-rich substrates Conway Granite and Waits River Formation, a metamorphic limestone, were crushed and layered with sterile perlite in seedling microcosms. The Conway Granite is a 180 Ma biotite granite (Eby et al. 1992) containing 0.04% to 0.6% apatite (estimated from total P reported by Billings and Wilson, 1965; major phases include quartz, alkali feldspar, plagioclase and up to 7% biotite, and up to 1% trace phases (titanite). Zircon, allanite, apatite, sphene, and fluorite are common accessory minerals (Creasy and Eby 1993). The Waits river formation is a meta-limestone with abundant carbonate, sparse pyroxene and occasional sulfide (Ferry 1992; Bailey et al. 2004). A layer of washed, wet-sieved bedrock, either Conway Granite (1- 2 mm and 2-4 mm size fraction) or Waits River Formation (2-4 mm size fraction) was placed in the rooting zone of the seedlings during the planting.

Nutrients were applied at a constant relative addition rate of 3% per day and the seedlings were harvested after 80 days. The nutrient solution contained 292μM K_2SO_4, 116μM K_2HPO_4, 1777μM $(NH_4)2SO_4$, 73μM $Ca(H_2PO_4)2{*}H_2O$, 123μM $MgSO_4{*}6H_2O$, 9.3μM H_3BO_3, 3.7μM $MnSO_4{*}H_2O$, 6.3μM $Fe(NO_3)_3{*}9H_2O$, 0.2μM $ZnSO_4{*}7H_2O$, 0.2μM $CuCl_2{*}2H_2O$, and 0.04μM $Na_2MoO_4{*}2H_2O$ (Hoff, 2009). The nutrient solution supplied to the plants contained less than 25 mg N L-1 and its pH was adjusted to 4.5 using hydrochloric acid In order to address differences in the nutrient requirements between the pine and maple seedlings, the amount of nutrient solution for maples was double that of the pine for 2 days, then tripled for a third day with an additional 9 mg of Ca applied daily to maples. Solutions eluting through the microcosms, percolate, were also collected throughout the course of the experiment for all samples as a representation of soil solutions. After 80 days the seedling samples were destructively harvested and separated out in to roots, shoots, and foliage and were digested in 15N nitric acid and heat for further analyses (Figure 2.1).

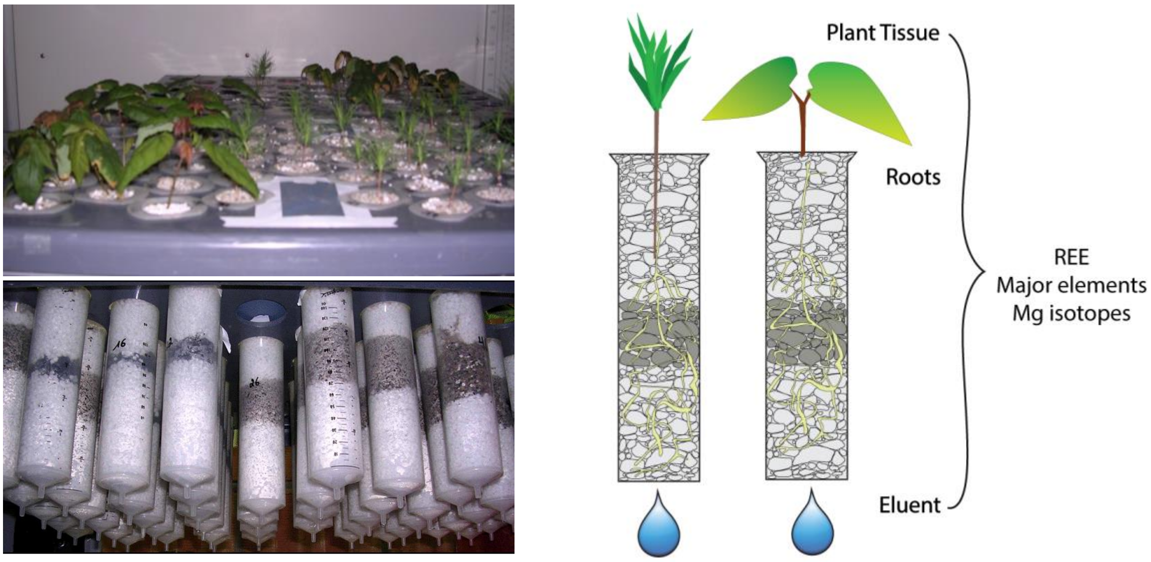


Figure 2.1: Photo of experimental set-up and methods schematic showing *Acer saccharum* and *Pinus sylvestris* seedlings grown in sterile perlite with bedrock chips as well as components collected and analyses preformed across all samples (Photo credit C.Hoff).

2.4.2 Analytical techniques

Aliquots of digested plant sample and percolates were taken for major element and REE analysis. Abundances of Mg, P, Ca , Mn and Fe were measured for both sites and rock types on an AttoM High Resolution inductively coupled plasma mass spectrometer at the University of New Hampshire. Accuracy and precision for were assessed for Mg and Ca at < 7% by replicate analyses of NIST 1643e and P was assessed at <6% error from an expected spike concentration.

To assess REE signals for apatite dissolution in a separate sample of Conway Granite, hand samples were collected from the abandoned Redstone Quarry (44.0184 ºN, 71.0978 ºW) and surface washed before grinding (Vadeboncoeur, 2013). Ground rock was passed through a series of stainless-steel sieves, and the fraction between 250 and 500 µm retained and thoroughly rinsed with deionized water (Vadeboncoeur, 2013). The un-weathered aliquot of granite chips was leached with 1 N nitric acid at 20 ºC for 24 hours to remove any surficial coatings, to extract apatite and other easily weathered accessory minerals, and to represent the apatite end member (Erel et al. 2004, Nezat et al. 2007). Concentrations of REEs were measured on aqueous samples diluted in 2% nitric acid with an AttoM high resolution single collector inductively coupled plasma mass spectrometer at the University of New Hampshire. A monitor sample with this matrix and 50 ppt REEs was run every 3-5 samples and used to correct for linear detector drift during the run. Analytic precision was < 5% for most REEs for granite leachates, and < 8% for Eu, Tm, Yb, Lu (Vadeboncoeur, 2013). The results of this are seen in Figure 2.5 to illustrate signals of apatite weathering from Conway Granite.

Aliquots of plant sample digested in 15N nitric acid and heat and percolates were processed for subsequent Mg isotope analysis using Mg separation procedures employing cation exchange chromatography with Bio-Rad AG50W-X12, following methods developed by Bolou-Bi et al. (2009). Mg isotopes were determined at ENS-Lyon on a NuPlasma, paired with a desolvating nebulizer using a sample-standard bracketing method (cf. Albarède et al. 2004) utilizing DSM-3. Most samples were analyzed with replicates to assess analytical precision.

2.5 Results and discussion

2.5.1 Major element enrichments

Fungal enrichment factors (FEF) were calculated for magnesium (Mg) and calcium (Ca) by taking the elemental concentration of the mycorrhizal sample and dividing it by the concentration of the non-mycorrhizal sample.

$$\text{FEF} = [\text{element}]_{\text{mycorrhizal sample}} / [\text{element}]_{\text{non-mycorrhizal sample}}$$

A value greater than one indicates a higher elemental concentration in the sample of a seedling grown in association with mycorrhizal fungi vs. the same sample grown without a mycorrhizal symbiont. FEFs were calculated for root, foliage, and percolate samples for both *Pinus sylvestris* and *Acer saccharum* grown on Waits River Formation (WRF) and Conway Granite rock substrates.

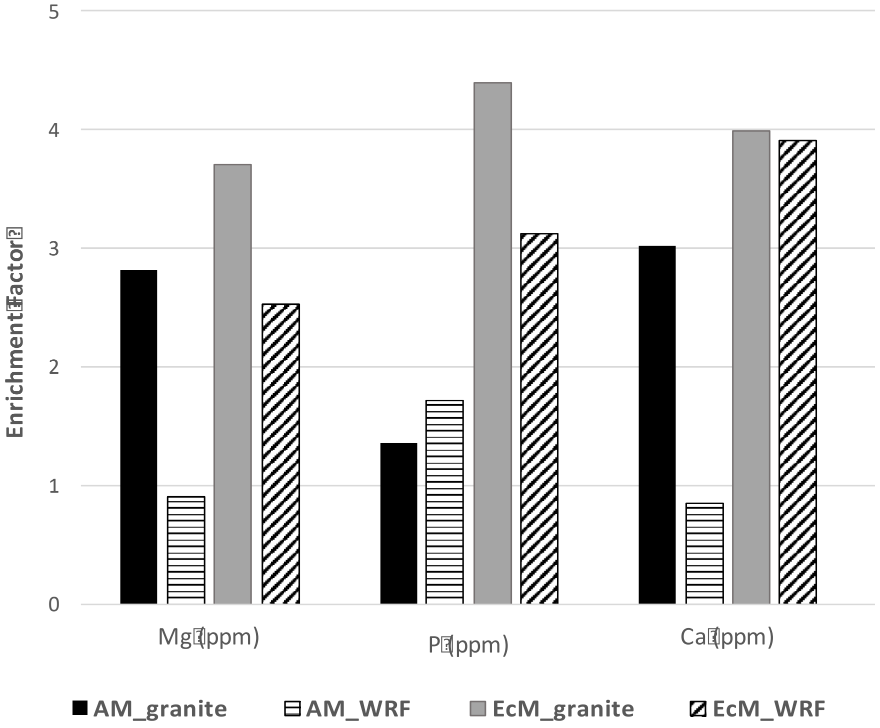


Figure 2.2: Enrichment factors for Mg, P, and Ca in root samples for *Pinus sylvestris* grown with and without *Suillus bovinus* and *Acer saccharum* grown with and without *Glomus intraradices*. Each bar represents an individual sample. Values > 1 for FEFs indicate higher elemental concentrations in the mycorrhizal samples than the non-mycorrhizal sample.

Acer saccharum seedlings grown with *G. intraradices* on Conway Granite bedrock are enriched (FEF > 1) in Mg and Ca when compared to the mycorrhizal *A. saccharum* seedlings grown on Waits River Formation (WRF) which show no elemental enrichments in the mycorrhizal seedlings compared to the non-mycorrhizal. In contrast *Pinus sylvestris* root samples show similar Ca, and Mg enrichments for seedlings grown on both WRF and Conway

Granite. The WRF, a calcareous rock, will dissolve easily under the relatively low pH (pH ~ 4.5) of the nutrient solution, creating access to nutrients in the soil solution without the need for additional fungal activity.

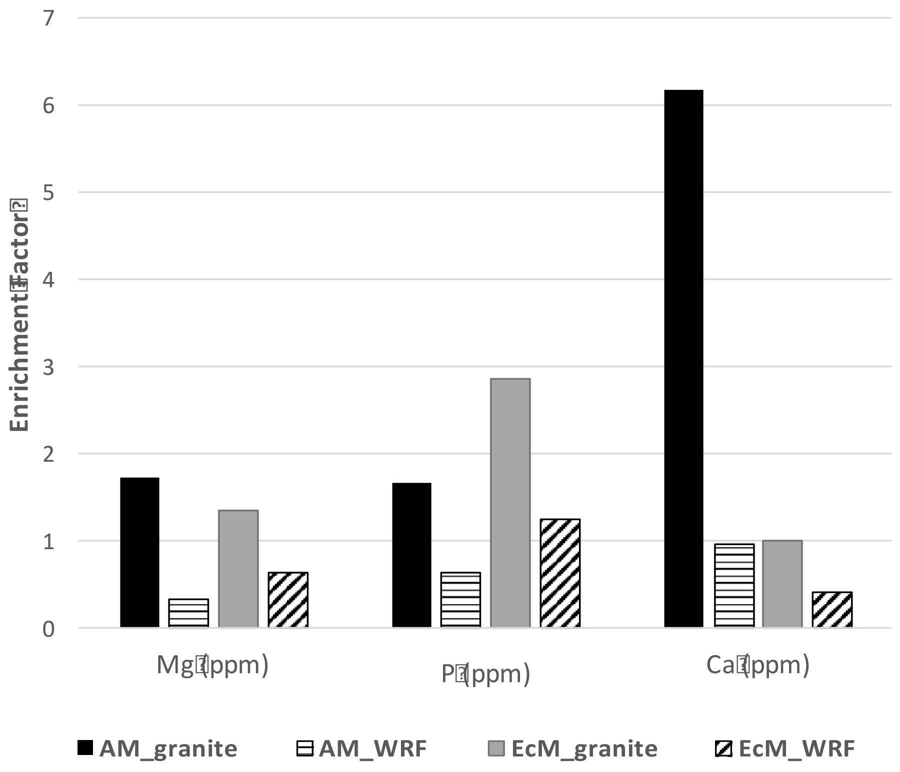


Figure 2.3: Foliar FEFs for Mg, P, and Ca in *Pinus sylvestris* grown with and without *Suillus bovinus* and *Acer saccharum* grown with and without *Glomus intraradices*. Each bar represents n=1 sample.

Fungal enrichment factors calculated for foliage samples of *A. saccharum* and *P. sylvestris* seedlings grown on WRF show no substantive enrichments in Mg, P, or Ca concentrations. In contrast foliage samples for *P. sylvestris* seedlings grown on Conway Granite show slight enrichment in Mg and larger enrichment in P. The *A. saccharum* seedlings grown on Conway Granite show slight enrichments in Mg and P and more suggestive enrichments in Ca.

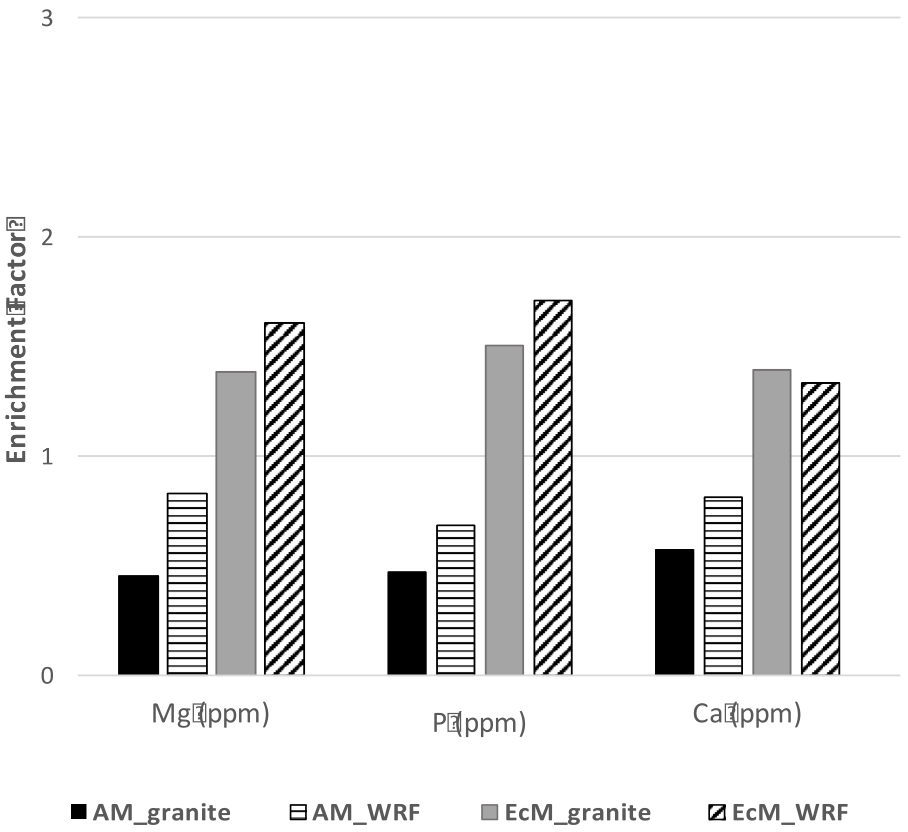


Figure 2.4: Enrichment factor in percolated solution collected from samples of *Pinus sylvestris* grown with and without *Suillus bovinus* and *Acer saccharum* grown with and without *Glomus intraradices*. Each bar represents n=1 sample. Values > 1 on the y-axis indicate larger elemental concentrations in the mycorrhizal samples than the non-mycorrhizal samples.

Elemental enrichments for waters collected during the growth period show slight enrichment in Mg, P, and Ca for all *P. sylvestris* samples regardless of rock type present and a signal for depletion in these three elements across all *A. saccharum* samples independent of rock type.

Taken together these FEF’s may suggest that when grown with access to a higher nutrient content and easily dissolvable rock type like the calcareous Waits River Formation, AM symbionts may not provide any additional access to nutrients like Ca, Mg, and P and therefore may not be actively weathering rock and minerals within the soil environment. This is illustrated by root and foliage FEF ≤ 1 for Ca and Mg in samples grown on WRF, indicating non-mycorrhizal had equal or higher concentrations of these elements in root and foliage samples when compared to the mycorrhizal counterparts. These FEFs may also lend support to the idea that, when grown on a nutrient-poor rock type, mycorrhizal fungi may access elements in the lithologic minerals to provide for their host. This can be seen especially in the case of calcium and magnesium enrichments in both the roots and the foliage for *A. saccharum* seedlings grown in association with *G. intraradices.*

2.5.2 Rare Earth Elements as a Proxy for Apatite Dissolution

In order to assess apatite weathering a nitric leach was applied to an abiotic granite sample. The 1 N nitric acid leach was intended to remove easily weatherable minerals from crushed rock, which we predicted would primarily comprise apatite (Nezat et al., 2007). Rare earth elements were measured on this abiotic leach and high La/Ba ratios (~23) relative to whole rock (~0.37) and low values of Ba in the leach solution could indicate a relatively small contributions from feldspar dissolution in this leaching process (Vadeboncoeur, 2013). Concentrations of REEs in the acid leach ranged from 110 ng Eu g$_{-1}$ to 173 µg Ce g$_{-1}$ in the granite (Table B.1 Vadeboncoeur, 2013).

The nitric acid leach shows high ratios of light REEs (LREEs, e.g. La, Ce) to heavy REEs (HREEs, e.g. Yb, La) compared with bulk Conway Granite and literature values for apatite (Table B.1). The La/Eu and Sm/Eu ratios are greater than in bulk rock, due to the wider range of mineral compatibilities for Eu compared to the other REEs (Gromet and Silver 1983, Bea et al. 1994). These may include monazite (REE phosphate), allanite (REE-rich epidote), and titanite (calcium-titanium orthosilicate); (Gromet and Silver, 1983; Harlavan and Erel 2002, Harlavan et al., 2009). Titanite and monazite tend to have low LREE/HREE relative to apatite (Adams et al., 1962; Gromet and Silver, 1983; Bea et al., 1994), making them a poor fit for the observed LREE/HREE.

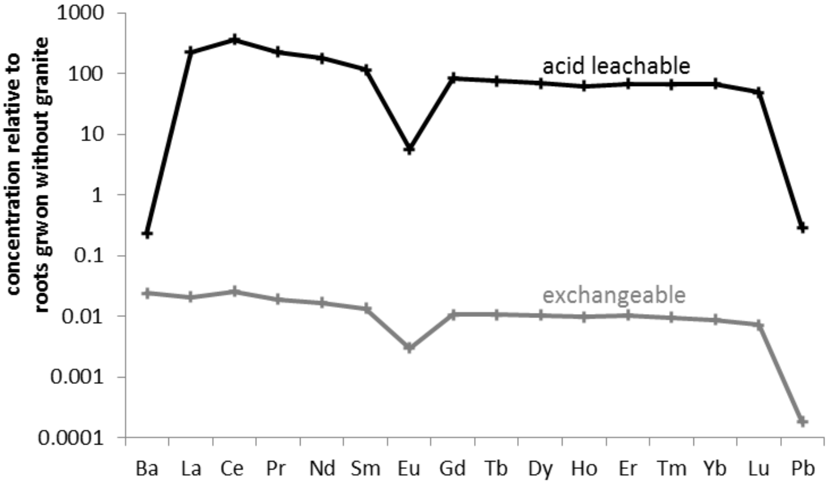


Figure 2.5: REE concentrations in acid-leachable fraction of fresh granite and exchangeable concentrations in the abiotic treatment (Vadeboncoeur, 2013).

Rare earth elements were analyzed for all samples and FEF's for REE's were calculated by dividing the concentration of REE in mycorrhizal samples by the REE concentration of non-mycorrhizal samples. A value over one indicates a higher concentration of REE's in the sample grown in association with mycorrhizal fungi vs. the same sample grown without a mycorrhizal symbiont.

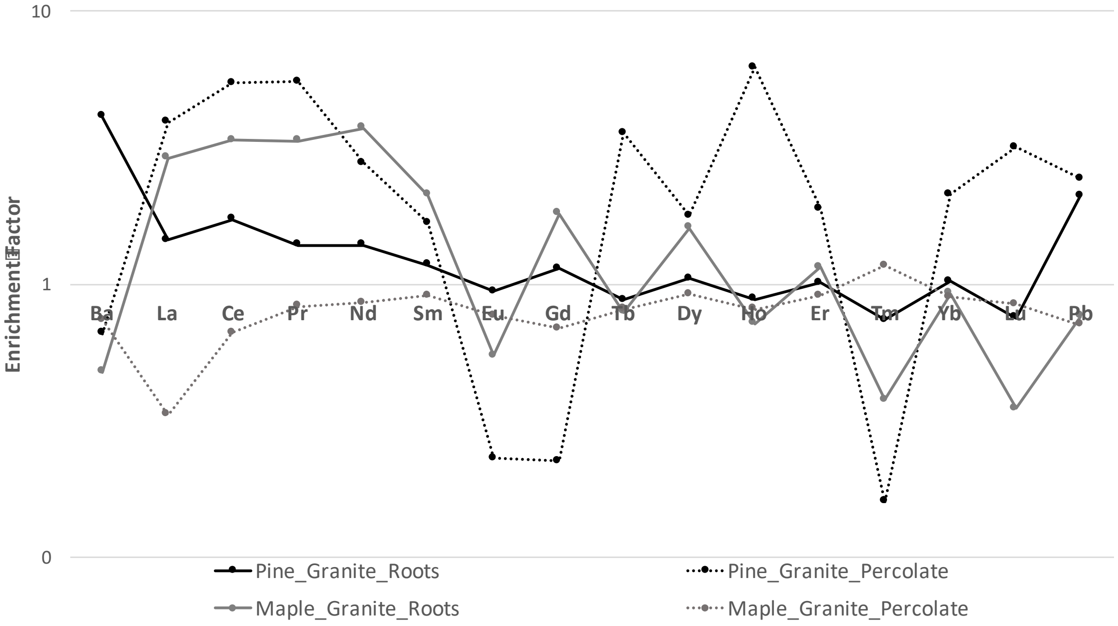
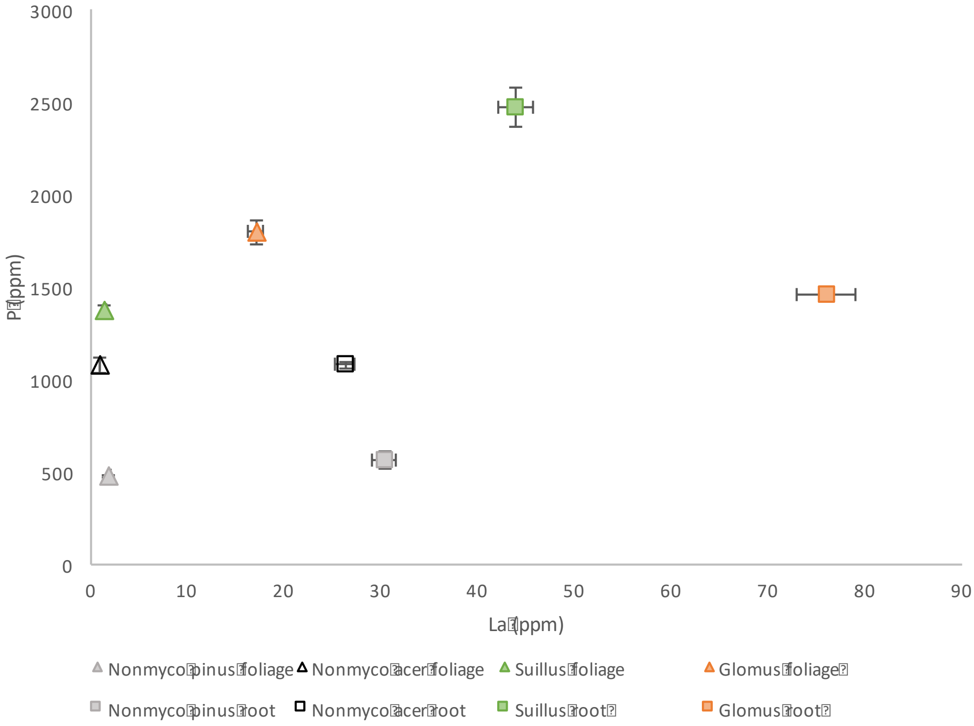


Figure 2.6: REE enrichment factors for P. sylvestris and A. saccharum samples grown on granite. Values over 1 on the y-axis indicate larger concentration of REE in the mycorrhizal samples than the non-mycorrhizal samples.

Europium (Eu) depletion, evident in root samples of *A. saccharum* grown on Conway Granite (Figure 2.6), is not apparent in *P. sylvestris* root samples grown with the same granite substrate. This pattern of a negative Eu anomaly indicates weathering of the mineral apatite which is present in Conway Granite (Figure 2.6). This signal for apatite weathering seen in the *A. saccharum* samples but not present in the *P. sylvestris* samples lends support to the patterns seen in the major enrichments that *G. intraradices* may be able to enhance weathering to obtain nutrients like Ca that the host tree needs to survive from nutrient-poor lithologies.

Rare earth elements in combination with major element concentrations can also help elucidate the presence of mineral weathering. In samples where access to phosphorus is limited, La may trace P mobilization from apatite (Figure 2.7a). Roots in both mycorrhizal treatments are characterized by enhanced La abundances. Foliage of mycorrhizal maple is also enriched in La and P relative to nonmycorrhizal maple, but foliage of mycorrhizal pine, while enriched in P, shows no enrichment in La. In samples grown on the Waits River formation where P is more broadly accessible La and P enrichments are mainly seen in the ectomycorrhizal cultures.



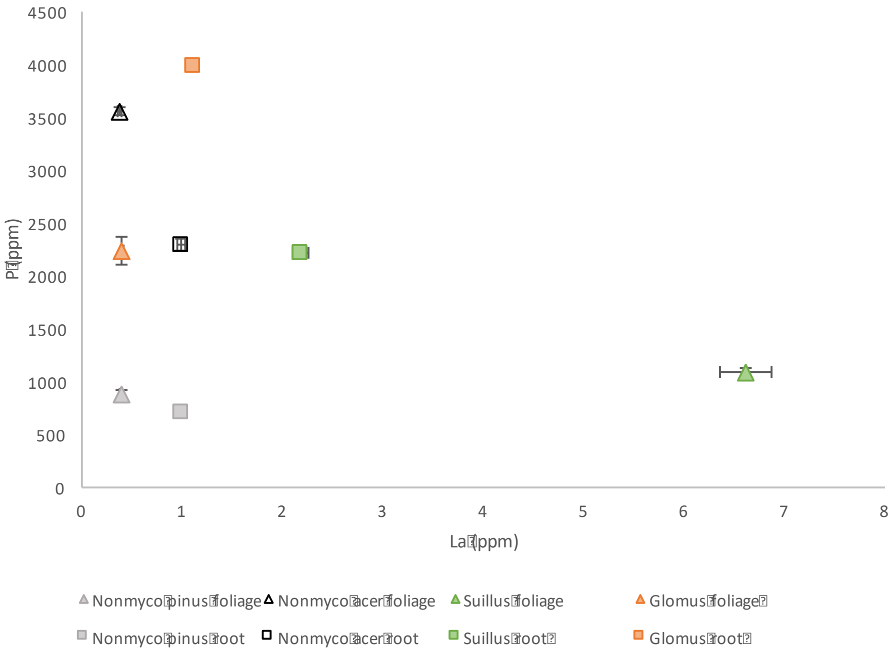


Figure 2.7: Phosphorus vs. Lanthanum concentrations for root and foliage samples of mycorrhizal and non-mycorrhizal Pinus and *Glomus* seedlings grown on a) Conway Granite and b) Waits River Formation bedrock.

As show in Figure 2.7a there are the largest La concentrations in the roots of mycorrhizal *A. saccharum* sample grown on the P-limited Conway Granite substrate when compared to both non-mycorrhizal *A. saccharum* samples and mycorrhizal and non-mycorrhizal *P. sylvestris* root samples. On the P-limited granite the mycorrhizal *A. saccharum* root sample also shows elevated P concentration when compared to the non-mycorrhizal root and taken together this could provide evidence for the weathering of apatite under fungal colonization when grown on a nutrient-limited lithology. The relationship between foliar P and La concentrations on Conway Granite samples (Figure 2.7a) also show a pattern of increased La and P in the mycorrhizal colonized *A. saccharum* seedling compared to their non-mycorrhizal counterpart. Low values of La in non-mycorrhizal *A. saccharum* and both mycorrhizal and non-mycorrhizal *P. sylvestris* foliage samples may indicate increased transport of weathered materials in maples colonized by *G. intraradices*. In contrast, when grown on a nutrient non-limited lithology, WRF, with easy dissolution and higher elemental abundance these same trends in La are not seen in the *A.saccharum* seedlings. This supports the thinking that mycorrhizal nutrient acquisition is dependent both on the host tree and the growth substrate available.

2.5.3 Mg isotopes

For maples seedlings grown without mycorrhizal fungi on the Conway Granite Mg isotope signatures were lower in foliage when compared to the roots (Figure 2.8). This aligns with studies that show lighter magnesium isotopes are enriched from roots to foliage through translocation (Black et al., 2008; Bolou-Bi et al. 2010). This enrichment in lighter isotopes moving from roots to the foliage was diminished in the maple seedlings grown with *G. intraradices* agrees with a recent study showing no fractionation in the Mg of maples in the field with AM fungi vs. those grown without AM fungi in a lab (Kimmig et al. 2018). Similarly, the systematic increase of δ26Mg values in vegetation relative to soil water was not seen in a tropical ecosystem study conducted by Schuessler and colleagues (2018).

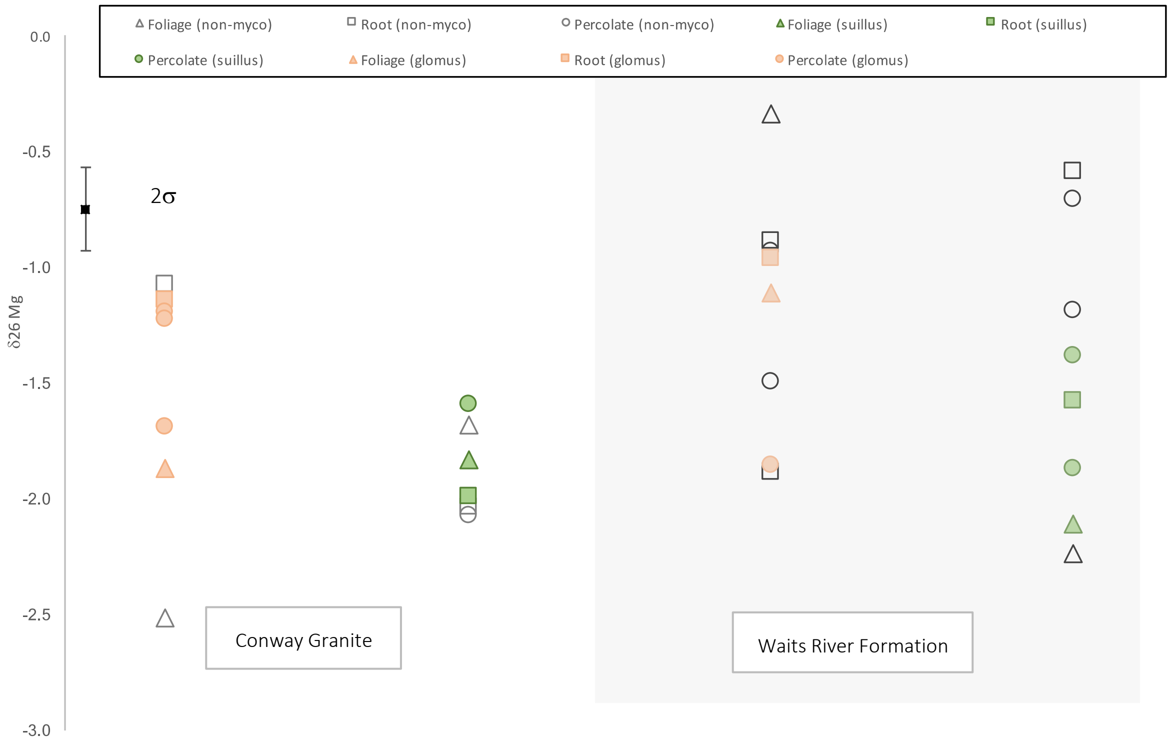


Figure 2.8: δ26Mg isotope ratios for pine and maple seedlings grown with and without mycorrhizal fungi on Conway Granite and Waits River Formation. Conway

Granite-hosted maple and pine seedlings (respectively, left) are depicted along with maple and pine seedlings grown in the WRF (respectively, right). Solid symbols indicate the presence of mycorrhizal fungi and open symbols represent non-mycorrhizal samples for both tree types. Triangles represent foliar samples, squares represent root samples, and circles represent percolates (a proxy for the eluting solution). 2-sigma error bar of average sample replication error represented in top left corner

When grown on a calcium- and magnesium-rich substrate like WRF nonmycorrhizal and mycorrhizal maple seedlings appear to follow the observed trend of preferentially taking up heavier Mg isotopes while still fractionating from roots to foliage, with lighter signatures in the foliage (Figure 2.8) (Black et al., 2008; Bolou-Bi et al. 2010, Bolou-Bi et al., 2016). In a Ca/Mg-rich rock substrate we see larger magnitude of depletion in non-mycorrhizal pine foliage with seedlings showing an arguable enrichment in the roots on when grown with mycorrhizal symbionts.

In Figure 2.8 the non-mycorrhizal maple foliage grown on WRF has a heavier signal than that of the foliage grown with *Glomus*. This might be explained in part by the differences in root biomass of the two systems (0.285g of non-mycorrhizal maple seedling roots versus 0.190g roots for the mycorrhizal seedling). The above ground biomass was comparable, 0.130g and 0.105g respectively. This isotopic signature of the foliage matches well with the isotopic signature of the nutrient solution, indicating that the increased rooting area's ability to uptake more nutrient solution may be responsible for the Mg supplied to the foliage. The difference in Mg isotopes in the mycorrhizal and non-mycorrhizal maple seedlings may also be dependent on tree health. In the study by Kimming and colleagues (2018) Mg isotope values for yellow leaves were reported at -0.96 ‰ while green leaves had a δ_{26}Mg of -1.12‰ indicating that yellow leaves have a heavier isotopic signature than green leaves. This could be linked to the health of the leaves, with non-mycorrhizal seedlings showing signs of stress, which could cause the chlorophyll to degrade and change the isotopic signature as they senesce. Black and colleagues found that magnesium in wheat chlorophyll was isotopically lighter than the whole leaf (2008). This chlorophyll Mg isotope signature is plant dependent and should be determined for maples (Black et al., 2007; Black et al., 2008) but a decrease in chlorophyll could explain an enrichment in heavier isotopes for maple seedlings growth without AM fungi. The variation in Mg isotopes signatures across different lithologies and fungal symbionts indicates that there is a multifactorial control on Mg isotope signatures that must be elucidated to help constrain Mg isotopes interpretations at the catchment scale.

2.6 Summary and Implications

Taken together, major elements, REEs, and Mg isotopes provide insights into the influence that rock type has on activating fungal weathering in AM symbionts. Fungal enrichment factors for *A. saccharum* seedlings grown on the nutrient-poor Conway Granite substrate exceed FEFs for *A. saccharum* seedlings grown in the nutrient-rich and easily dissolved Waits River Formation in both roots and foliage. Conversely, root and foliar FEFs for the two rock types were quite similar for *P. sylvestris*. In plants grown on Conway Granite, foliage FEFs for *A. saccharum* exceeded those of *P. sylvestris*. This could be a signal of the importance of Ca for maple tree health (e.g. Hallet et al., 2006; Vadeboncoeur, 2010; Battles et al., 2014) or indicate increased ion transport from AM fungi to host plants (Long et al., 2009). The FEFs alone cannot fully support the idea that AM fungi when grown on a nutrient-poor substrate can increase weathering to gain access to nutrients for their hosts but REE’s also show patterns of mineral dissolution under fungal colonization. The 1 N nitric acid leach of the Conway Granite was used to investigate REE signals for apatite dissolution in the substrate. Low Europium concentrations in the roots and foliage of AM-colonized *A.saccharum* seedlings were interpreted as indicating apatite weathering in the Conway Granite. This apatite signal was not present in non-mycorrhizal seedlings of either type or in EcM-colonized *P. sylvetris* seedlings grown on Conway Granite. In combination, the Mg isotopes support the idea that AM fungi are important in for how maple trees can access critical nutrients like Ca and Mg from minerals present in recently glaciated soils. The lack of Mg isotope fractionation in maple seedlings grown with AM fungi compared to those grown without could indicate the AM fungi alter how the host plant is obtaining and processing Mg.

The data indicate that rock type, more specifically the presence of plant-necessary nutrients, taken in conjunction with the nutrient status of the growth medium may influence intensity of fungal weathering. It has been shown that nutrient mobilization could be governed by element supply from parent mineral and plant physiological requirement (Zaharescu et al. 2017). This work may suggest that biological weathering is enhanced when nutrients are not already readily available to the system and could affect how we think about the importance of biological weathering. AM fungi associated with a nutrient-sensitive plants like sugar maple may be able to increase their weathering ability when key elements like Ca and Mg are deficient in the soil. More research regarding gene activity in fungal symbionts should be conducted to see if lithologic conditions can trigger weathering mechanisms in AM fungi. Future studies considering varied plant nutrient requirements and growth habits may help further tease apart the importance of fungi vs. the host plant itself. It is important to understand the differences in weathering potential of AM and EcM fungi and how they might change based on both the lithology underlying the ecosystem and the nutrient cycling and limiting nutrients in the ecosystem (Yanai et al., 2005; Goswami et al., 2018). This pairing of biogeochemical cycling and underlying lithology could help to support effective models of mineral weathering and enhance predictions of nutrient cycling in evolving ecosystems.

CHAPTER 3: MICROBIAL COMMUNITY COMPOSITION AND WEATHERING REACTIONS ACROSS A GEOLOGIC NUTRIENT GRADIENT

3.1 Abstract

As ecosystems shift under changing climate, understanding how the nutrient content of underlying lithologies interact with microbial communities in the soil will be key for accurately modeling nutrient dynamics. Fungi and bacteria interact with minerals in the rhizosphere, but the influence of mineral nutrient content on these interactions is less clear. Naturally occurring isotopes together with element abundances can assess biologic influence on nutrient mobilization and element cycling. Specifically, elemental concentrations (Mg, Sr, and Rb) and Pb isotope ratios in solutions extracted from two distinct lithologies with different nutrient content provide insight into both short-term and long-term nutrient availability under biologic influence. Prokaryotic community composition was assessed via 16S rRNA sequencing for both lithologies planted at two sites at Hubbard Brook Experimental Forest and one site in Fairfield, Vermont. These sites were selected because they had varied dominant vegetation which could be used to determine how vegetation with known fungal symbioses and minerology influences microbial abundance. Prokaryotic communities grouped by site using Bray-Curtis dissimilarity metrics on the sequenced data. At the phyla level *Proteobacteria* accounted for more than 20% of the relative abundance for both lithologies but that relative abundance differed between sites depending on dominant tree species. The distinct microbial populations did not differ in mineral weathering based on Pb isotope signatures, which were instead driven by rock type. Rb/Sr values from nitric leaches of mineral ingrowth bags indicated the possible enhancement of biotite weathering under willow-dominated ecosystems. Biotic enrichment factors for Mg indicated that weathering liberated Mg from nutrient-poor

lithologies in maple-dominated ecosystems. Taken together this study shows that for large-scale mineral weathering reactions, abiotic lithologic properties may control weathering, but increased weathering may be an important mechanism to increase nutrient availability for nutrient-poor lithologies.

3.2 Introduction

Soil conditions, a critical but complex component of the terrestrial ecosystem, contribute to models of vegetation health and productivity and they are also an important interface for weathering reactions but are poorly understood in vegetation models (Prentice et al., 2004; Taylor et al., 2009). Minerals housed within soils and bedrock underlying shallow soils offer a reservoir of base cations that can be accessed through mineral breakdown reactions facilitated by plants and microbes (Blum et al., 2002; Koele et al., 2009; Calvaruso et al., 2013; Nicolitch et al., 2019; Wild et al., 2019). The poorly quantified role of fungal and bacterial components in driving weathering fluxes make it challenging to translate these observations for implementation in a predictive framework (e.g., Taylor et al., 2012). These shortcomings integrating fungi into current carbon cycle models are even more apparent when the role of climate fluctuations is considered. With the predicted changes in AM- and EcM- dominated vegetation in the future under climate change it is important to understand and quantify any differences in prokaryotic community composition in the field as well as any differential influence they may have on mineral dissolution and nutrient mobilization (Uroz et al., 2015; Steidinger et al., 2019; Wild et al., 2019).

The nutrients contained in minerals and their varied dissolution rates offer different reactive surfaces for microbes, including bacteria and fungi to interact with (Uroz et al., 2015). There has been research to suggest that certain minerals can favor their own specific community of microbes due to the nutrient availability and dissolution properties of the minerals (ex. Barton et al., 2007; Carson et al., 2007; Ding et al., 2013). The question of how minerals impact community composition and microbial abundance are important lines of investigation that is still being researched (Uroz et al., 2015; Lladó et al., 2017). Microbial colonization of minerals may be influence by external environmental properties or internal mineral characteristics. In a recent synthesis by Uroz and colleagues they propose the idea of the “mineralosphere” which is an abiotic foil to the rhizosphere (Uroz et al., 2015). The “mineralosphere” describes the interface between mineral surfaces and the surrounding soil where bacteria are impacted by the physiochemical properties of the minerals themselves. These properties include things like surface area, surface charge, and nutrient content. The physical structure of a minerals surface can provide protection from predation and a stable area for bacteria to grow, it has been shown that mineral edges and high porosity minerals have preferential bacterial colonization (Barker et al., 1998; Abdulla, 2009). The chemical properties and surface kinetics can also drive microbial colonization of minerals (Barton et al., 2007). Philips-Lander et al., 2013; Santelli et al., 2009; Uroz et al., 2009). Enrichment of proteobacteria were seen on metamorphic minerals when compared to $CaCO_3$ (Barton et al.,2007), while P rich minerals have been seen to exhibit the ability to preferentially host bacteria (Philips-Lander et al., 2013). Uroz and colleagues (2009) determined that apatite minerals were more highly weathered and saw an enrichment of Betaproteobaterica with an overall decrease in diversity on the mineral grains (Uroz et a., 2009). All of these studies point to the possibility of mineral chemistry impacting bacterial community composition and subsequent weathering ability.

Previous studies of elemental and isotopic tracers of weathering at these Hubbard Brook sites have focused on implied fungal associations in the dominant vegetation but expanding this view to include bacteria is important. Bacteria have been found around mycorrhizal associations and could be impacted by the fungal exudates, not just plant root exudates and Fontaine colleagues found fluorapatite-solubilizing bacteria in the hydrosphere of EcM fungus associated with spruce trees (Bennet et al., 2001; Fontaine et al., 2016). Research by Vik and colleagues indicated that EcM hyphae create a distinct microbiome and supports the idea that bacteria may use EcM hyphae as a transport vector (2013). This combination of plant and fungal symbionts interacting with a bacterial community in the rhizosphere may be an important factor in tree health and nutrient acquisition.

The use of individual minerals in studies may over-simplify the dynamics that occur in the rhizosphere and “mineralsophere”. In this study lithologies with varied mineral contents were utilized and whole rock samples were taken for microbial community composition assessment to see if changes in microbial populations were dependent on the whole-rock composition. Bacterial weathering in the “mineralosphere” may be an important source in addition to fungal contributions for plants on nutrient poor soils (Uroz et al., 2009; Uroz et al., 2015). The role of mineral weathering by heterotrophic bacteria remains poorly understood compared to fungal communities (Uroz et al., 2015). This work utilizes geochemical analyses and 16s data to describe microbial communities across geologic gradients under variable plant colonization and to further examine any differences in mineral breakdown reactions.

This work addressed the follow hypotheses:

- EcM dominant ecosystems will show signs of enhanced apatite/P-bearing mineral weathering compared to AM dominated ecosystems.
- Weathering in AM dominated forest stands will be elevated on nutrient poor rocks when compared to EcM dominated forests.
- The microbial community composition will vary depending on the dominant tree type and the lithology in the in-growth bag.

3.3 Methods

3.3.1 Experimental design and field methods

This work builds on previous studies at Hubbard Brook to look at the weatherability of different rocks under varied fungal symbionts (Remiszewski et al., 2016). Mesh in-growth bags, with the same lithologies designed to exclude plant roots but allow the entry of hyphae and bacteria with 50μm mesh, were planted in the field following procedures adapted from Wallander et al. (2001) (Remiszewski et al., 2016). These field experiments took place in Hubbard Brook Experimental Forests (HBEF; 43.9490 N, 71.7852 W) and a willow farm in Fairfield, VT (44.7687N, 72.9251W). These sites were selected due to the dominant tree species and their ability to associate with EcM and/or AM fungi. Hubbard Brook Experimental Forest contains both hardwoods and conifers and is a Long-Term Ecological Research (LTER) Program site. Hubbard Brook receives an average of 1395 mm of precipitation per year with a mean annual temperature of 5.5ºC, ranging from a mean of -8.5ºC in January to a mean of 18.8ºC 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 *p*H ranging between 3.5-4.5 (Bourgault et al., 2015). Soils are thin on upper slopes with bedrock exposed in stream channels and along ridgelines (Bailey et al., 2014). The willow farm in Fairfield, VT is not a highly monitored site but instead was selected due to the presence of a large number of *S.repens*, a species known to have the ability to host both AM and EcM fungi (van der Heijden, 2001). Fairfield is located in northern VT and receives 1016-1270mm of precipitation each year (NOAA National Weather Service, 2019). The soil at the site is a spodosol, Westbury stony fine sand-loam with 8-15% slopes (USDA Natural Resources Conservation Service, 2019). The Fairfield Pond Formation, comprised of quartz-sericite-chlorite, phyllite and foliated quartzite, underlies the site (Ratcliffe et al., 2011).

These sites were selected to test *in situ* weathering across plots dominated by EcM or AM fungal symbioses. The sites at Hubbard brook contain young soils with shallow depth to bedrock and the presence of well-documented sites dominated by vegetation known to associate with AM and EcM fungi (Schwarz et al., 2003; vanDoorn et al., 2011). Hubbard Brook site 206 is a mixed beech/birch plot dominated by beech (*Fagus grandifolia*) and birch (*Betula sp.*), which are known to associate with ectomycorrhizal fungi. Site 237 is dominated by sugar maple (*Acer saccharum*), which associates with AM fungi. Both plots include a mix of AM and EcM plant species but are distinct based on the dominance of each group. Trees were selected in both plots based on their size to avoid seedlings, and their proximity to non-dominant vegetation to control for fungal type.

Mesh bags were buried in August 2018 in Hubbard Brook Experimental Forest at the base of birch/beech trees in site 206 and at the base of maple trees in site 237. In September 2018 mesh in-growth bags were installed at a willow farm in Fairfield, VT beneath a plantation of *Salix repens* specimens. In both cases bags were buried in the organic horizon at 10 cm depth or where the Organic Horizon met the mineral A Horizon, whichever occurred first. Upon planting soil samples from the base of representative trees were collected with sterile trowel and stored at -80$_0$C for future microbial community composition analyses. Mesh in-growth bags were collected from Hubbard Brook sites 206 and 237 in June of 2019 while samples were retrieved from VT in July 2019. Soil samples were obtained again at the time of retrieval with a sterile trowel and stored along with the mesh in-growth bags at -80$_0$C for community composition analysis.

The lithologies for the mesh bags replicate earlier work at HBEF (Remiszewski et al., 2016). Conway Granite with low MgO, CaO, and P_2O_5 content (0.47, 0.20, and 0.03 wt. % respectively) collected from Grafton County was selected to represent low-nutrient substrate (Barker NHGS, 2013). Biotite tonalite with high MgO, CaO, and P_2O_5 content (2.3, 3.03, and 0.91 wt. % respectively) collected from Strafford County was used as a nutrient-rich substrate (Barker NHGS, 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 250-500μm and acid washed (24 h in 1N nitric acid) and rinsed with 18MΩ DI water. Aliquots (~ 10g) of acid-washed rock chips were then sealed into double-layered mesh bags and buried. Mesh bags of both lithologies were withheld as “abiotic” controls and stored at 20°C 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.

3.3.2 Analytical methods

Bags were retrieved from the field sites and stored in a -80°C freezer to stop biological activity and preserve genetic material for sequencing. Aliquots of crushed rock were removed from the bags and DNA was extracted from the soil surrounding the mesh ingrowth bags and the crushed rock samples contained within the bags using the PowerSoil DNA Isolation Kit (MoBio Laboratories, Carlsbad, California, USA). Sequencing of 16S rRNA was performed using the Illumina HiSeq2500 platform at the Hubbard Center for Genome Studies at the University of New Hampshire. The 16S rRNA amplicon sequences of each sample were imported into the Quantitative Insights into Microbial Ecology (QIIME) 2 environment for processing and analysis. Taxonomy was classified in Qiime2 using the SILVA database version 138. Native-Bayes was used to train the feature classifier on the representative sequences and the data was normalized by sample total and rarified at 1700 reads per sample. Community beta diversity between sites was measured by the Bray-Curtis distance metric and was ordinated through Principle Coordinates Analysis (PCoA) using EMPeror. (Bray and Curtis, 1957; Vazquez-Baeza et al., 2017).

Aliquots (~ 1 g) of rock chips were subsampled from mesh bags. Sequential extraction techniques (Blum et al., 2002, Nezat et al., 2007) 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 pH= 7 in the UNH Geochemistry Clean laboratory. An additional 24-hour 1.0 N nitric acid leach allowed for assessment of the fraction that may weather over longer time scales. Leachate volumes (~10 mL) collected after both steps were subsampled and analyzed for elemental contents and isotopic compositions.

Abundances of Mg, Sr, and Rb were assessed for both sites and rock types on an AttoM High Resolution (HR)- ICP-MS at the University of New Hampshire. Accuracy and precision for Mg, was assessed at ≤ 16% by replicate analyses of NIST 1643f and Rb/Sr were assessed at ≤ 1% by replicate analyses of NIST 1643f. Lead (Pb) isotope ratios were analyzed in order to identify minerals contributing to the weathering solute fluxes (e.g., Erel and Blum, 2007; Remiszewski et al., 2016). 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. Lead purification was carried out using standard separation procedures on AG1-X8 anion-exchange columns (e.g., Bryce and DePaolo, 2004). Collected solutions were dried down and re-dissolved in 2% HNO_3 for analysis on the Nu plasma II ES multi-collector inductively coupled plasma mass spectrometer (MC-IPC-MS). Instrumental mass fractionation for lead isotopes were corrected externally via Tl normalization (White et al. 2000), and isotope ratios were further adjusted for instrumental drift using sample-standard bracketing (e.g. Albarède et al. 2004) using NIST SRM values reported by Eisele et al. (2003). Eight NIST SRM 981 analyzed as “samples” in addition to the bracketing standards produced averages (and $2\sigma_{external}$) of $^{208}Pb/^{204}Pb$ = 36.726 (0.025), $^{207}Pb/^{204}Pb$ = 15.498 (0.008), $^{206}Pb/^{204}Pb$ = 16.941 (0.007), $^{207}Pb/^{206}Pb$ = 2.297 (.069), $^{208}Pb/^{207}Pb$ = 2.370 (0.0003), and $^{207}Pb/^{207}Pb$ = 1.093 (0.0002).

3.4 Results

3.4.1 Microbial community

In order to determine how samples differed by site, and therefore dominant vegetation type, the beta diversity of the microbial communities was analyzed. Bray-Curtis dissimilarity metrics were calculated and ordinated using PCoA (Figure 3.1). In both ordinations, the samples formed distinct groupings based on site. Axis 1 accounted for the largest amount of community variation in 15.7%. The field sites show separation along axis 1 and 2 which indicate that there are distinct communities at each site (Figure 3.1a). This is important to note, especially for Hubbard Brook site 206 and 237 which are geographically close but marked by different dominant tree vegetation. Unlike the site locations the soil samples and differing rock types do not visibly group out based on sample type as shown in Figure 3.1b.

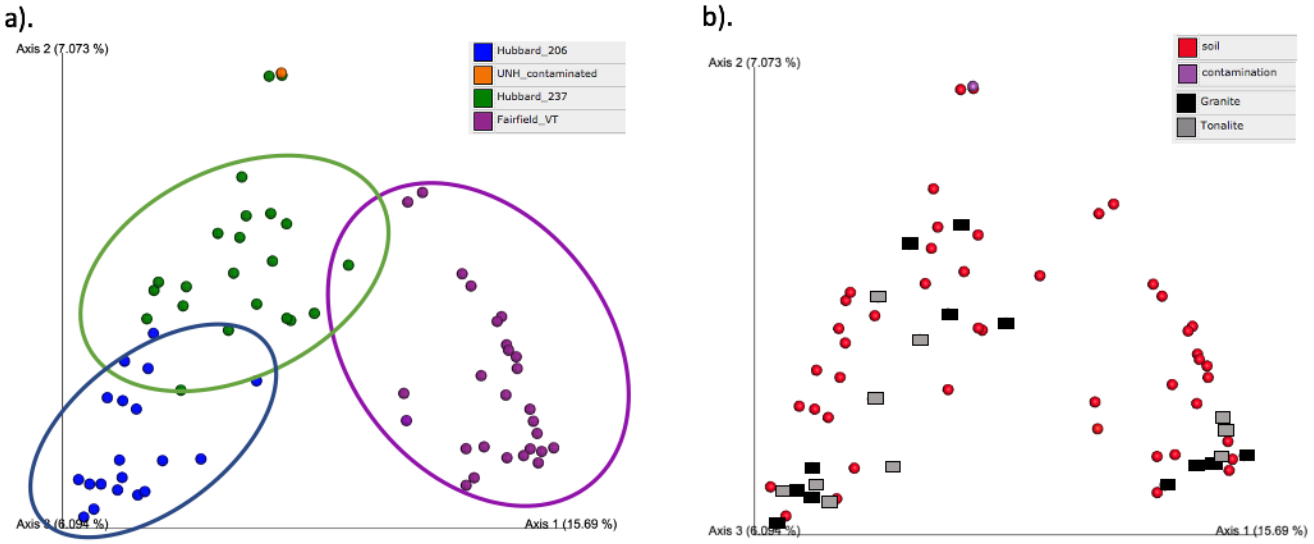


Figure 3.1: PCoA ordination of Bray-Curtis dissimilarity metrics for a). each field site and purposeful human contamination of crushed rock samples b). sample types distinguished between granite, tonalite, soil and purposeful human contamination

Percent abundance was calculated for both tonalite and Conway Granite samples retrieved from all three sites with varying dominant vegetation. The phyla classifications in Figure 3.2

are represented vertically in the stacked bar plots. The "other" category is a compilation of the remaining 51 phyla that were identified but composed less than 1% of abundance for each phylum. The table of abundance which includes all identified phyla can be found in Appendix C (Table C.6).

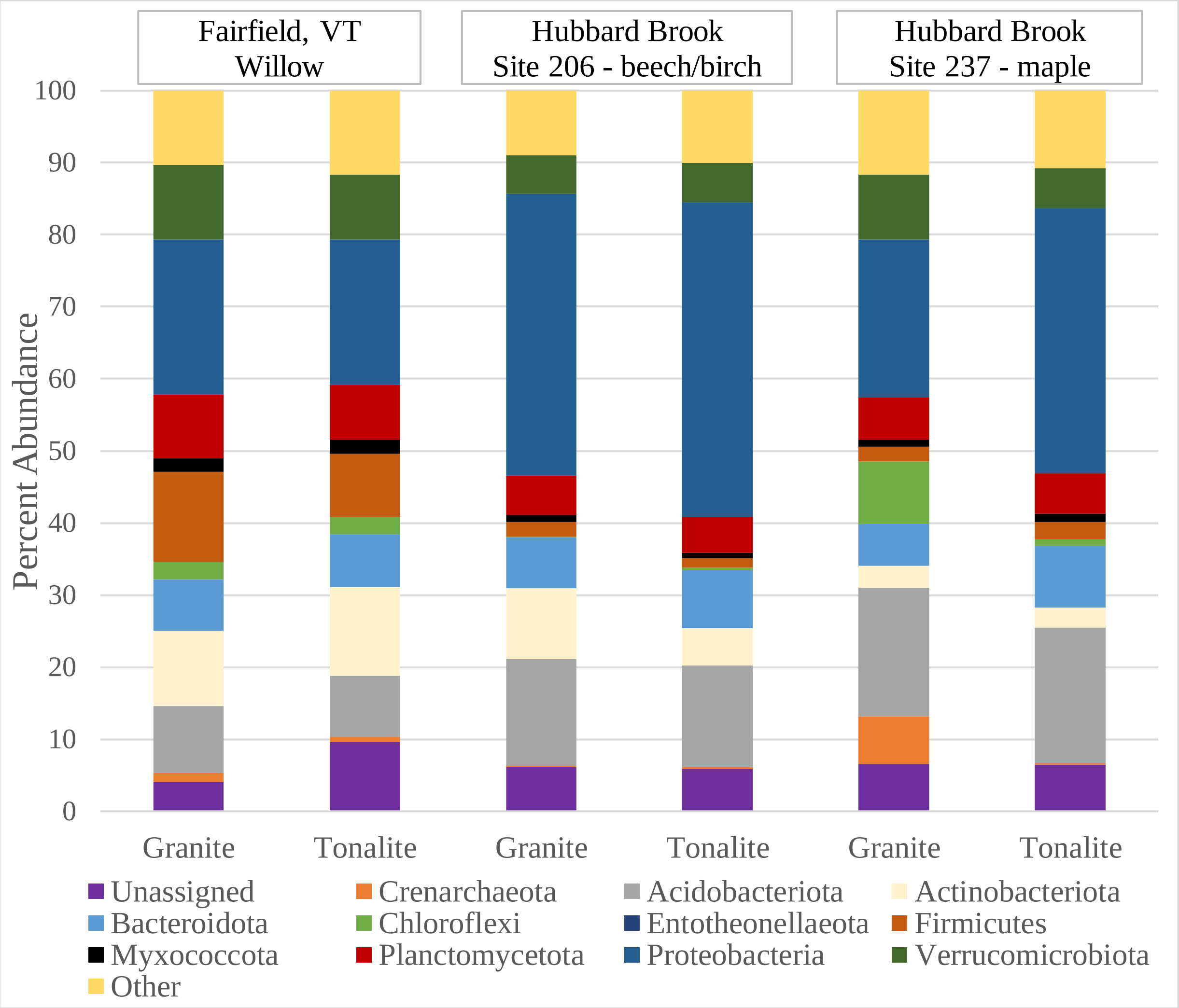


Figure 3.2: Phylum-level taxonomic classification of microbial community across both rock types and field sites with differing dominant vegetation.

The overall taxonomic composition of these rock microbial communities at the phylum level indicates that *Proteobacteria* are the most abundant, accounting for more than 20% of the communities for both lithologies across all sites (Figure 3.2), with a range of values depending on location and rock type from 20.2% on the tonalite buried in a willow dominated plot in VT to 43.6% on the tonalite buried in a beech/birch dominated plot in Hubbard Brook site 206

(Table 3.1). The second largest classification across sites was *Acidobacteriota*, representing a range of 8.5 – 18.9% across the sites and rock types (Table 3.1).

Table 3.1: Percent abundance at the phyla-level› in crushed rock samples of both lithologies across all three field sites.

	Fairfield VT		Site 206		Site 237	
	Granite	Tonalite	Granite	Tonalite	Granite	Tonalite
Unassigned	4.0	9.6	6.1	5.9	6.5	6.4
Crenarchaeota	1.3	0.6	0.1	0.3	6.1	0.2
Acidobacteriota	9.3	8.5	14.9	14.1	17.9	18.9
Actinobacteriota	10.4	12.4	9.9	5.2	3.0	2.8
Bacteroidota	7.11	7.32	7.01	8.03	5.84	8.54
Chloroflexi	2.4	2.3	0.1	0.4	8.6	0.9
Firmicutes	12.5	8.8	2.0	1.3	2.1	2.4
Myxococcota	1.9	1.9	1.0	0.7	1.0	1.2
Planctomycetota	8.8	7.6	5.4	5.0	5.8	5.6
Proteobacteria	21.5	20.2	39.1	43.6	21.9	36.8
Verrucomicrobiota	10.4	9.1	5.4	5.5	9.0	5.6
Other	10.3	11.7	9.0	10.1	11.7	10.8

The differences across the field sites were pronounced and showed increasing abundance moving from the willow dominated plot to the beech/birch and finally maple dominated plots (Table 3.1). It is interesting to note that both the location of samples and the rock type influence the percent abundance (Figure 3.2). In the case of *Proteobacteria* in Hubbard Brook sites, which are two sites within the same forest ecosystem, beech-/birch- dominated forest stands show a larger abundance of the bacteria compared to maple-dominated forests but, in both sites, crushed tonalite rocks host a larger percentage of the bacteria compared to Conway Granite. *Proteobacteria* have been shown to be abundant in most soils and *Betaproteobacteria*, a class of *Proteobacteria*, are recognized as efficient mineral weathering bacteria (Lladó et al., 2017). *Actinobacteriota*, also present in the rock samples to varying degrees based on location and rock type (Table 3.1), are thought to enhance rock weathering (Cockell et al., 2013). Through the release of chelator substances some strains of *Actinobacteria* can solubilize P from rocks and are being investigated as a way to enhance nutrient availability in P-limited environments (Hamdali et al., 2012).

3.4.2 Geochemical signals

Weathering enrichment factors (WEF) were calculated for magnesium (Mg) in the NH_4Cl leach, representing the easily exchangeable fraction, by taking the elemental concentration of a sample exposed to biology in the field and dividing it by the concentration of the control sample which had been stored in a cool dry space.

$$\mathrm{WEF} = [\mathrm{Mg}]_{\text{biotic sample}} / [\mathrm{Mg}]_{\text{abiotic sample}}$$

A value greater than one indicates a higher elemental concentration in the leachate for the sample planted in the field vs. the abiotic control. This could be a sign, especially in the nitric leach, that exposure to the soil biological community enhanced future available stores of nutrients via weathering. A value less than one indicates that the abiotic control sample had higher concentrations of an element than the sample exposed to biology in the field. In the ammonium chloride leach especially, this could indicate that nutrients were removed from the mineral system and were taken up or lost from the rhizosphere. WEFs were calculated for all field sites and for both Conway Granite and tonalite samples.

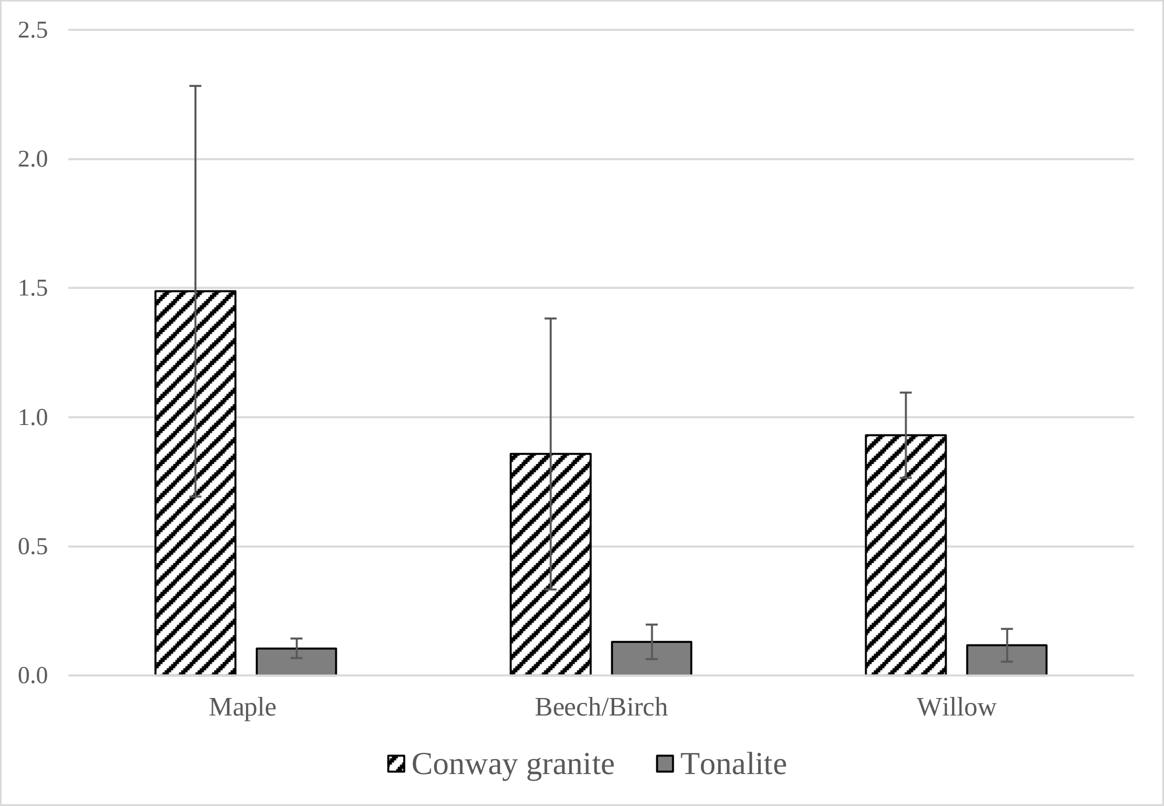


Figure 3.3: Weathering enrichment factors for Mg NH_4Cl leach representing easily exchangeable nutrient stores. Values > 1 for WEFs indicate higher elemental concentrations in the biotic samples than the control.

Conway Granite in-growth bags in Hubbard Brook site 237, dominated by maples, are enriched (WEF > 1) in Mg when compared to the tonalite planted in the same site. Neither the beech-/birch- dominated nor the willow- dominated site showed enrichment for Conway Granite samples in the easily exchangeable fraction though they are elevated compared to the tonalite. Across all sites the tonalite do not show signs of biologic enrichment when field samples are compared to the biologic control. Tonalite is a nutrient -rich rock when compared to the Conway Granite which may allow for access to nutrients without the need for additional biologic activity from fungi and bacteria. Additionally, its susceptibility to decompose when subjected to a solution (~pH 7) is enhanced compared to the Conway Granite.

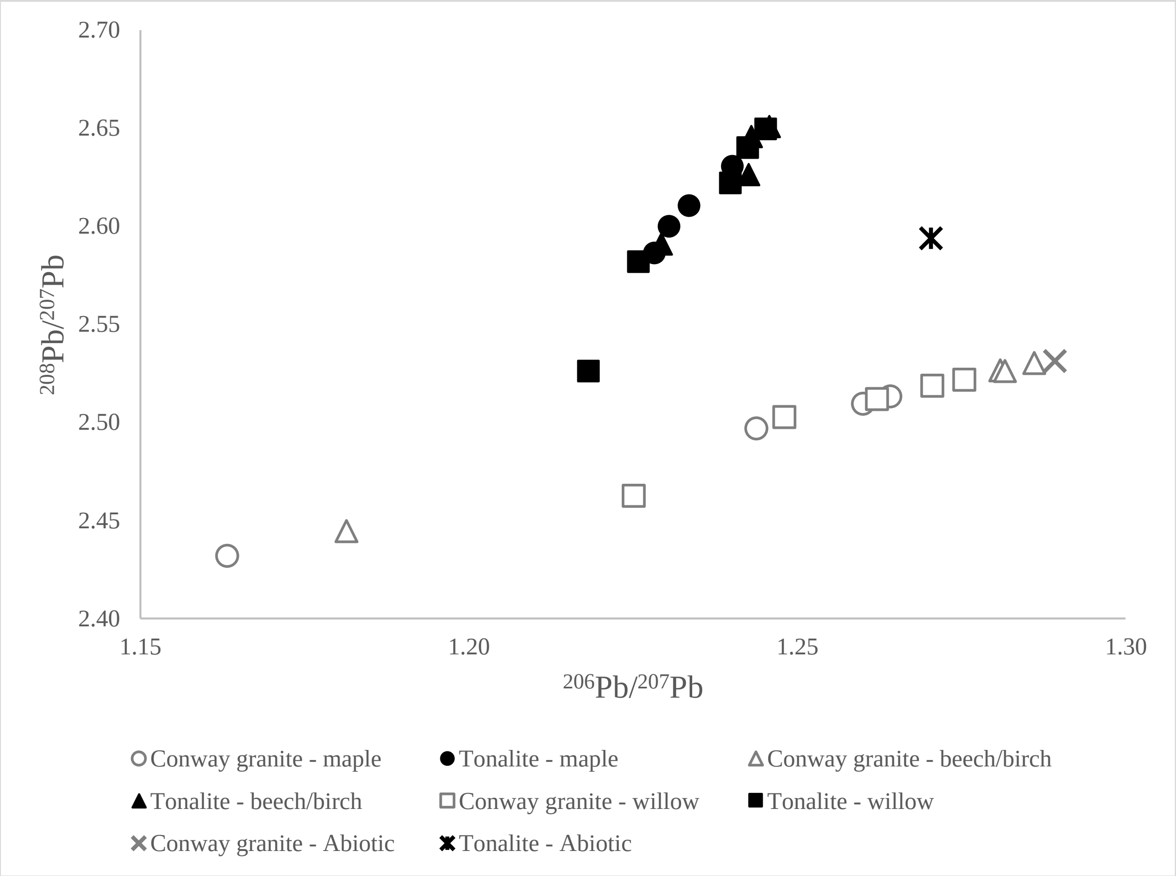


Figure 3.4: ^{208}Pb/^{207}Pb vs. ^{206}Pb/^{207}Pb in the nitric leach, representing future available stores, for granite and tonalite samples from both AM- and EcM-dominated sites.

Tonalite samples show higher levels of ^{208}Pb/^{207}Pb compared to the Conway Granite (Figure 3.4). The increased ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb ratios could indicate apatite weathering or could be attributed to a higher contribution of Pb from Th-rich minerals like monzanite (Erel et al., 1994; Harlavan and Erel, 2002). In a study by Erel and colleagues they show biotite weathering under sequential acid leaching has been shown to have elevated ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb signatures of 1.274 and 2.656 respectively (Erel et al., 2004).

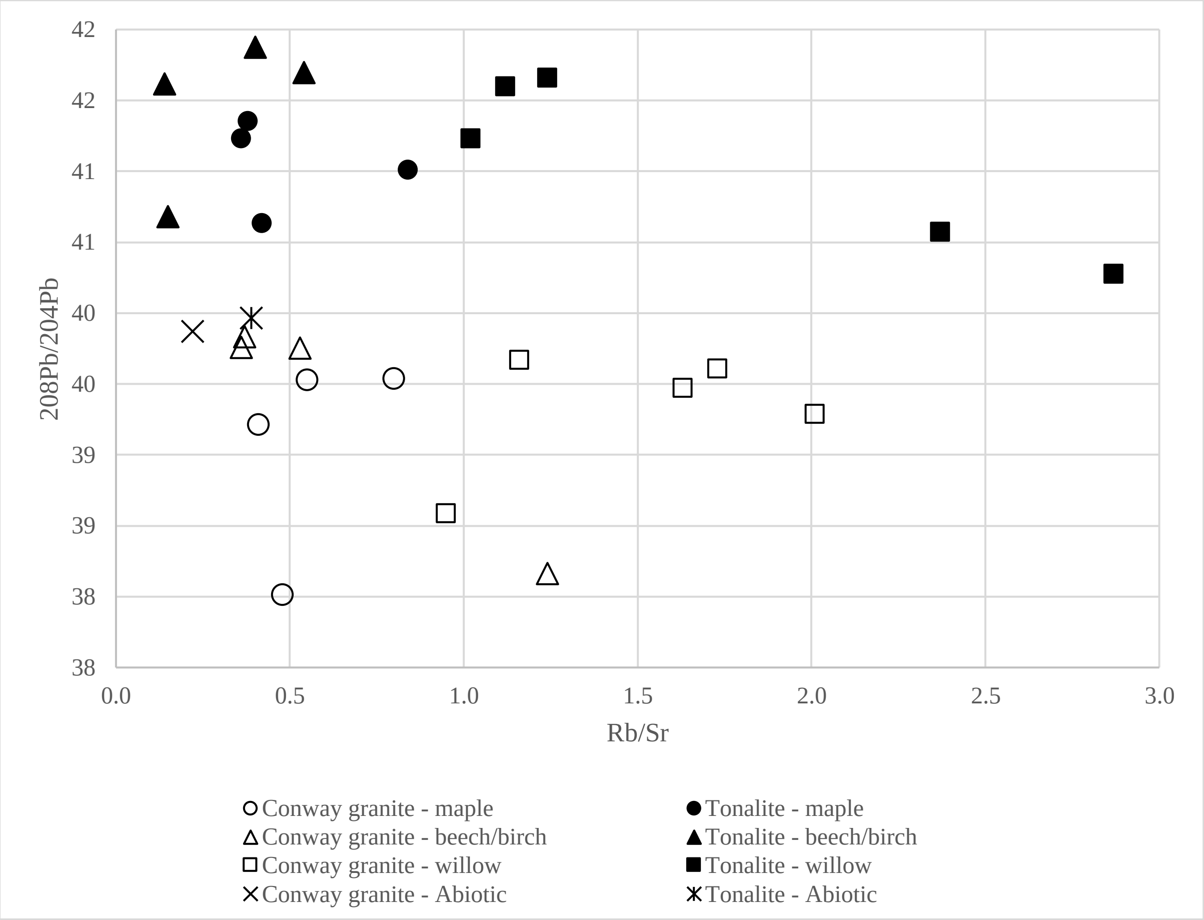


Figure 3.5: ^{208}Pb/^{207}Pb vs. Rb/Sr from the nitric leach, representing future available stores, in granite and tonalite samples from both AM- and EcM-dominated sites.

The increasingly radiogenic Pb isotopic values are consistent with increasing apatite contributions and Rb/Sr can be used to trace biotite as Rb/Sr is elevated in biotite compared to other minerals like plagioclase. Tonalite samples show increased ^{208}Pb/^{207}Pb values compared to the Conway Granite but the Rb/Sr data vary, suggesting that rock type is not the primary distinguishing factor (Figure 3.5). The signals for these mineral dissolution reactions are not significantly different based on the dominant fungal symbioses of the Hubbard Brook sites though it is interesting to see that willow samples show signs of higher Rb/Sr than both maple and beech/birch dominated sites (Figure 3.5). Solute generated from a control aliquot of chips not subjected to 10 months of field exposure was also found to plot within the range of the field-deployed samples though Rb/Sr indicate that the time spent in-situ has an impact on mineral dissolution reactions.

3.5 Implications

Prokaryotic community composition, assessed via 16S rRNA sequencing, grouped distinctly between field sites using Bray-Curtis dissimilarity metrics. At the phyla level, *Proteobacteria* are the dominant taxon but abundances varied based on both the dominant vegetation at the sample location and the type of rock within the in-growth bags. These findings show that dominant plant species, and perhaps their associated fungal symbionts, drive compositional changes in the community. The variable presence of many taxa, including actinobacteria which are shown to enhance weathering, could suggest that weathering of the samples at a microscale may vary across different dominant vegetation and rock types.

Isotopic signatures of the in-growth bag rocks provide evidence for similar mineral decomposition reactions at both sites. Radiogenic ^{208}Pb/^{207}Pb and ^{206}Pb/^{207}Pb at both sites support the idea that apatite dissolution as the dominant reaction in the Conway Granite, with this dissolution independent of site variability in microbial communities. Rock type was the most important factor controlling the Pb isotopic signatures of the solute whereas dominant plant type, fungal symbiont type, or bacterial community appeared to have no effect over the 10-month treatment. Elevated Rb/Sr in field sites dominated by the willow *S.repens* suggests enhanced biotite weathering. Our findings may suggest that varied biologic communities across dominant forest ecosystems are equally efficient at obtaining the nutrients that their host plants need from minerals within the soil; alternatively, sparse intensive weathering agents (ex. EcM species within AM-dominated plots) may serve to enhance weathering.

This work improves our understanding of nutrient cycling under different lithologic nutrient gradients. Data from this study will contribute significantly to debates about relative importance of bacteria and fungi in field-scale weathering reactions pairing both geochemical tracers and 16S rRNA data (Taylor et al., 2012; Uroz et al., 2015; Finlay et al., 2020). Results of this study will also provide important baseline data from a single host plant and natural mixed forest stands regarding the relative impact of AM-dominated vs. EcM-dominated rhizosphere communities in mineral weathering across varied substrates.

CHAPTER 4: NASA GLOBE STUDENT RESEARCH SYMPOSIUM PROGRAM– A FRAMEWORK FOR HOW CITIZEN SCIENCE PROJECTS CAN SUPPORT EXPERIENTIAL LEARNING AND IMPROVE CONFIDENCE IN SCIENCE AND SCIENCE PRACTICES

4.1 Introduction

Science is an integral part of everyday life and now, more than ever, it is crucial that citizens are knowledgeable in science (National Academies of Science, 2016). Student interest and engagement in science overall is low, with students often finding the sciences boring or thinking it "isn't for them" which impacts student retention in science, technology, engineering and math (STEM) programs and careers (Aschbacher et al., 2014). It is key to have a science literate population in a democratic society because science literacy can provide a strong foundation for addressing societal problems and allow citizens to make intelligent and informed decisions on issues like climate change or natural hazards, and other issues that impact them and future generations (Miller 2016; Tomovick et al., 2017; Zen, 2018). Scientific knowledge is one of the factors that can be important in influencing attitudes toward science, but it is not the only one (Sturgis and Allum, 2004). 'Attitudes toward science' is a complex concept that includes the enjoyment of science learning, an interest in science activities, and an interest in pursuing science as a career (Tytler and Osborne, 1998). Attitude toward science is also a critical aspect to consider when gauging overall understanding of science (Sinatra et al., 2014). There is a shortage of studies regarding the attitudes of participants in citizen science programs, in part because of the difficulties surrounding the measurement of attitude (Phillips et al., 2012). Though there is some evidence that supports overall scientific attitudes change positively when participating in inquiry-based science projects, additional research regarding the public's understanding of science suggests the need to focus on the mechanisms that underlie the association between knowledge and attitudes about science (Allum et al., 2008; Price and Lee, 2013). It has been suggested that making science more approachable and accessible to both students and instructors is an important step for encouraging engagement with science and could help improve attitudes toward science (Bandura, 1993; Zimmerman, 2000). There are many ways to approach the goal of increasing student interest in science but both citizen science and experiential education programs have shown themselves to be aligned to support public engagement with science. The NASA GLOBE (Global Learning and Observations to Benefit the Environment) program has the capacity to positively impact students' ability to use scientific data in decision-making in its role both in the context of citizen science projects and through the experiences of the GLOBE Student Research Symposium (SRS). The SRS brings together students from across the United States and gives them the opportunity to share the results of field investigations using GLOBE protocols at one of six face-to-face regional Student Research Symposia. The agenda for individual symposia vary but all include presentations from scientists at the host institution, poster presentation and review sessions, and student discussions with scientists. The poster presentations given by students are reviewed by professionals in the field and substantive feedback is given to each group after presentation awards.

Inquiry, as a pedagogical concept, is recognized as a key component for science instruction and experiential education as it allows students to ask questions, construct and communicate findings, and gives students an active role in their learning (NRC, 2012; Joplin, 1981; Kolb, 1984). The GLOBE program utilizes inquiry to engage students with the NGSS Science Practices in formal classrooms and informal afterschool settings and offers an example of the role citizen science projects could have in supporting experiential education within schools and in a scientific symposium setting. The program does this by providing a framework of data collection by students for the purpose of contributing to a repository of GLOBE data which can be used to answer authentic research questions. This is paired with student support and the chance to synthesize and publicly present data. The use of GLOBE protocols in data collection and subsequent analysis helps connect students share and argue their ideas with peers, use evidence to back up their claims, and come to their own understanding of the science. (Furtak and Penuel, 2018). This combination of citizen science and experiential learning practices make NASA’s GLOBE SRS a unique opportunity to investigate what impacts these factors can have on student attitudes toward science. The objective of this study is to understand how participation in the SRS impacts students’ interest in science as well as their confidence in NGSS science practices. It is also to offer a model of how the GLOBE citizen science program can be used to support experiential education within the classroom and structure of K-12 public education with the goal of improving student attitudes toward science.

4.1.1 Experiential education

“Experience alone is insufficient to be called experiential education, and it is the reflection process which turns experience into experiential education” (Joplin, 1981). Experiential learning, according to Kolb (1984), is a four-part process that asks the learner to engage themselves in a new experience, actively reflect on that experience, conceptualize that experience, and integrate it with past experiences. In her five-stage model Joplin (1981), building from Kolb’s construction of experiential education, presents a structure for designing experiential moments in a more structured classroom setting. These include beginning with a focus, giving the student responsibility in the phase of acquiring new skills and knowledge. Support and feedback are important components of the model, allowing students to continue to try and move forward with the information. Debriefing the students in the final component of the model is key because it is in this part that the knowledge is reorganized, articulated, and made public (Joplin, 1981). In addition to the model, Joplin provides characteristics that are key to ensuring a successful experiential education for students. Many of these characteristics (e.g. student-driven, organized around experience, process and product driven) are also keys for successful citizen science projects and are exemplified by the NASA GLOBE program. Experiential education settings allow for a student-centered learning environment and provide students with autonomy over their own learning, encouraging inquiry and meaning making (Barron et al., 2017). There are many studies that support the idea that the structure of experiential education and citizen science projects can engage students more deeply in the subject matter and provide a sense of meaning which can sometimes be lacking in traditional learning models (Barron et al., 2017; Hasni and Potvin, 2015; Luehmann, 2009; Price and Lee, 2013).

4.1.2 Citizen science

Citizen science is a broad category of work but can be thought of as the partnership of professional scientists and the general public to collect large amounts of data in addition to providing a pathway to increase public involvement in science and issues related to their environment (Irwin, 1995; Bonney, 1996; Bonney et al., 2009). Citizen science projects can result in participants gaining scientific knowledge and insight into the scientific process which does not always occur by “feeding” scientific information to the public (Allum et al., 2008; Bonney et al., 2016). Citizen science projects that focus on youth and include rigorous data collection, disseminating scientific findings to authentic external audiences, and investigating complex social-ecological systems can foster engagement with current science and build capacity for future action (Ballard et al., 2017). Citizen science projects that can best support youth’s learning are those that are driven by research questions the sponsoring agency has and clearly inform participants that the data being collected will be used to address these questions via analysis and publication and involved active and continual engagement of nonscientists (Bonney and Dickinson, 2012; National Academies of Science, 2018). Another important trait of a successful citizen science project is the presence of easy to perform and clear protocols that participants can use to collect data for the project (Bonney and Dickinson, 2012). Communicating and using the results of the project, especially within the scientific community, has also been identified as a key trait of a citizen science project (National Academies of Science, 2018). These traits of a successful citizen science project are exemplified by NASA's GLOBE program which has developed data collection protocols for classrooms and citizens as well as the GLOBE Observer app which allows anyone with a smart phone to participate in data gathering. These protocols paired with the Student Research Symposium (SRS), which gathers students together to communicate their findings with peers and professional scientists, engage students in many aspects of a successful citizen science project.

4.1.3 GLOBE program

The GLOBE program is an international science and education program that provides students and the public worldwide with the opportunity to participate in data collection and the scientific process and contribute meaningfully to our understanding of the Earth system and global environment. At GLOBE's core students learn how science and math can be applied to monitor the environment while collecting data that can be used for both their own studies and studies by professional earth systems researchers (Howland and Becker, 2002). The GLOBE program community is dedicated to providing these authentic science experiences and has the essential tools to foster project-based scientific learning for K-12 students. The GLOBE community includes 114 countries with over 28,000 K-12 schools, and 21,000 teachers around the world. Students and teachers are using GLOBE protocols that have been designed by scientists and field-tested by classroom teachers to study the atmosphere, biosphere, hydrosphere and pedosphere. Teachers and students have entered data into the GLOBE database that has grown to over 130 million measurements since the program's inception. There are 90 active U.S. Partnerships recruiting, training and mentoring teachers in inquiry and research investigations using GLOBE protocols. Another 40 partners are now actively recruiting and providing training but continue to mentor teachers. GLOBE partnerships are located at many types of organizations; including colleges and universities, state and local professional development centers, NASA education centers, informal science centers, and individual schools and school districts. Through the GLOBE website and with the assistance of GLOBE Partners, teachers and students have the resources and tools to explore the local environment, ask questions, design investigations, carry out data collection, and enter data into a publicly accessible repository. The website enables students to compare their data to data collected by other students around the world and collaborate and publish results from student investigations.

GLOBE Student Research Symposia (SRS) is a program bringing together GLOBE teachers and their students with GLOBE partners in six regions across the United States to present student research. The program began in 2015 and six regional science fairs were coordinated across the United States in the Spring of 2019 at which 262 students presented the results of their investigations using GLOBE data and protocols to peers and scientists across the six regions. One objective of these GLOBE SRS is to increase student confidence in using the NGSS science practices and conducting research investigations with GLOBE protocols. During the SRS students present their GLOBE research to judges and community members and interact with scientists and peers. Research has shown that students who engage in authentic research experiences are more likely to be engaged in their lessons (Pruneau et al., 2003). The NASA GLOBE program and their Student Research Symposium (SRS) provide students with the opportunity to interact with scientists and their peers in a form consistent with that of a career scientist. The GLOBE program fits well within the framework proposed by Bonney and colleagues' model for citizen science projects and supports student learning (Bonney et al., 2009). GLOBE focusses on specific questions using refined protocols and vast educational support materials. Students not only collect data according to GLOBE protocol but also share their data with the GLOBE database, as well as disseminate the results including through the Student Research Symposia which helps to increase the impact it can have on students and their science learning (National Academies of Science, 2018).

GLOBE has the capacity to positively impact students' ability to use scientific data in decision-making and on students' scientifically informed awareness of the environment (Butler and Macgregor, 2003). Teachers of GLOBE participating students reported a high interest in GLOBE activities from their students and the program improved their students' use of NGSS science practices, observation, and using technology (Butler and Macgregor, 2003). Students appreciated being able to collect data that would be useful to real scientists and would contribute to a greater understanding of how the world works (Butler and Macgregor, 2003). It has been proposed by Trautmann and colleagues that depending on the degree to which students design their own investigations and analyze and interpret the results, their involvement in citizen science could lead to an increase in science process understandings (e.g., NGSS science practices) and analytical reasoning skills (Trautmann et al., 2012). There has been some evidence that scientific competency is increased by participation in citizen science (Bonney et al., 2009; Perelló et al., 2017; Phillips et al., 2018) but this isn't a guaranteed outcome and is something that should be evaluated (Brossard et al., 2005). The ability of citizen science projects to increase science process understanding is an important point of investigation and one that this work examining the GLOBE SRS may help to support. Another way in which citizen science projects can help students experience the full research experience is by providing a forum for presenting results which the GLOBE SRS offer to student participants (Trautmann et al., 2012; National Academies of Science, 2018).

The GLOBE program and the Student Research Symposia follow best practices for citizen science and experiential education programs with its well-developed data collection protocols, project support and feedback, and the opportunity for students to interact with professional scientists and present their synthesized work. Experiential education programs emphasize student directed work and inquiry and have been pointed to as ways to increase scientific knowledge in participants (Eyler, 2009; Djonko-Moore et al., 2018) as have citizen science programs (Brossard et al., 2005; Bonney et al., 2009; Crall et al., 2013). The GLOBE SRS also support the key “debriefing” portion the experiential education model posed by Joplin as the students make their work public to professional scientists in the field (Joplin, 1981). The interest of this work is to see the impact that participation in GLOBE Student Research Symposia had on students’ attitudes towards science with the goal that programs like the GLOBE SRS could be implemented and evaluated as a way to increase student interest in science and self-confidence in NGSS science practices.

4.2 Methods

4.2.1 Data Collection Instruments and Procedure

Data was gathered from students attending the 2019 GLOBE Student Research Symposia (SRS), which was conducted across the country, and was analyzed to determine the impact participation in this program had on students’ attitudes toward science and their confidence with NGSS science practices. The 2019 SRS were held in the spring in six regions across the U.S. A total of 262 students, 65 teachers, 41 GLOBE partners, 14 scientists and reviewers, and 93 other attendees were registered (Table 4.1). Out of the two hundred and sixty-two students registered, 228 consented and were permitted by their parents to participate in this research.

Table 4.1: Attendance at regional GLOBE SRS 2019

Region & Dates	Location	Students	Teachers	Partners	Other
Midwest April 5-6	University of Northern Iowa, Cedar Falls, IA	36	5	5	9
Northeast/Mid-Atlantic May 31-June 1	Boston University, Boston, MA	78	19	11	42
Northwest May 2-4	Seattle, WA	11	4	6	2
Pacific April 26-27	Nature Bridge of Golden Gate, Sausalito, CA	71	13	7	9
Southeast May 10-11	Atlanta, GA	26	9	5	9
Southwest May 17-19	Mescalero, NM	40	15	7	22
TOTAL		**262**	**65**	**41**	**93**

4.2.2 Student questionnaires

Questions were designed that specifically asked students to rate their agreement with statements regarding their ability in and value for science. Students who agreed to participate were asked to complete questions assessing their feelings towards science before their regional SRS. At the end of their participation in the 1.5 day Student Research Symposium participants were asked to complete the post questionnaire. For complete instrument please see Figure D.1.

The student survey questionnaire included 17 statements with repeated measure at pre-test and post-test to assess changes in value for and confidence in science resulting from participation in the SRS. Students rated each item from 1 ‘strongly disagree’ to 6 ‘strongly agree.’ A summed score was computed for the 17 items, with items #14-17 reverse coded (because lower scores indicate positive responses and higher scores are negative for those items).

4.2.3 Statistical analysis:

Pre- and post- SRS surveys were matched up for each participating student. The average score for each question for all participants across all regions was calculated. Paired t-tests were performed to test for changes in the average of participating students' confidence with science practices and attitudes towards science among the participants both before and after the symposium using these total participant averages. Significant ($p< 0.05$) differences between average pre- score for a question and the average post- score were determined in paired two tail t-tests.

4.3 Results

To understand how the experience of participating in GLOBE's Student Research Symposium improved student's attitude toward science we examined student responses to several items in the survey instrument including "being good at science is important", "I am proud of my accomplishments in science…." And "I am worried I won't learn all of the things I'm supposed to in science", and "I get embarrassed in science". In order to assess confidence with NGSS science practices instrument items including "I am able to interpret data in science research" and "I am able to analyze data to do science research" were evaluated. All items were measured using a 6-point Likert type rating scale, where 1 = Strongly Disagree and 6 = Strongly Agree. When referring to students as "agreeing" or "disagreeing" with a particular statement, we are referring to those who responded 5 'agree' or 6 'strongly agree,' or 2 'disagree' or 1 'strongly disagree,' without reverse coding. We describe the results for disagreement instead of agreement where disagreement is the desired response and increased disagreement indicates a positive change.

Two hundred sixty-two students registered for the 2019 symposia, but not all registrants participated in the survey or provided consent to use their survey results for research purposes, and not all survey questionnaires included the registration code to use for pre-post matching. These results focus on 140 student cases with pre-test and post-test data matched using their SRS registration codes.

4.3.1 Does the process of following GLOBE protocols and participating in the symposium allow students to gain confidence their use of NGSS science practices?

Analysis of the pre-post student survey data found a significant ($p < .05$) increase in agreement with statements that indicate confidence in science practices (Table 4.2). This is also shown by Figure 4.1 showing the percentage of agreement that students have with various statements, including “I am able to construct scientific arguments” and “I am able to interpret data in science research” indicating confidence in science practices before and after the experience of attending the research symposium.

Table 4.2: Average scores for participants on questions that examined confidence with science practices. Includes p-value results from t-tests on student survey scores Pre- and Post- symposium participation. 2 tailed paired t-test. **p-values < 0.001 *p-values < 0.05 (n=140).

Instrument questions “I am able to...”	Average pre-SRS score	Average post-SRS score	P-value
learn new things in science.	5.51	5.69	0.0003**
ask good questions to do science research.	5.01	5.19	0.004**
analyze data to do science research.	5.23	5.34	0.06
interpret data in science research.	5.01	5.21	0.007**
construct scientific arguments	4.81	4.96	0.047*

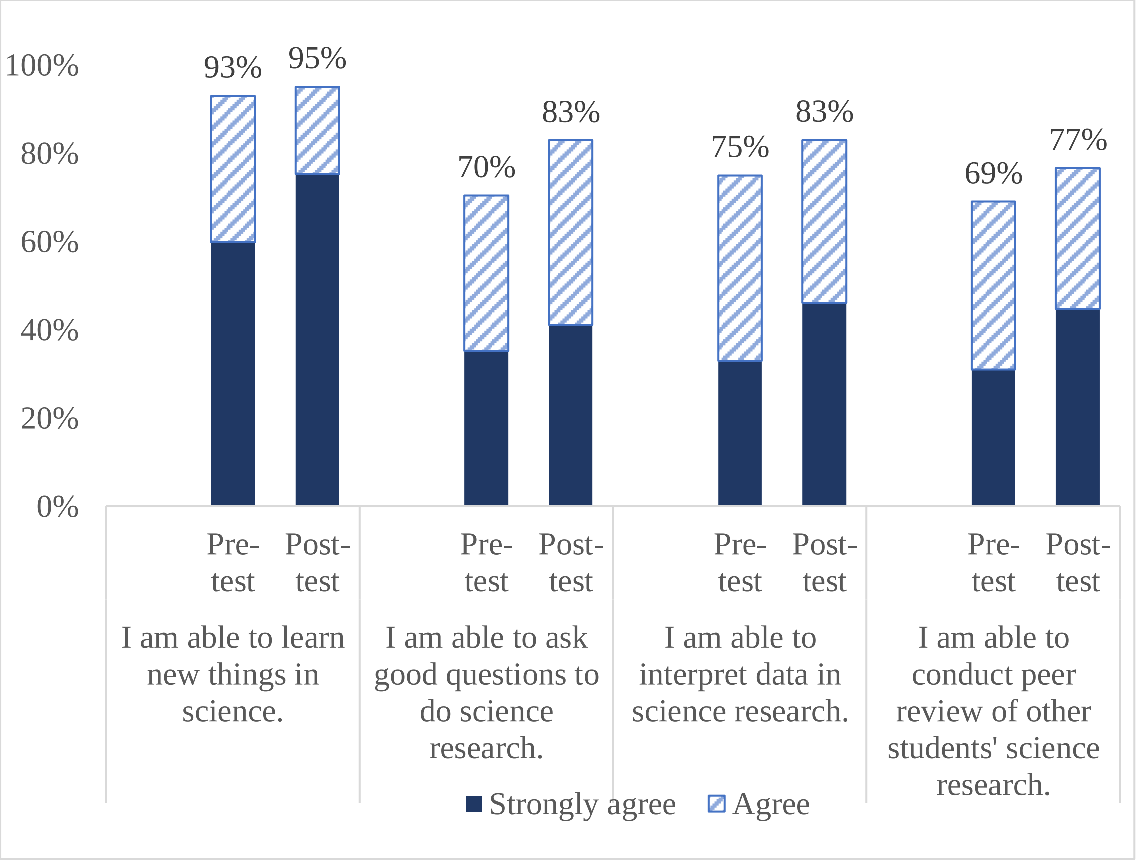


Figure 4.1: The percentage of agreement that students have with various statements indicating confidence in science practices in both pre- and post- tests (n=140).

4.3.2 Can the experience of participating in GLOBE's Student Research Symposium improve student's engagement with or interest in science?

In order to examine students' positive attitudes towards science and try to gauge their interest in the subject the pre- and post- surveys were analyzed for increases in the numbers assigned to affirming statements like "I am good at science".

It is possible that students who elected to attend the symposium may have already self-selected for having an enjoyment of science. Additionally, this snapshot of pre and post symposium survey does not take into account any change or growth in interest for students as they went through the GLOBE program to collect and analyze data ahead of the symposium.

Table 4.3: Average scores for participants on questions that examined positive feelings and attitudes towards science. Includes p-value results from t-tests on student survey scores Pre- and Post- symposium participation (n=140). 2 tailed paired t-test. **p-values ≤ 0.01 *p-values ≤ 0.05

Instrument question assessing positive feelings about science	Pre	Post	P-value
I am good at science	5.14	5.29	0.02*
I am good at learning new things	5.31	5.37	0.22
Being good at science is important	5.34	5.37	0.63
I enjoy science	5.43	5.43	1
I want to have a career in science someday	4.61	4.69	0.37
I am proud of my accomplishments in science	5.35	5.53	0.01**

We can also look at negative statements like "I am worried I won't learn all of the things I'm supposed to in science" to evaluate feelings toward science, where increased disagreement would indicate a more positive relationship to science.

Table 4.4: Average scores for participants on questions that examined negative feelings around science. Includes p-values results from two tailed paired t-tests on student survey scores Pre- and Post- symposium participation. *p-values ≤ 0.05

Instrument question assessing negative feelings about science	Average pre-SRS score	Average post-SRS score	P-value
I am worried I won't learn all of the things I'm supposed to in science	2.60	2.33	0.03*
I get bored in science	2.10	1.92	0.10
I get embarrassed in science	1.61	1.61	0.93
I get angry when I don't understand something in science	2.10	1.92	0.10

4.3.3 Positive responses to the experience provided by SRS

We wanted to evaluate more broadly the experience students had collecting data following GLOBE protocols in conjunction with the analysis and data presentation at the SRS to determine if the SRS offers another type of "experiential education" that can be implemented by other citizen science programs. In order to do this, we examined survey questions regarding student experience at the SRS event.

When students were asked what "part of SRS did you enjoy the most?" the SRS events selected by students as those they enjoyed most involved interaction with scientists. Meeting scientists was selected most frequently (84), followed by review from scientists (82), and research presentations to the reviewers (77). When answering the open-ended question "Did participating in the research symposium impact your understanding of the scientific process and what it's like to do science research?" 79% of students of the 140 who answered responded in the affirmative.

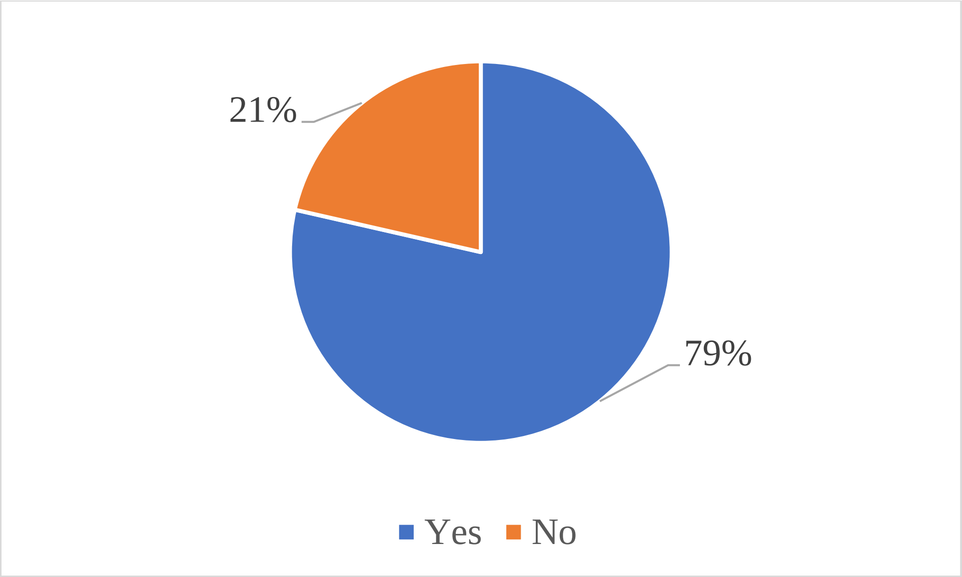


Figure 4.2: Participant responses to the question “Did participating in the research symposium impact your understanding of the scientific process and what it’s like to do science research?”

Twenty-nine comments focused on gaining science and research skills, for example:

> *Yes, it impacted my understanding of the scientific process and what it’s like to do science research. It gave me a better perspective on science.*

> *I enjoyed using new tools to find and collect data. There were many aspects to the data collection I thought were interesting.*

> *Yes; it gave me more information and knowledge to improve research as well as how to do additional research based on conclusions.*

> *Participating was a great experience and I learned a lot about the scientific process.*

Participants (n=25) also described being inspired and having fun at the event. Some were inspired to pursue careers in science or to engage in new scientific research projects.

> *Yes, this event verified that I have a passion for research, and that I will definitely pursue research in college.*

> *Participating in this year's SRS has given me more inspiration and ideas on the scientific process. Doing science research for my project was fun and interesting.*

> *Yes, the research symposium impacted [my understanding of] the scientific process. It was awesome, exciting and fun to do the science research.*

> *YES! I've learned soo [sic] much today and it really gave me more inspiration and more topics to think about in future research.*

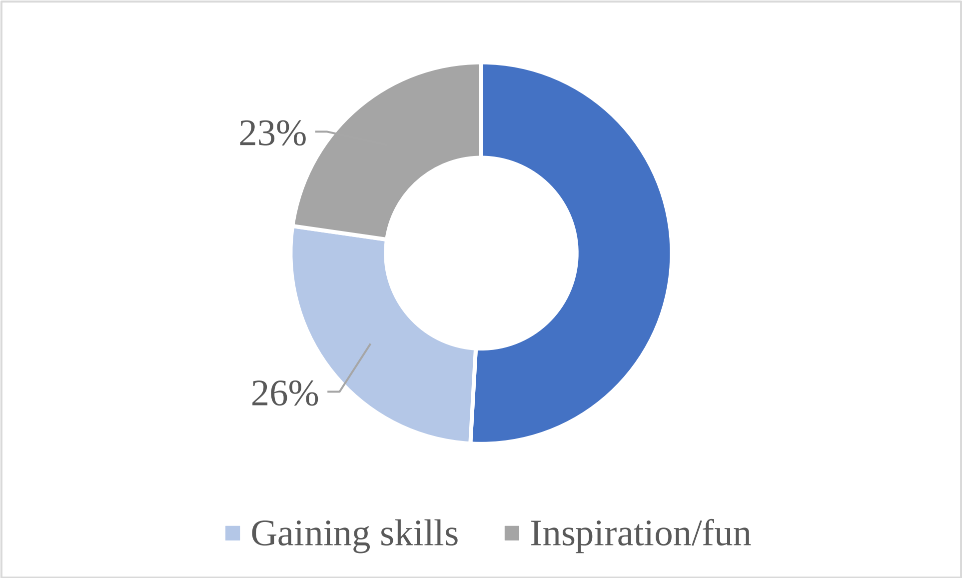


Figure 4.3: Breakdown of common themes indicated in "yes" responses by participants who answered yes to the question "Did participating in the research symposium impact your understanding of the scientific process and what it's like to do science research?"

Students were also asked to complete the statements, "before the student research symposium I thought … but now I know …" Many of their 'before … after' statements illustrate how the SRS increased their confidence to participate in science (n=25), for example:

> *I was bad at science anything. … I am capable of science.*

> *I wasn't good at science. … Everyone can be good at science.*

> *I thought that I would be scared. ... I know that I can achieve my goals in science.*

> *I won't make it because my English not really good, scientist will ask me a question and have a big word in science, that I don't understand. ... Even though, my English is not good, I still can learn a lot from the science.*

Another theme students expressed in the "before and after" open ended question was the idea of a reinvigorated sense of excitement or interest in science and the hope to do more science (n=33):

> *That science was boring. ... That science is fun.*

> *That I wouldn't want to do Globe and that I wouldn't learn anything new. ... That Globe is about having fun and learning new things and that I want to come back to Globe.*

> *That it was going to be a waste of time. ... that experiences like these will help me find out about what I want to do for a career.*

> *Before the symposium I wasn't very interested in the field of science or what it had to offer me personally. ... The scientific area can now help me learn, explore, and it can help impact my life in many ways.*

4.4 Discussion and Implications

The GLOBE program is a citizen science initiative, encouraging students and adults alike to collect meaningful data to answer pertinent research questions. The GLOBE Student Research Symposia expose students to experiential learning by encouraging student directed research, providing feedback and support to students during data collection, and allowing them to synthesize and debrief this data in a public forum. In particular, the student poster presentations to scientists with scientist feedback are an example of the "debriefing" portion of the experiential education model (Joplin, 1981). The importance of providing students the ability to legitimately participate in many dimensions of science work including the conceptual, social, and material, is key for learning science-as-practice (Lehrer and Schauble, 2006; Trautmann et al., 2012). The experience of collecting data following GLOBE protocols, communicating their projects, as well as participating in the peer review and review by a scientist at the SRS enhanced students' understanding of the investigation process and allows them to engage in science practices. As a result of SRS, students reported an increased confidence in applying NGSS science practices like "analyzing and interpreting data" and "obtaining, evaluating, and communicating information". The experience of communicating about their research with the scientists in a poster presentation format could highlight for the students their abilities in NGSS science practices, which may have contributed to significant increases in agreement from pre to post SRS.

Through participation in this SRS students also saw an increase in positive attitudes towards science shown by the decrease in agreement with negative statements regarding attitudes in science as well as an increase in their self-identified perception of being "good at science". The increase in confidence levels, as shown by more disagreement with the statement "I am worried I won't learn all of the things I'm supposed to in science" could point to the importance of the experience of presenting information for peer review and scientist feedback as a way to improve confidence in science for students.

The combined experience of students collecting data following GLOBE protocols along with analyzing and presenting data in the symposium offers another type of "experiential education" that can be implemented by other citizen science programs. The GLOBE SRS program is designed for learning as it builds upon the concept of teachers using GLOBE protocols to get their students experience with data collection, an example of citizen science used for learning, and combines it with the experience of analyzing and presenting the data to scientists for increases in confidence with NGSS science practices (National Academies of

Science, 2018). The data used in this study is a snapshot of students' perceptions just before and after participating in the SRS and as such it has limited ability to make claims beyond the impact of the two-day event but it does highlight the impact that debriefing data collected by students with scientists can have. GLOBE SRS could be a model for other programs who may have the ability to offer this experience to other students, centering citizen science designed for students to enhance science learning and improve attitudes toward science. It is important that we provide students with meaningful experiences that can foster positive relationships with scientific process and support students' identities as it relates to the discipline.

4.5 Future Work

More work needs to be done to determine what if any benefits are seen by students in the long term regarding their attitude toward sciences and their confidence with science practices. Collecting data from students at different stages of the GLOBE investigation process would help us better understand how individual components of the GLOBE SRS (i.e. data collection, poster creation) help influence their self-confidence and views towards science. In the future demographic data could also be collected to ascertain if there is a subset of students that is seeing an increased interest in science or confidence with NGSS science practices compared to others. This will help us to better understand how individuals may benefit from an experience like the GLOBE Student Research Symposium and allow other community science programs to target populations that may benefit the most from their involvement. Students who are traditionally underrepresented in the sciences see varied outcomes after the experience of a GLOBE SRS than their peers which will be critical to identify in order to build more inclusive and robust science experiences for all students in the future.

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APPENDIX A: CHAPTER 1 SUPPLEMENTARY MATERIALS

Figure A.1: Schematic of bag placement at Hubbard Brook maple dominated Site 237. Labels C1-C15 and T1-T15 represent in-growth bags containing the Conway Granite and tonalite substrates respectively. Black X's represent locations where bags were not relocated for retrieval at day 100.

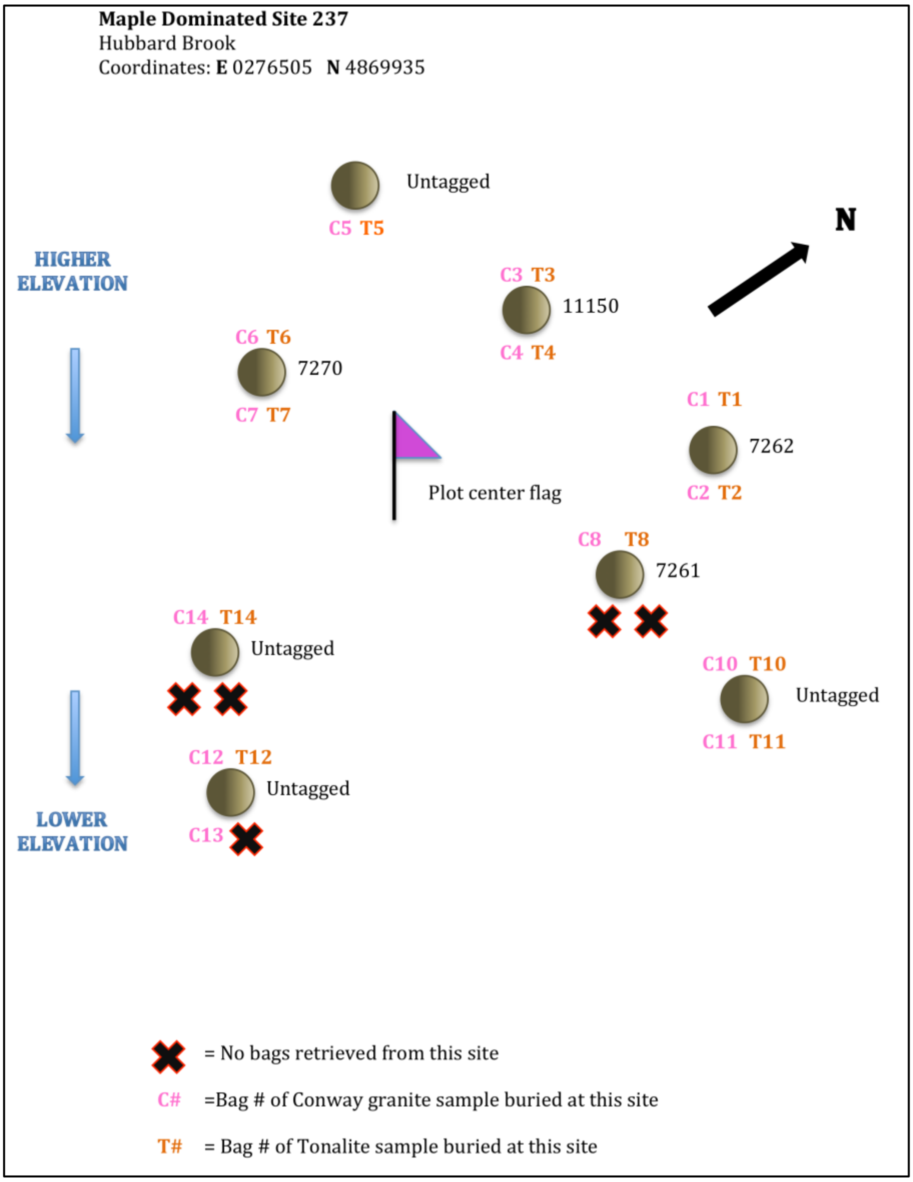

Figure A.2: Schematic of bag placement at Hubbard Brook beech and birch dominated Site 206. Labels C16-C30 and T16-T30 represent in-growth bags containing the Conway Granite and tonalite substrates respectively. Black X’s represent locations where bags were not relocated for retrieval at day 100.

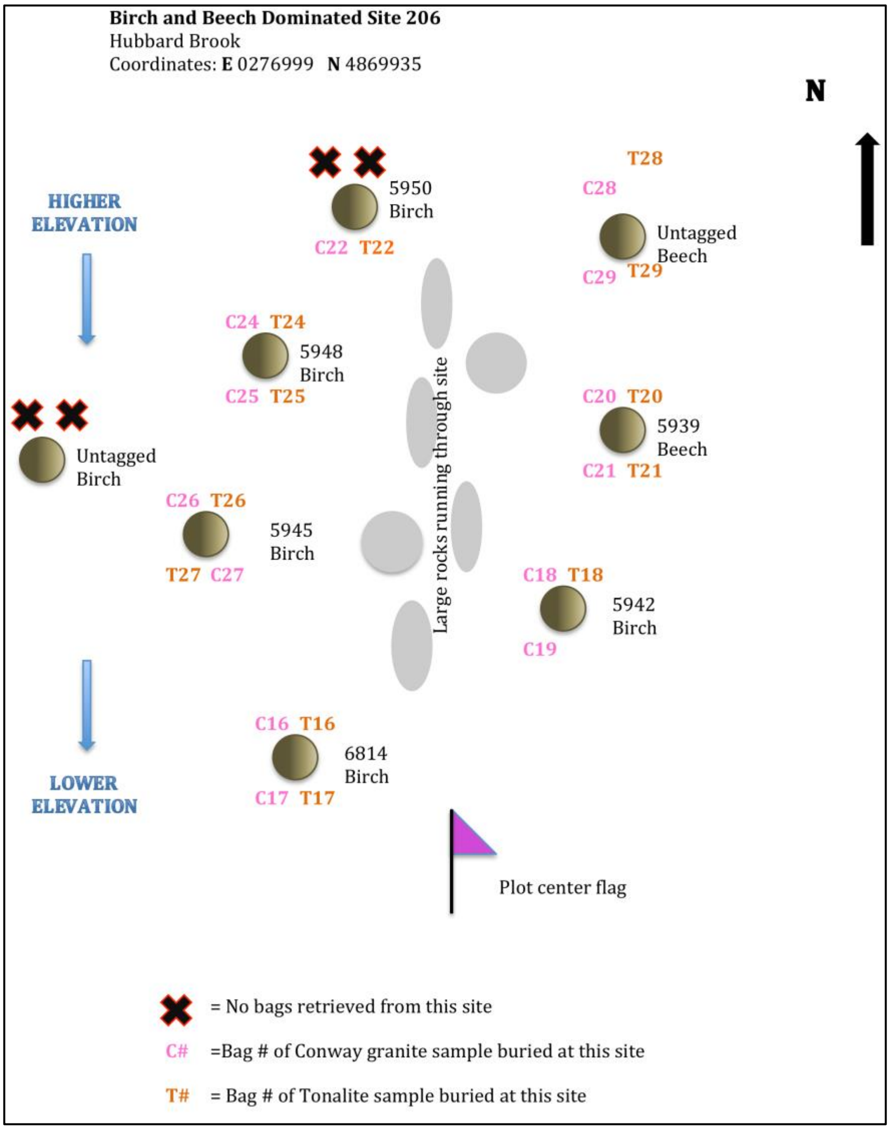

Table A.1: Concentrations of Mg, P, and Ca in μmol/g for both EcM and AM sites and leachates, NH_4Cl and nitric (HNO_3-) obtained from ICP-MS analyses.

Fungal type	**Leachate and Rock Type**	**Bag code**	**Mg μmol/g**	**P μmol/g**	**Ca μmol/g**
AM	Conway Granite	CG5	0.1679	0.0065	0.7489
	NH_4Cl	CG2	0.1677	0.0049	0.5852
		CG10	0.1484	0.0010	0.4900
		CG6	0.1537	0.0019	0.6897
		CG3	0.1233	0.0012	0.3905
		CG13	0.1440	0.0033	0.6107
		CG14	0.1337	0.0001	0.5063
		CG1	0.1065	0.0070	0.4003
	Tonalite	T12	0.4118	0.0547	2.4064
	NH_4Cl	T4	0.5430	0.0179	2.8476
		T5	0.3498	0.0074	1.4180
		T6	0.4488	0.0185	2.1558
		T8	0.2724	0.0189	2.0037
		T1	0.4597	0.0434	1.6123
		T14	0.0847	0.0126	1.0026
		T11	0.1504	0.0345	1.4809
	Conway Granite	CG5	2.6974	0.2454	8.5374
	HNO_3-	CG2	2.3422	0.0844	10.3513
		CG10	2.4550	0.6057	13.6420
		CG6	3.4148	0.8465	17.3830
		CG3	2.0711	0.2271	8.2948
		CG13	2.5400	0.4440	10.8942
		CG14	2.4716	0.2137	9.3235
		CG1	4.1087	1.2713	24.3376

	Tonalite	T12	7.2922	33.8407	72.0496
	HNO_{3-}	T4	6.0448	35.6114	69.8470
		T5	9.9246	47.9326	101.4972
		T6	5.9775	31.3625	64.4395
		T8	11.0532	57.1388	117.3414
		T1	6.1308	42.2473	79.8430
		T14	8.0552	46.9047	95.0947
		T11	6.6589	41.3028	81.9990
EcM	Conway Granite	CG16	0.2198	0.0240	1.0720
	NH_4Cl	CG19	0.1630	0.0048	0.5894
		CG21	0.7771	0.0416	2.7535
		CG22	0.1902	0.0135	0.4675
		CG25	0.2311	0.0113	0.7872
		CG26	0.1026	0.0022	0.3630
		CG28	0.1131	0.0111	0.3766
	Tonalite	T17	0.4242	0.0787	1.6197
	NH_4Cl	T18	0.2790	0.0249	0.8711
		T21	0.2764	0.0231	1.4373
		T22	0.1119	0.0099	0.3766
		T25	0.2865	0.0233	0.8131
		T26	0.7171	0.0686	1.0406
		T29	0.2779	0.0087	0.7135
	Conway Granite	CG16	1.6413	0.2148	7.2248
	HNO_{3-}	CG19	1.3789	0.2451	6.0539
		CG21	1.2532	0.2490	5.7742
		CG22	1.7942	0.3361	7.0393
		CG25	1.7486	0.2644	7.0280

		CG26	1.4932	0.2403	6.9466
		CG28	1.6551	0.1978	6.4207
	Tonalite	T17	6.0725	36.9325	63.7073
	HNO_{3-}	T18	5.3486	33.2778	60.1371
		T21	6.9379	38.7655	65.3617
		T22	6.5312	35.3769	63.0847
		T25	6.2608	36.0334	62.0558
		T26	6.6045	38.6302	67.7153
		T29	5.2357	36.4029	61.2702
	Conway Granite control NH_4Cl		0.8628	0.0040	0.8285
	Tonalite control NH_4Cl		0.5267	0.0962	2.4061
	Conway Granite control HNO_{3-}		1.8484	0.2423	7.2719
	Tonalite control HNO_{3-}		4.8489	36.5663	59.6936

Table A.2: Sr and Pb isotopic rations measured via MC-ICP-MS for Conway Granite and tonalite in-growth bags and controls subjected to NH_4Cl and nitric (HNO_{3-}) leaches across both AM and EcM dominated sites.

Dominant Fungal type	**Bag code**	**Leachate and Rock type**	**^{208}Pb/^{204}Pb**	**^{207}Pb/^{204}Pb**	**^{206}Pb/^{204}Pb**	**^{207}Pb/^{206}Pb**	**^{208}Pb/^{206}Pb**	**^{87}Sr/^{86}Sr**
AM	CG5	Conway Granite	39.083	15.938	18.909	0.842	2.067	0.71889
	CG2	NH_4Cl	38.720	15.649	18.922	0.827	2.046	0.71841
	CG10		38.696	15.630	18.825	0.830	2.056	0.71827
	CG6		39.040	15.665	19.088	0.821	2.045	0.71771
	CG3		38.921	15.623	19.089	0.818	2.039	0.71863
	CG13		38.969	15.622	19.159	0.815	2.034	0.71688
	CG14		39.267	15.653	19.362	0.808	2.028	0.71654
	CG1		38.768	15.652	18.965	0.825	2.044	0.71702
	T12	Tonalite	39.079	15.669	18.740	0.836	2.085	0.71684
	T4	NH_4Cl	39.440	15.705	19.082	0.823	2.067	0.71843
	T5		39.650	15.699	18.729	0.838	2.117	0.71870
	T6		39.502	15.686	18.624	0.842	2.121	0.71868
	T8		39.166	15.620	18.482	0.845	2.119	0.71837
	T1		38.988	15.632	18.601	0.840	2.096	0.71602
	T14		39.793	15.677	18.720	0.837	2.126	0.72053
	T11		39.372	15.685	18.785	0.835	2.096	0.71991
	CG5	Conway Granite	41.373	15.801	21.492	0.735	1.925	0.71677
	CG2	HNO_{3-}	41.550	15.783	21.638	0.729	1.920	0.71586
	CG10		41.944	15.833	22.115	0.716	1.897	0.71646
	CG6		42.101	15.831	22.260	0.711	1.891	0.71752
	CG3		42.004	15.832	22.071	0.717	1.903	0.71687
	CG13		41.708	15.801	21.736	0.727	1.919	0.72794
	CG14		42.108	15.830	22.286	0.710	1.889	0.71617

	CG1		42.065	15.820	22.209	0.712	1.894	0.71631
	T12	Tonalite	41.609	15.721	19.558	0.804	2.127	0.71420
	T4	HNO_3^-	41.694	15.720	19.562	0.804	2.131	0.71359
	T5		41.633	15.716	19.499	0.806	2.135	0.71336
	T6		42.380	15.720	19.721	0.797	2.149	0.71422
	T8		42.521	15.737	19.779	0.796	2.150	0.71364
	T1		42.008	15.730	19.633	0.801	2.140	0.71373
	T14		42.113	15.732	19.678	0.799	2.140	0.71395
	T11		42.339	15.722	19.704	0.798	2.149	0.71385
EcM	CG16	Conway Granite	39.737	15.736	18.973	0.915	2.095	0.72085
	CG19	NH_4Cl	38.901	15.647	18.955	0.915	2.052	0.71912
	CG21		39.043	15.652	19.116	0.915	2.041	0.72023
	CG22		39.370	15.655	19.457	0.805	2.024	0.72219
	CG25		39.328	15.647	19.464	0.817	2.021	0.71842
	CG26		38.977	15.687	18.923	0.860	2.060	0.71750
	CG28		38.549	15.644	18.862	0.805	2.044	0.72120
	T17	Tonalite	39.557	15.693	18.649	0.915	2.121	0.72512
	T18	NH_4Cl	38.662	15.579	18.668	0.915	2.071	0.72247
	T21		39.370	15.652	18.767	0.834	2.098	0.72167
	T22		40.342	15.639	18.954	0.834	2.128	0.72056
	T25		39.998	15.673	18.954	0.834	2.110	0.72295
	T26		41.489	15.692	19.195	0.817	2.161	0.72661
	T29		39.829	15.654	18.896	0.915	2.108	0.72565
	CG16	Conway Granite	41.557	15.797	21.791	0.831	1.929	0.71716
	CG19	HNO_3^-	42.417	15.848	22.445	0.706	1.890	0.71648
	CG21		42.549	15.851	22.589	0.767	1.893	0.71911

	CG22		42.404	15.842	22.524	0.764	1.907	0.71600
	CG25		42.327	15.765	21.356	0.703	1.878	0.71652
	CG26		42.479	15.855	22.639	0.871	2.057	0.71693
	CG28		41.888	15.824	21.995	0.786	1.920	0.71676
	T17	Tonalite	42.514	15.722	19.702	0.944	2.369	0.71472
	T18	HNO_3^-	40.566	15.674	19.254	0.814	2.107	0.71451
	T21		42.552	15.713	19.769	0.795	2.152	0.71609
	T22		42.195	15.725	19.701	0.798	2.142	0.71641
	T25		42.461	15.726	19.751	0.937	2.295	0.71543
	T26		42.388	15.726	19.697	0.798	2.152	0.71506
	T29		41.432	15.701	19.493	0.805	2.126	0.71387
	C. granite control	NH_4Cl	39.621	15.667	19.703	0.829	2.011	0.71713
	Tonalite control	NH_4Cl	39.529	15.679	18.619	0.842	2.123	0.71530
	C. granite Control	HNO_3^-	42.151	15.826	22.274	0.711	1.892	0.71634
	Tonalite control	HNO_3^-	42.470	15.726	19.744	0.797	2.151	0.71395

Table A.3: Pb isotopic ratios measured via MC-ICP –MS for sporocarp samples collected from Hubbard Brook Experimental Forest and Bartlett Experimental Forest. Taxon abbreviations in the table are as follows: Cort = *Cortinarius violaceus*, Lact = *Lactarius camphoratus,* Lecc = *Leccinum* spp. (at least 3 spp that could not be identified based on sequences)

Sample	**Site**	**Taxon**	**208Pb/204Pb**	**207Pb/204Pb**	**206Pb/204Pb**	**207Pb/206Pb**
733	HBM	Lact	38.351	15.639	18.677	0.8373
798	HBM	Lecc	38.421	15.64	18.724	0.8353
862	HBM	Lecc	38.448	15.646	18.742	0.8348
927	HBM	Lecc	38.357	15.637	18.644	0.8387
950	HBM	Cort	38.29	15.632	18.636	0.8389
750	HBO	Lecc	38.382	15.65	18.72	0.836
794	HBO	Lact	38.389	15.64	18.669	0.8378
820	HBO	Lecc	38.332	15.637	18.707	0.8359
882	HBO	Lecc	38.338	15.638	18.671	0.8376
943	HBO	Cort	38.328	15.638	18.713	0.8357
711	C9	Cort	38.412	15.642	18.739	0.8348
713	C8	Lecc	38.396	15.631	18.664	0.8375
722	C6	Lecc	38.406	15.641	18.69	0.8369
725	C6	Cort	38.348	15.633	18.685	0.8366
732	C9	Lact	38.463	15.646	18.761	0.8339
743	C6	Lact	38.506	15.646	18.735	0.835
751	C6	Cort	38.345	15.648	18.643	0.8394
781	C8	Lecc	38.496	15.645	18.762	0.8339
782	C6	Lecc	38.357	15.638	18.71	0.8358
793	C8	Lact	38.386	15.658	18.658	0.8394
829	C9	Lecc	38.455	15.646	18.775	0.8336
878	C6	Cort	38.344	15.631	18.679	0.8368
887	C9	Lecc	38.514	15.643	18.746	0.8345

896	C9	Lact	38.422	15.643	18.708	0.8362
920	C4	Lecc	38.802	15.654	18.921	0.8273
937	C6	Cort	38.433	15.643	18.721	0.8356
939	C8	Lact	38.333	15.641	18.521	0.8444
942	C4	Cort	38.382	15.635	18.667	0.8376
955	C9	Lecc	38.469	15.647	18.762	0.834
956	C4	Cort	38.359	15.632	18.693	0.8362
958	C4	Lact	38.365	15.641	18.667	0.8379
962	C4	Lecc	38.366	15.642	18.677	0.8375

APPENDIX B: CHAPTER 2 SUPPLEMENTARY MATERIALS

Table B.1: Acid-leachable and whole rock Ba, REE, and Pb concentrations. Concentrations in apatite are estimated from the acid leach; literature values for apatite samples from other granites are listed for comparison. See also Hughes et al. (1991).

	ug g^{-1} granite			**ug g^{-1} apatite**					
	acid leachable	XRF total *		This study (estimated)	Kyushu (Nagasawa 1970)	Peninsular Range (Gromet and Silver 1983)	Sierra Nevada (Sawka and Chappell 1988)	Peña Negra (Bea et al. 1994)	Madagascar (Hagerberg et al. 2003)
Ba	4.0	191		4,200					
La	93	70		98,800			1131	903	1,200
Ce	173	148		184,000	1490	509	1404	2,158	
Pr	17			17,800				291	300
Nd	49	51*		52,000	1360	302	458	1,300	1,200
Sm	6.9	98*		7,300	543	53	66	409	100
Eu	0.11	0.4	*	120	3.3	15	10	17	10
Gd	5.3			5,600			60	448	100
Tb	0.69	1.5	*	730			6.6	73	10
Dy	3.71			3,900	615	32		456	40
Ho	0.70			740			8.7	94	7
Er	1.96			2,080	256	17		254	20
Tm	0.28			300				37	
Yb	1.72	5.0	*	1,820	188	14	21	222	10
Lu	0.22	0.6	*	240	25		4.0	30	
Pb	1.72	16		1,800				1.4	
La/Lu		112		416			283	31	
La/Yb		14		54			53	4	120

Ce/Yb	27	101	8	37	66	10	
La/Eu	156	845			116	54	120
Sm/Eu	22	62	165	3.5	6.7	25	10

* values are estimated from those reported by Eby (1992), scaled to La determined by XRF analysis on our sample.

Table B.2: Fungal enrichment factors calculated for major elements. Values calculated by dividing elemental concentration of samples grown with mycorrhizal symbionts by concentrations of those non-mycorrhizal samples.

Tree Type	**Sample type**	**Rock type**	**Mg**	**P**	**Ca**
Pine	Foliage	Waits	0.640	1.242	0.419
Pine	Root	Waits	2.521	3.119	3.902
Pine	Stem	Waits	1.279	1.953	0.751
Pine	Average Percolate	Waits	1.605	1.711	1.332
Pine	Foliage	Granite	1.349	2.867	1.006
Pine	Root	Granite	3.704	4.391	3.988
Pine	Stem	Granite	1.324	3.558	2.184
Pine	Average Percolate	Granite	1.380	1.501	1.392
Maple	Foliage	Waits	0.326	0.629	0.956
Maple	Root	Waits	0.898	1.718	0.843
Maple	Average Percolate	Waits	0.831	0.680	0.813
Maple	Foliage	Granite	1.720	1.665	6.168
Maple	Root	Granite	2.815	1.354	3.021
Maple	Average Percolate	Granite	0.455	0.473	0.571

Table B.3. Mg isotopes for mycorrhizal and non-mycorrhizal pine and maple samples grown on WRF and Conway Granite.

Tree Type	**Type**	**Mycorrhizal**	**Rock type**	**Sample**	**d26/24 Mg**	**d25/24 Mg**	**d26/25 Mg**
Pine	Foliage	Nonmyco	Waits	22 Pine, Foliage	-2.23	-1.16	-1.06
Pine	Root	Nonmyco	Waits	22 Pine, Root	-0.58	-0.36	-0.25
Pine	Stem	Nonmyco	Waits	22 Pine, Stem	-1.60	-0.87	-0.75
Pine	percolate	Nonmyco	Waits	22 (percolate)	-0.70	-0.38	-0.30
Pine	percolate	Nonmyco	Waits	22 (percolate)	-1.19	-0.71	-0.48
Pine	Foliage	*Suillus*	Waits	12 Pine, Foliage	-2.11	-1.12	-0.98
Pine	Root	*Suillus*	Waits	12 Pine, Root	-1.57	-0.83	-0.74
Pine	Stem	*Suillus*	Waits	12 Pine, Stem	-1.96	-1.03	-0.95
Pine	percolate	*Suillus*	Waits	12 (percolate)	-1.38	-0.74	-0.64
Pine	percolate	*Suillus*	Waits	12 (percolate)	-1.87	-0.98	-0.88
Pine	Foliage	Nonmyco	Granite	24 Pine, Foliage	-1.68	-0.92	-0.75
Pine	Root	Nonmyco	Granite	24 Pine, Root	-2.10	-1.11	-0.98
Pine	percolate	Nonmyco	Granite	24 (percolate)	-2.07	-1.11	-0.96
Pine	Foliage	*Suillus*	Granite	2 Pine, Foliage	-1.83	-0.98	-0.86
Pine	Root	*Suillus*	Granite	2 Pine, Root	-1.99	-1.06	-0.93
Pine	Stem	*Suillus*	Granite	2 Pine, Stem	-1.59	-0.84	-0.75
Pine	percolate	*Suillus*	Granite	2 (percolate)	-1.39	-0.74	-0.65
Pine	percolate	*Suillus*	Granite	2 (percolate)	-1.78	-0.96	-0.83
Maple	foliage	Nonmyco	Granite	62 Acer, NM, (low), G, foliage	-2.51	-1.55	-0.95
Maple	root	Nonmyco	Granite	62 Acer, NM, (low), root	-0.96	-0.53	-0.44

Maple	foliage	*Glomus*	Granite	39 Acer, Glom, (low), G, foliage	-1.87	-1.00	-0.87
Maple	root	*Glomus*	Granite	39 Acer, Glom, (low), G, root	-1.14	-0.61	-0.54
Maple	percolate	*Glomus*	Granite	39 (percolate)	-1.19	-0.73	-0.49
Maple	percolate	*Glomus*	Granite	39 A1 (percolate)	-1.23	-0.68	-0.54
Maple	percolate	*Glomus*	Granite	39 (percolate)	-1.69	-0.94	-0.75
Maple	foliage	Nonmyco	Waits	67 Acer, NM, (low), foliage	-0.34	-0.16	-0.18
Maple	root	Nonmyco	Waits	67 Acer, NM, Ca rich, root	-1.88	-0.96	-0.92
Maple	root	Nonmyco	Waits	67 Acer, NM, Ca rich, root	-0.89	-0.47	-0.41
Maple	percolate	Nonmyco	Waits	67 (percolate)	-0.93	-0.48	-0.43
Maple	percolate	Nonmyco	Waits	67 A1 (percolate)	-1.49	-0.79	-0.69
Maple	foliage	*Glomus*	Waits	51 Acer, Glom, Ca, (low)	-1.11	-0.57	-0.53
Maple	root	*Glomus*	Waits	51 Acer, MYC, *Glomus*, Ca rich, (low), root	-0.96	-0.50	-0.47
Maple	percolate	*Glomus*	Waits	51 (percolate)	-1.86	-1.00	-0.87
Abiotic	percolate		granite	53 (percolate) big bottle	-0.40	-0.32	-0.09
Abiotic	percolate		granite	53 (percolate) small bottle	-1.08	-0.56	-0.52
Abiotic	percolate		Waits	52 (percolate) small bottle	-0.57	-0.39	-0.14

Table B.4: Elemental concentrations in ppm

Tree Type	**Mycorhizal**	**Rock type**	**Sample**	**Mg (ppm)**	**Std dev**	**P (ppm)**	**Std dev**	**Ca (ppm)**	**Std dev**
Pine	Nonmyco	Waits	22 Pine, Foliage	1510.043	20.216	884.003	30.654	15002.489	272.743
Pine	*Suillus*	Granite	2 Pine, Root	1277.673	72.775	2475.021	110.412	2881.246	358.649
Pine	*Suillus*	Waits	12 Pine, Root	1593.837	24.577	2222.937	59.508	18682.142	192.015
Pine	Nonmyco	Waits	22 Pine, Root	632.132	11.230	712.802	29.850	4787.916	97.444
Pine	*Suillus*	Granite	2 Pine, Foliage	995.623	18.852	1379.610	25.020	2753.295	232.565
Pine	*Suillus*	Granite	2 Pine, Stem	2062.833	30.624	2183.914	88.290	2383.872	180.651
Pine	*Suillus*	Waits	12 Pine, Foliage	966.136	15.047	1098.159	37.692	6283.467	190.499
Pine	Nonmyco	Granite	24 Pine, Foliage	738.186	8.555	481.133	3.985	2736.252	122.285
Pine	Nonmyco	Granite	24 Pine, Root	344.931	8.274	563.611	48.477	722.452	273.187
Pine	Nonmyco	Granite	24 Pine, Stem	1558.226	31.546	613.890	32.507	1091.306	239.534
Pine	*Suillus*	Waits	12 Pine, Stem	2506.562	25.113	2058.230	121.157	5074.330	134.193
Pine	Nonmyco	Waits	22 Pine, Stem	1959.571	30.170	1054.123	31.026	6754.879	985.611
Pine	*Suillus*	Waits	12 (percolate)	3.323	0.054	2.483	0.027	31.179	0.378
Pine	Nonmyco	Waits	22 (percolate)	1.485	0.026	1.767	0.008	13.516	0.191

Pine	Nonmyco	Granite	24 (percolate)	1.410	0.015	1.547	0.015	8.307	0.101
Pine	*Suillus*	Granite	2 (percolate)	2.664	0.006	3.490	0.081	13.681	0.757
Pine	Nonmyco	Waits	22 (percolate)	2.088	0.047	1.629	0.044	25.102	0.370
Pine	*Suillus*	Waits	12 (percolate)	2.413	0.019	3.326	0.004	20.275	0.182
Pine	Nonmyco	Granite	24 (percolate)	2.010	0.013	2.203	0.037	11.316	0.062
Pine	*Suillus*	Granite	2 (percolate)	2.057	0.020	2.137	0.047	13.631	0.383
Maple	Nonmyco	Granite	62 Acer, NM, (low), G, foliage	1314.837	22.256	1080.481	39.831	1061.798	273.607
Maple	Nonmyco	Granite	62 Acer, NM, (low), root	925.093	21.666	1080.427	14.956	431.806	245.668
Maple	*Glomus*	Waits	51 Acer, Glom, Ca, (low)	2033.748	71.774	2237.800	62.004	9148.116	1183.615
Maple	*Glomus*	Granite	39 Acer, Glom, (low), G, foliage	2260.938	29.603	1799.259	61.017	6549.208	159.075
Maple	Nonmyco	Waits	67 Acer, NM, Ca rich, root	3397.499	49.090	2415.266	45.062	9396.649	151.790
Maple	Nonmyco	Waits	67 Acer, NM, Ca rich, root	2827.394	31.473	2239.243	65.945	8520.467	188.584

Maple	*Glomus*	Granite	39 Acer, Glom, (low), G	2604.214	99.177	1463.351	37.963	1304.554	158.603
Maple	*Glomus*	Waits	51 Acer, MYC, Glomus, Ca rich, (low), root	2796.050	81.503	3998.208	77.024	7551.873	245.664
Maple	Nonmyco	Waits	67 Acer, NM, (low), foliage	6239.810	11.563	3557.306	129.059	9573.079	398.055
Maple			Blank (digest)	1.68946	0.02480	0.99020	0.09037	5.01503	2.22176
Maple	Abiotic	granite	53 (percolate) small bottle	5.102	0.021	3.946	0.057	26.994	0.100
Maple	Nonmyco	Granite	62 A1 (percolate)	5.086	0.049	3.277	0.005	31.525	0.094
Maple	Abiotic	granite	53 (percolate) big bottle	0.060	0.003	0.051	0.001	0.189	0.078
Maple	*Glomus*	Granite	39 A1 (percolate)	3.442	0.014	2.844	0.017	25.762	0.320
Maple			Blank 2 (percolate)	0.2434	0.0030	0.1533	0.0055	1.0007	0.3922
Maple	Nonmyco	Granite	62 (percolate)	2.896	0.043	3.868	0.121	11.743	0.426
Maple	*Glomus*	Waits	51 (percolate)	3.095	0.027	2.678	0.023	33.357	0.361
Maple	Nonmyco	Waits	67 (percolate)	3.028	0.040	2.782	0.044	47.592	0.102

Maple	*Glomus*	Granite	39 (percolate)	0.537	0.018	0.658	0.009	3.407	0.157
Maple	Abiotic	Waits	52 (percolate) small bottle	0.046	0.002	0.043	0.004	0.266	0.035
Maple	Nonmyco	Waits	67 A1 (percolate)	5.255	0.067	4.783	0.076	44.386	0.384
Maple	Abiotic	Granite	54 (percolate)	1.439	0.008	1.317	0.027	5.808	0.369
Maple	*Glomus*	Waits	51 A1 (percolate)	3.788	0.057	2.469	0.008	41.403	1.325
Maple	*Glomus*	Granite	39 (percolate)	1.470	0.037	1.563	0.036	7.867	0.173

Table B.5: Accuracy and precision against NIST standards.

Standard	**Element**	**Accepted value**	**Experimental value**	**Percent Error**
1643f	Mg	7.454	7.448	0.08
1643f	Ca	29.430	31.354	6.54
P spiked 1643f	P	0.777	0.731	5.90

Table B.6 – Table of biomass of seedlings collected at harvest

Tree Type	Mycorrhizal	Rock type	Foliage (g)	Stem (g)	Roots (g)
Pine	Non-myco	Waits	0.076	0.039	0.236
Pine	Suillus	Waits	0.060	0.032	0.165
Pine	Non-myco	Granite	0.077	0.033	0.240
Pine	Suillus	Granite	0.069	0.028	0.075
Maple	Non-myco	Waits	0.130	0.118	0.285
Maple	Glomus	Waits	0.105	0.063	0.190
Maple	Non-myco	Granite	0.134	0.085	0.350
Maple	Glomus	Granite	0.250	0.088	0.853

Table B.7: Rare earth elements (ppm)

	Type	Mycorrhizal	Rock type	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Pb
Pine	Foliage	Nonmyco	Waits	13.7339	0.3807	0.3036	0.2292	0.2743	0.3035	0.2275	0.3116	0.1752	0.2758	0.1979	0.2569	0.1991	0.314	0.203	13.8465	0.5232
Pine	Root	Nonmyco	Waits	10.3558	0.9898	1.1247	0.2475	0.6539	0.2633	0.1627	0.2746	0.1127	0.2361	0.1262	0.1912	0.1176	0.2156	0.1201	25.8449	0.9813
Pine	Stem	Nonmyco	Waits	36.1809	1.4756	0.8774	0.7564	0.9007	1.0361	0.7458	0.9913	0.5934	0.9195	0.6718	0.8686	0.6754	1.0553	0.6886	below detection	1.3409
Pine	percolate	Nonmyco	Waits	0.0154	0.0004	0.0006	0.0003	0.0009	0.0003	0.0002	0.0003	0.0002	0.0002	0.0002	0.0002	0.0002	0.0003	0.0002	0.0012	0.001
Pine	percolate	Nonmyco	Waits	0.0084	0.0001	0.0001	0	0.0001	0.0001	0.0004	0.0006	0	0.0001	0	0.0001	0.0006	0.0001	0	0.0056	0.0004
Pine	av percolate			0.0119	0.0003	0.0003	0.0002	0.0005	0.0002	0.0003	0.0004	0.0001	0.0002	0.0001	0.0002	0.0004	0.0002	0.0001	0.0034	0.0007
Pine	Foliage	Suillus	Waits	39.6458	6.6054	1.1094	0.8495	1.0073	1.1523	0.82	1.1886	0.671	1.0352	0.7565	0.9741	0.7625	1.1885	0.7776	25.9157	1.8168
Pine	Root	Suillus	Waits	37.1147	2.1694	1.7265	0.5669	1.11	0.6319	0.4498	0.6521	0.3267	0.5726	0.3705	0.5076	0.3629	0.6038	0.3688	27.9801	1.8772
Pine	Stem	Suillus	Waits	63.0577	4.8193	1.545	1.2963	1.5642	1.7641	1.2208	1.8312	1.0196	1.5822	1.147	1.483	1.1613	1.8101	1.177	23.828	3.6672
Pine	percolate	Suillus	Waits	0.0136	0.0001	0.0001	0	0.0001	0.0001	0.0001	0.0001	0	0.0001	0	0.0001	0.0009	0.0001	0	0.0064	0.0004
Pine	percolate	Suillus	Waits	0.02	0.0014	0.0005	0.0003	0.0004	0.0004	0.0002	0.0003	0.0002	0.0003	0.0002	0.0003	0.0002	0.0003	0.0002	0.0039	0.0061
Pine	Av percolate			0.0168	0.0007	0.0003	0.0002	0.0003	0.0002	0.0002	0.0002	0.0001	0.0002	0.0001	0.0002	0.0006	0.0002	0.0001	0.0052	0.0033
Pine	Foliage	Nonmyco	Granite	22.0763	1.8937	1.0718	0.5616	0.9869	0.6314	0.4352	0.6267	0.3557	0.5768	0.4036	0.5373	0.401	0.6503	0.4096	6.474	0.7639
Pine	Root	Nonmyco	Granite	21.5381	30.3135	30.8906	6.2492	20.5556	3.9827	0.7036	3.4212	0.7308	2.8772	0.8312	1.8471	0.5501	1.833	0.5464	3.8684	5.5181
Pine	Stem	Nonmyco	Granite	37.3271	4.1176	1.1193	0.8475	1.0862	1.1172	0.8034	1.0787	0.6426	1.0067	0.7279	0.9462	0.7299	1.1516	0.7454	1.2332	1.8859
Pine	percolate	Nonmyco	Granite	0.0459	0.0004	0.0003	0.0001	0.0004	0.0003	0.0014	0.0022	0.0001	0.0002	0	0.0002	0.0018	0.0002	0.0001	0.0053	0.0014
Pine	percolate	Nonmyco	Granite	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection	below detection
Pine	Foliage	Suillus	Granite	16.7987	1.4225	0.5015	0.3434	0.431	0.4408	0.3237	0.4369	0.2528	0.3966	0.2876	0.376	0.2888	0.4523	0.294	20.5273	0.7675
Pine	Stem	Suillus	Granite	23.6709	1.0987	0.7234	0.4997	0.6379	0.6518	0.4645	0.6776	0.3733	0.585	0.4233	0.5481	0.4252	0.669	0.4338	1.0699	1.0363
Pine	percolate	Suillus	Granite	0.0363	0.0015	0.0016	0.0005	0.0011	0.0005	0.0003	0.0005	0.0003	0.0004	0.0003	0.0004	0.0003	0.0005	0.0003	0.0046	0.0031
Pine	percolate	Suillus	Granite	0.0103	0.0002	0.0003	0.0002	0.0007	0.0002	0.0001	0.0002	0.0001	0.0002	0.0001	0.0002	0.0001	0.0002	0.0001	0.0054	0.0003
Pine	Av percolate			0.0233	0.0008	0.001	0.0004	0.0009	0.0004	0.0002	0.0003	0.0002	0.0003	0.0002	0.0003	0.0002	0.0003	0.0002	0.005	0.0017
Maple	foliage	Nonmyco	Granite	23.2989	0.927	0.8824	0.5171	0.7028	0.6525	0.4797	0.6756	0.3715	0.5825	0.419	0.543	0.422	0.6583	0.4293	12.3496	0.9755
Maple	root	Nonmyco	Granite	93.4688	26.2046	22.0333	4.2608	12.5121	3.1074	1.2383	2.9117	0.9534	2.3625	1.0843	1.7599	0.9236	1.9126	0.9382	95.3395	13.6651
Maple	percolate	Nonmyco	Granite	0.0409	0.0016	0.0008	0.0004	0.0006	0.0006	0.0004	0.0006	0.0003	0.0005	0.0004	0.0005	0.0004	0.0006	0.0004	0.0539	0.0012
Maple	percolate	Nonmyco	Granite	0.0316	0.0002	0.0002	0.0001	0.0003	0.0003	0.0006	0.001	0	0.0002	0	0.0002	0.0016	0.0002	0.0001	0.0072	0.0007
Maple	Av percolate			0.0363	0.0009	0.0005	0.0003	0.0005	0.0004	0.0005	0.0008	0.0002	0.0004	0.0002	0.0003	0.001	0.0004	0.0002	0.0306	0.0009

Maple	foliage	Glomus	Granite	14.8421	17.0082	11.0264	1.7836	5.0816	0.5036	0.095	0.4569	0.0807	0.2093	0.0789	0.1278	0.0604	0.111	0.0588	2.4239	0.2143
Maple	root	Glomus	Granite	32.4322	75.9338	74.1308	14.2569	46.7464	6.5878	0.6772	5.2809	0.7515	3.796	0.7791	2.0308	0.3469	1.7665	0.3283	26.4674	10.6983
Maple	percolate	Glomus	Granite	0.0115	0.0002	0.0002	0.0001	0.0003	0.0002	0.0001	0.0002	0	0.0002	0	0.0002	0.0014	0.0002	0.0001	0.0153	0.0002
Maple	percolate	Glomus	Granite	0.0301	0.0005	0.0005	0.0005	0.0005	0.0006	0.0005	0.0006	0.0004	0.0006	0.0004	0.0005	0.0004	0.0007	0.0004	0.0496	0.0008
Maple	percolate	Glomus	Granite	0.0446	0.0003	0.0002	0.0001	0.0003	0.0003	0.0006	0.0009	0.0001	0.0002	0	0.0002	0.0017	0.0002	0.0001	0.0129	0.0011
Maple	Av percolate			0.0287	0.0003	0.0003	0.0002	0.0004	0.0004	0.0004	0.0005	0.0002	0.0003	0.0002	0.0003	0.0012	0.0004	0.0002	0.0259	0.0007
Maple	foliage	Nonmyco	Waits	29.4285	0.3673	0.344	0.1587	0.2316	0.2027	0.1357	0.214	0.1131	0.1776	0.1278	0.1655	0.1278	0.2012	0.1304	10.7647	0.3744
Maple	root	Nonmyco	Waits	34.4858	1.0993	1.6412	0.3836	0.943	0.4116	0.2557	0.4174	0.178	0.3398	0.1997	0.2775	0.1907	0.3321	0.1941	33.5486	3.1437
Maple	root	Nonmyco	Waits	21.9407	0.8752	1.35	0.3422	0.8824	0.3514	0.2126	0.3421	0.1532	0.2945	0.1712	0.244	0.164	0.2865	0.1669	11.7278	2.0076
Maple	percolate	Nonmyco	Waits	0.0245	0.0001	0.0001	0.0001	0.0002	0.0002	0.0003	0.0004	0	0.0002	0	0.0001	0.0012	0.0002	0.0001	0.0123	0.0003
Maple	percolate	Nonmyco	Waits	0.0251	0.0001	0.0001	0.0001	0.0002	0.0002	0.0001	0.0002	0	0.0002	0	0.0001	0.0013	0.0002	0.0001	0.007	0.0004
	avg percolate			0.0248	0.0001	0.0001	0.0001	0.0002	0.0002	0.0002	0.0003	0	0.0002	0	0.0001	0.0013	0.0002	0.0001	0.0097	0.0004
	avg root			28.2133	0.9873	1.4956	0.3629	0.9127	0.3815	0.2342	0.3797	0.1656	0.3171	0.1854	0.2607	0.1773	0.3093	0.1805	22.6382	2.5756
Maple	foliage	Glomus	Waits	12.2217	0.3968	0.2557	0.1275	0.1844	0.1645	0.1185	0.1715	0.092	0.1527	0.1036	0.1386	0.1027	0.1656	0.1043	16.5202	0.3491
Maple	root	Glomus	Waits	20.0114	1.1028	2.0077	0.4299	1.2091	0.4465	0.2455	0.4363	0.179	0.3691	0.2001	0.2919	0.1868	0.3294	0.1899	14.7477	1.5325
Mapl	percolate	Glomus	Waits	0.0225	0.0001	0.0002	0.0001	0.0003	0.0002	0.0001	0.0002	0	0.0002	0	0.0001	0.0013	0.0002	0.0001	0.0045	0.0002
Maple	percolate	Glomus	Waits	0.0178	0.0001	0.0001	0.0001	0.0002	0.0002	0.0001	0.0002	0	0.0002	0	0.0002	0.0014	0.0002	0.0001	0.0095	0.0002
	avg percolate			0.0202	0.0001	0.0001	0.0001	0.0002	0.0002	0.0001	0.0002	0	0.0002	0	0.0002	0.0013	0.0002	0.0001	0.007	0.0002
Abiotic	percolate		Granite	0.0175	0.0003	0.0004	0.0004	0.0004	0.0005	0.0005	0.0014	0.0003	0.0005	0.0003	0.0004	0.0004	0.0005	0.0004	0.0004	0.0003
Abiotic	percolate		Granite	0.0416	0.0008	0.0009	0.0004	0.0009	0.0005	0.0003	0.0005	0.0003	0.0004	0.0003	0.0004	0.0003	0.0005	0.0003	0.003	0.0038
Abiotic	percolate		Granite	0.0251	0.0001	0.0001	0.0001	0.0003	0.0003	0.0008	0.0037	0.0001	0.0003	0	0.0002	0.0019	0.0002	0.0001	0.0239	0.0001
Abiotic	percolate		Waits	0.0073	0.0015	0.0001	0.0001	0.0003	0.0002	0.0001	0.0002	0	0.0002	0	0.0002	0.0013	0.0002	0.0001	0.0327	0.0023

APPENDIX C: CHAPTER 3 SUPPLEMENTARY MATERIALS

Table C.1 – Average Mg FEF for easily exchangeable (NH_4Cl) leach

Rock type	Dominant Tree	Leachate	Average Mg BEF	Standard Deviation
Conway Granite	Maple	NH_4Cl	1.49	0.80
Tonalite	Maple	NH_4Cl	0.11	0.04
Conway Granite	Beech/Birch	NH_4Cl	0.86	0.52
Tonalite	Beech/Birch	NH_4Cl	0.13	0.07
Conway Granite	Willow	NH_4Cl	0.93	0.17
Tonalite	Willow	NH_4Cl	0.12	0.06

Table C.2 – Average Mg FEF for future available (nitric) leach

Rock type	Dominant Tree	Leachate	Average Mg BEF	Standard Deviation
Conway Granite	Maple	Nitric	2.23	2.08
Tonalite	Maple	Nitric	0.31	0.10
Conway Granite	Beech/Birch	Nitric	0.60	0.50
Tonalite	Beech/Birch	Nitric	0.33	0.14
Conway Granite	Willow	Nitric	2.17	0.65
Tonalite	Willow	Nitric	1.23	1.20

Table C.3 – Magnesium BEF for all samples and leachates, calculated by dividing Mg concentration of the samples by the Mg concentration of the abiotic sample for both lithologies and leach types.

Rock type	**Dominant Tree**	**Leachate**	**Mg BEF**
Conway Granite	Maple	NH4Cl	1.84
Conway Granite	Maple	NH4Cl	0.92
Conway Granite	Maple	NH4Cl	2.44
Conway Granite	Maple	NH4Cl	0.75
Tonalite	Maple	NH4Cl	0.10
Tonalite	Maple	NH4Cl	0.16
Tonalite	Maple	NH4Cl	0.08
Tonalite	Maple	NH4Cl	0.08
Conway Granite	Beech/Birch	NH4Cl	0.51
Conway Granite	Beech/Birch	NH4Cl	1.63
Conway Granite	Beech/Birch	NH4Cl	0.74
Conway Granite	Beech/Birch	NH4Cl	0.55
Tonalite	Beech/Birch	NH4Cl	0.07
Tonalite	Beech/Birch	NH4Cl	0.16
Tonalite	Beech/Birch	NH4Cl	0.21
Tonalite	Beech/Birch	NH4Cl	0.08
Conway Granite	Willow	NH4Cl	1.10
Conway Granite	Willow	NH4Cl	0.77
Conway Granite	Willow	NH4Cl	0.92
Tonalite	Willow	NH4Cl	0.08
Tonalite	Willow	NH4Cl	0.19
Tonalite	Willow	NH4Cl	0.08

Conway Granite	Maple	Nitric	0.80
Conway Granite	Maple	Nitric	4.61
Conway Granite	Maple	Nitric	1.27
Tonalite	Maple	Nitric	0.24
Tonalite	Maple	Nitric	0.30
Tonalite	Maple	Nitric	0.46
Tonalite	Maple	Nitric	0.24
Conway Granite	Beech/Birch	Nitric	0.40
Conway Granite	Beech/Birch	Nitric	1.32
Conway Granite	Beech/Birch	Nitric	0.49
Conway Granite	Beech/Birch	Nitric	0.19
Tonalite	Beech/Birch	Nitric	0.40
Tonalite	Beech/Birch	Nitric	0.12
Tonalite	Beech/Birch	Nitric	0.37
Tonalite	Beech/Birch	Nitric	0.42
Conway Granite	Willow	Nitric	2.98
Conway Granite	Willow	Nitric	1.79
Conway Granite	Willow	Nitric	2.08
Conway Granite	Willow	Nitric	1.36
Conway Granite	Willow	Nitric	2.64
Tonalite	Willow	Nitric	0.37
Tonalite	Willow	Nitric	1.38
Tonalite	Willow	Nitric	0.84
Tonalite	Willow	Nitric	3.24
Tonalite	Willow	Nitric	0.32

Table C.4: Rb/Sr and $^{208}Pb/^{207}Pb$ values for all samples of nitric leachate which represents future available stores.

Rock type	**Dominant tree type**	**Leachate**	**Rb/Sr**	**$^{208}Pb/^{207}Pb$**
Conway Granite	Abiotic	Nitric	0.22	2.531
Tonalite	Abiotic	Nitric	0.39	2.594
Conway Granite	Maple	Nitric	0.80	2.513
Conway Granite	Maple	Nitric	0.55	2.510
Conway Granite	Maple	Nitric	0.41	2.497
Conway Granite	Maple	Nitric	0.48	2.432
Tonalite	Maple	Nitric	0.36	2.600
Tonalite	Maple	Nitric	0.84	2.611
Tonalite	Maple	Nitric	0.38	2.631
Tonalite	Maple	Nitric	0.42	2.586
Conway Granite	Beech/Birch	Nitric	1.24	2.445
Conway Granite	Beech/Birch	Nitric	0.36	2.527
Conway Granite	Beech/Birch	Nitric	0.53	2.526
Conway Granite	Beech/Birch	Nitric	0.37	2.530
Tonalite	Beech/Birch	Nitric	0.40	2.626
Tonalite	Beech/Birch	Nitric	0.14	2.646
Tonalite	Beech/Birch	Nitric	0.54	2.651
Tonalite	Beech/Birch	Nitric	0.15	2.591
Conway Granite	Willow	Nitric	0.95	2.463
Conway Granite	Willow	Nitric	1.73	2.519
Conway Granite	Willow	Nitric	2.01	2.503
Conway Granite	Willow	Nitric	1.63	2.512

Conway Granite	Willow	Nitric	1.16	2.522
Tonalite	Willow	Nitric	1.12	2.640
Tonalite	Willow	Nitric	2.87	2.526
Tonalite	Willow	Nitric	1.02	2.622
Tonalite	Willow	Nitric	2.37	2.582
Tonalite	Willow	Nitric	1.24	2.649

Table C.5: $^{208}\mathrm{Pb}/^{207}\mathrm{Pb}$ and $^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$ values for all samples of nitric leachate which represents future available stores.

Rock type	**Dominant tree type**	**$^{208}\mathrm{Pb}/^{207}\mathrm{Pb}$**	**$^{206}\mathrm{Pb}/^{207}\mathrm{Pb}$**
Conway Granite	Abiotic	2.531	1.289
tonalite	Abiotic	2.594	1.270
Conway Granite	Maple	2.513	1.264
Conway Granite	Maple	2.510	1.260
Conway Granite	Maple	2.497	1.244
Conway Granite	Maple	2.432	1.163
tonalite	Maple	2.600	1.231
tonalite	Maple	2.611	1.234
tonalite	Maple	2.631	1.240
tonalite	Maple	2.586	1.228
Conway Granite	Beech/birch	2.445	1.181
Conway Granite	Beech/birch	2.527	1.281

Conway Granite	Beech/birch	2.526	1.282
Conway Granite	Beech/birch	2.530	1.286
tonalite	Beech/birch	2.626	1.243
tonalite	Beech/birch	2.646	1.243
tonalite	Beech/birch	2.651	1.246
tonalite	Beech/birch	2.591	1.229
Conway Granite	Willow	2.463	1.225
Conway Granite	Willow	2.519	1.271
Conway Granite	Willow	2.503	1.248
Conway Granite	Willow	2.512	1.262
Conway Granite	Willow	2.522	1.275
tonalite	Willow	2.640	1.243
tonalite	Willow	2.526	1.218
tonalite	Willow	2.622	1.240
tonalite	Willow	2.582	1.226
tonalite	Willow	2.649	1.245

Table C.6: Percent abundance for all identified phyla.

	Willow granite	Willow tonalite	Beech/birch granite	Beech/birch tonalite	Maple granite	Maple tonalite
Unassigned_	4.03	9.64	6.14	5.89	6.54	6.44
Archaea_	0.18	0.04	0.03	0.00	0.00	0.04
Archaea_Crenarchaeota	1.26	0.64	0.12	0.25	6.61	0.21
Archaea_Euryarchaeota	0.01	0.01	0.01	0.02	0.02	0.00
Archaea_Halobacterota	0.03	0.04	0.00	0.00	0.00	0.00
Archaea_Nanoarchaeota	0.00	0.00	0.00	0.00	0.00	0.00
Archaea_Thermoplasmatota	0.00	0.01	0.00	0.02	0.03	0.01
Bacteria_	3.27	5.93	3.72	4.68	5.76	5.10
Bacteria_Abditibacteriota	0.02	0.03	0.00	0.04	0.00	0.04
Bacteria_Acidobacteriota	9.34	8.48	14.86	14.05	17.91	18.85
Bacteria_Actinobacteriota	10.41	12.39	9.86	5.23	2.99	2.78
Bacteria_Armatimonadota	0.38	0.32	0.51	0.66	0.20	0.34
Bacteria_Bacteroidota	7.11	7.32	7.01	8.03	5.84	8.54
Bacteria_Bdellovibrionota	1.06	0.68	0.75	0.86	0.47	0.59
Bacteria_Campilobacterota	0.00	0.00	0.00	0.00	0.00	0.00
Bacteria_Chloroflexi	2.44	2.33	0.13	0.38	8.60	0.90
Bacteria_Cyanobacteria	0.38	0.22	0.21	0.15	0.18	0.16
Bacteria_Deferribacterota	0.01	0.02	0.00	0.02	0.00	0.00
Bacteria_Deinococcota	0.02	0.00	0.00	0.00	0.00	0.00
Bacteria_Dependentiae	0.36	0.13	0.60	0.32	0.22	0.39
Bacteria_Desulfobacterota	0.83	0.55	0.00	0.01	0.25	0.19
Bacteria_Elusimicrobiota	0.31	0.31	0.09	0.14	0.32	0.20

Bacteria_Entotheonellaeota	0.00	0.02	0.00	0.00	0.00	0.00
Bacteria_FCPU426	0.01	0.01	0.09	0.20	0.05	0.09
Bacteria_Fibrobacterota	0.05	0.22	0.13	0.10	0.16	0.21
Bacteria_Firmicutes	12.51	8.80	2.00	1.27	2.07	2.42
Bacteria_GAL15	0.00	0.00	0.00	0.00	0.01	0.00
Bacteria_Gemmatimonadota	0.85	1.27	0.28	0.35	0.83	0.63
Bacteria_Hydrogenedentes	0.01	0.00	0.00	0.00	0.00	0.00
Bacteria_Latescibacterota	0.05	0.11	0.00	0.00	0.03	0.03
Bacteria_MBNT15	0.00	0.02	0.00	0.00	0.16	0.15
Bacteria_Methylomirabilota	0.10	0.14	0.00	0.00	0.43	0.31
Bacteria_Myxococcota	1.91	1.92	1.04	0.72	1.02	1.15
Bacteria_NB1-j	0.00	0.00	0.00	0.00	0.04	0.03
Bacteria_Nitrospinota	0.00	0.01	0.00	0.00	0.00	0.00
Bacteria_Nitrospirota	0.54	0.38	0.00	0.00	0.28	0.08
Bacteria_Patescibacteria	0.51	0.28	0.09	0.17	0.08	0.15
Bacteria_Planctomycetota	8.84	7.59	5.43	5.01	5.84	5.64
Bacteria_Proteobacteria	21.45	20.16	39.05	43.64	21.91	36.77
Bacteria_RCP2-54	0.29	0.16	0.37	0.50	1.28	0.71
Bacteria_SAR324clade(MarinegroupB)	0.00	0.00	0.00	0.00	0.00	0.01
Bacteria_Spirochaetota	0.02	0.16	0.13	0.11	0.10	0.20
Bacteria_Sumerlaeota	0.00	0.01	0.00	0.00	0.00	0.00
Bacteria_Synergistota	0.00	0.00	0.00	0.00	0.00	0.00
Bacteria_Verrucomicrobiota	10.39	9.06	5.35	5.48	8.97	5.57
Bacteria_WPS-2	0.00	0.03	0.49	0.45	0.17	0.21
Bacteria_WS2	0.00	0.01	0.00	0.00	0.00	0.00
Bacteria_WS4	0.00	0.01	0.00	0.00	0.00	0.00

Eukaryota_	0.24	0.34	0.95	0.67	0.33	0.21
Eukaryota_Apicomplexa	0.00	0.00	0.00	0.00	0.00	0.06
Eukaryota_Arthropoda	0.00	0.02	0.02	0.05	0.05	0.00
Eukaryota_Ascomycota	0.12	0.03	0.08	0.12	0.02	0.08
Eukaryota_Basidiomycota	0.52	0.06	0.17	0.22	0.01	0.14
Eukaryota_Cercozoa	0.00	0.00	0.00	0.04	0.00	0.00
Eukaryota_Chytridiomycota	0.00	0.00	0.04	0.00	0.00	0.00
Eukaryota_Ciliophora	0.00	0.06	0.08	0.04	0.18	0.37
Eukaryota_Euglenozoa	0.00	0.00	0.00	0.00	0.00	0.01
Eukaryota_Gastrotricha	0.04	0.00	0.05	0.05	0.00	0.00
Eukaryota_Myxogastria	0.00	0.00	0.01	0.00	0.00	0.00
Eukaryota_Nematozoa	0.00	0.00	0.10	0.06	0.00	0.00
Eukaryota_Phragmoplastophyta	0.09	0.00	0.00	0.00	0.03	0.00
Eukaryota_Platyhelminthes	0.00	0.00	0.02	0.00	0.00	0.00
Eukaryota_Rotifera	0.00	0.00	0.00	0.00	0.00	0.00
Eukaryota_Vertebrata	0.00	0.00	0.00	0.00	0.01	0.00

APPENDIX D: CHAPTER 4 SUPPLEMENTARY MATERIALS

Figure D.1 Instrument used to assess students before and after participation in the SRS. Includes student assessment form.

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ASSENT FORM FOR STUDENTS

15 MARCH 2019

Dear Student,

We are education researchers at the University of New Hampshire studying how new ways your teacher uses GLOBE in class helps you learn about doing science. You are being asked to participate in this project because your teacher is learning about new ways to teach science.

If you decide to participate, you will allow us to use the surveys that you complete as data in our research study. **Your responses will be grouped with all the student responses we receive to look at how using data in your class helped you understand how to think scientifically. We are not interested in individual answers so your name will not appear with any of our data when we write our reports or present our work to other researchers. When we ask for personal information, it is so that we can keep all of your work together in one file. All of your surveys will receive a code number.**

You don't have to give us permission to use your work if you don't want to. **Your grades in the class will not be affected by your decision, whether you choose to participate or not.** Even if you decide that you want to do it and then change your mind, you can decide to stop at any time. You just need to tell your teacher or email us and we will not use your work.

Your parent/guardian has already given us permission to ask you to participate, so it is up to you.

Sincerely,

Jennifer Bourgeault	Haley Wicklein
U.S. GLOBE Country Coordinator	U.S. GLOBE Office
jen.bourgeault@unh.edu	Haley.Wicklein@unh.edu

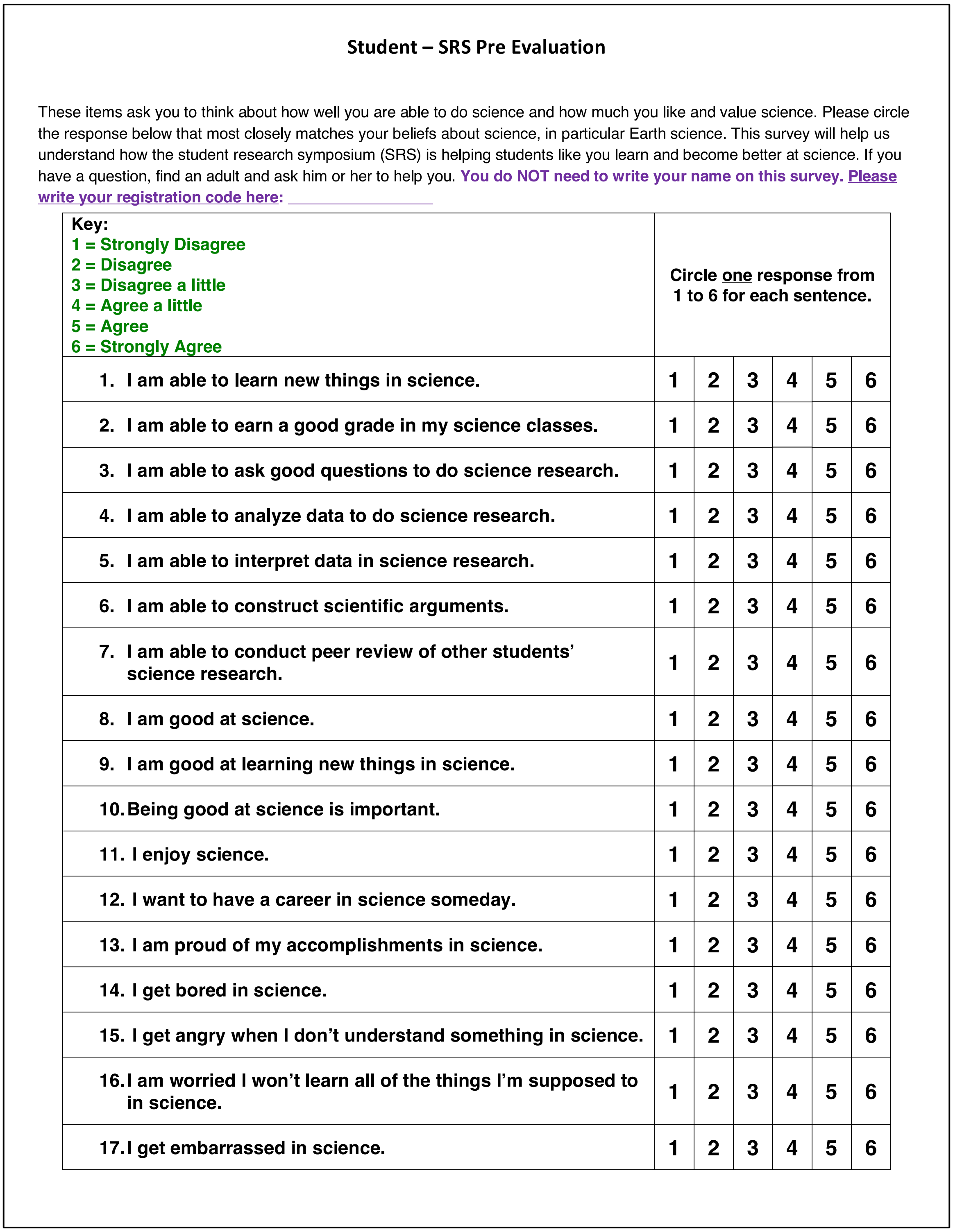
My registration code (see nametag) **is** ___________________________

Check one box below:

☐ **Yes**, I want to participate in this research project.

☐ **No,** I do not want to participate in this research project.

Figure D.2 Student pre-assessment form.

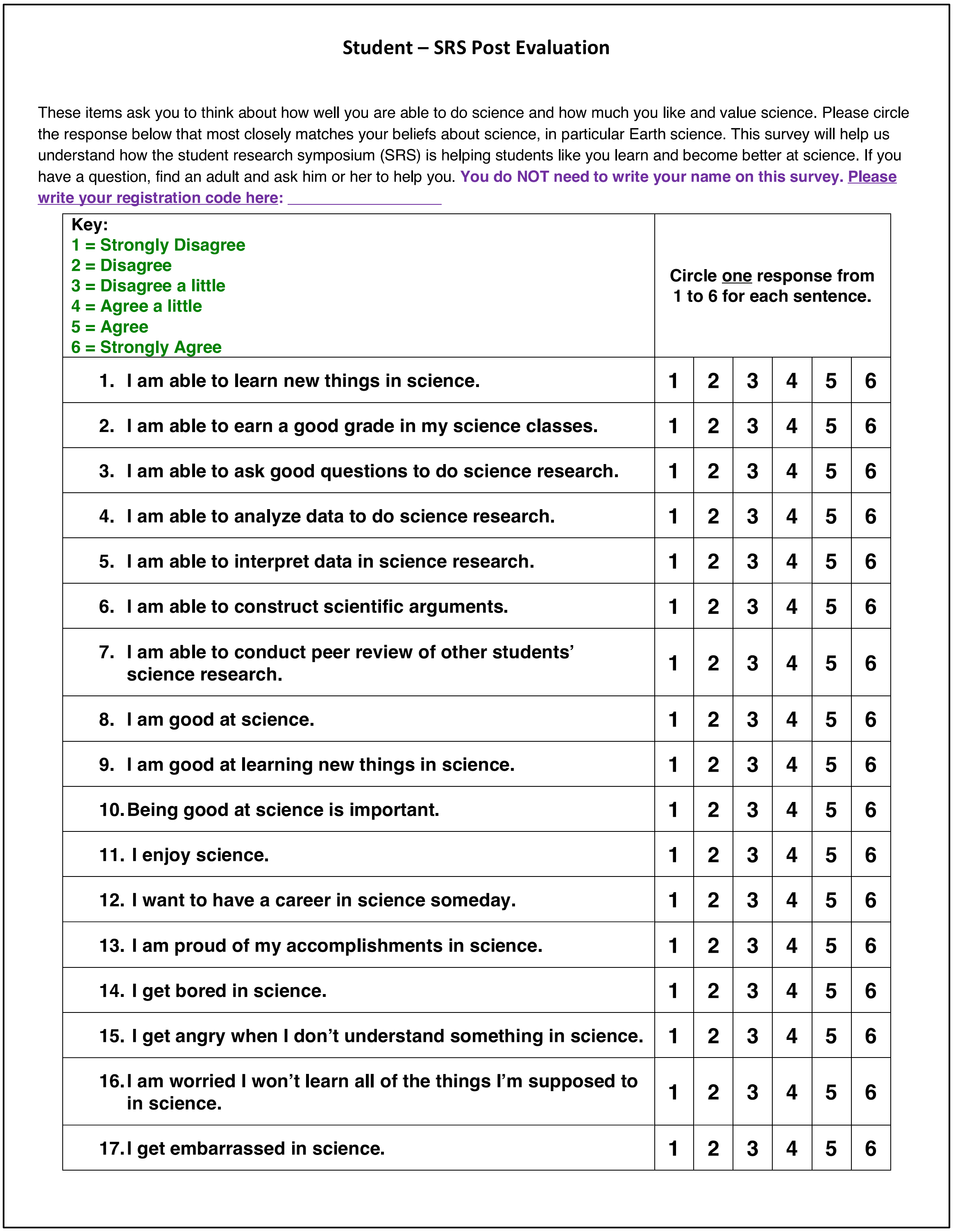


Student – SRS Pre Evaluation

These items ask you to think about how well you are able to do science and how much you like and value science. Please circle the response below that most closely matches your beliefs about science, in particular Earth science. This survey will help us understand how the student research symposium (SRS) is helping students like you learn and become better at science. If you have a question, find an adult and ask him or her to help you. **You do NOT need to write your name on this survey. Please write your registration code here: __________________**

Key: **1 = Strongly Disagree** **2 = Disagree** **3 = Disagree a little** **4 = Agree a little** **5 = Agree** **6 = Strongly Agree**	**Circle one response from 1 to 6 for each sentence.**					
1. I am able to learn new things in science.	**1**	**2**	**3**	**4**	**5**	**6**
2. I am able to earn a good grade in my science classes.	**1**	**2**	**3**	**4**	**5**	**6**
3. I am able to ask good questions to do science research.	**1**	**2**	**3**	**4**	**5**	**6**
4. I am able to analyze data to do science research.	**1**	**2**	**3**	**4**	**5**	**6**
5. I am able to interpret data in science research.	**1**	**2**	**3**	**4**	**5**	**6**
6. I am able to construct scientific arguments.	**1**	**2**	**3**	**4**	**5**	**6**
7. I am able to conduct peer review of other students' science research.	**1**	**2**	**3**	**4**	**5**	**6**
8. I am good at science.	**1**	**2**	**3**	**4**	**5**	**6**
9. I am good at learning new things in science.	**1**	**2**	**3**	**4**	**5**	**6**
10. Being good at science is important.	**1**	**2**	**3**	**4**	**5**	**6**
11. I enjoy science.	**1**	**2**	**3**	**4**	**5**	**6**
12. I want to have a career in science someday.	**1**	**2**	**3**	**4**	**5**	**6**
13. I am proud of my accomplishments in science.	**1**	**2**	**3**	**4**	**5**	**6**
14. I get bored in science.	**1**	**2**	**3**	**4**	**5**	**6**
15. I get angry when I don't understand something in science.	**1**	**2**	**3**	**4**	**5**	**6**
16. I am worried I won't learn all of the things I'm supposed to in science.	**1**	**2**	**3**	**4**	**5**	**6**
17. I get embarrassed in science.	**1**	**2**	**3**	**4**	**5**	**6**

Figure D.2 Student two-page post-assessment form.



Student – SRS Post Evaluation

These items ask you to think about how well you are able to do science and how much you like and value science. Please circle the response below that most closely matches your beliefs about science, in particular Earth science. This survey will help us understand how the student research symposium (SRS) is helping students like you learn and become better at science. If you have a question, find an adult and ask him or her to help you. **You do NOT need to write your name on this survey. Please write your registration code here: __________________**

Key: **1 = Strongly Disagree** **2 = Disagree** **3 = Disagree a little** **4 = Agree a little** **5 = Agree** **6 = Strongly Agree**	**Circle one response from 1 to 6 for each sentence.**					
1. I am able to learn new things in science.	**1**	**2**	**3**	**4**	**5**	**6**
2. I am able to earn a good grade in my science classes.	**1**	**2**	**3**	**4**	**5**	**6**
3. I am able to ask good questions to do science research.	**1**	**2**	**3**	**4**	**5**	**6**
4. I am able to analyze data to do science research.	**1**	**2**	**3**	**4**	**5**	**6**
5. I am able to interpret data in science research.	**1**	**2**	**3**	**4**	**5**	**6**
6. I am able to construct scientific arguments.	**1**	**2**	**3**	**4**	**5**	**6**
7. I am able to conduct peer review of other students' science research.	**1**	**2**	**3**	**4**	**5**	**6**
8. I am good at science.	**1**	**2**	**3**	**4**	**5**	**6**
9. I am good at learning new things in science.	**1**	**2**	**3**	**4**	**5**	**6**
10. Being good at science is important.	**1**	**2**	**3**	**4**	**5**	**6**
11. I enjoy science.	**1**	**2**	**3**	**4**	**5**	**6**
12. I want to have a career in science someday.	**1**	**2**	**3**	**4**	**5**	**6**
13. I am proud of my accomplishments in science.	**1**	**2**	**3**	**4**	**5**	**6**
14. I get bored in science.	**1**	**2**	**3**	**4**	**5**	**6**
15. I get angry when I don't understand something in science.	**1**	**2**	**3**	**4**	**5**	**6**
16. I am worried I won't learn all of the things I'm supposed to in science.	**1**	**2**	**3**	**4**	**5**	**6**
17. I get embarrassed in science.	**1**	**2**	**3**	**4**	**5**	**6**

Student – SRS Post Evaluation

18. What part of the SRS did you enjoy the most? You may choose more than one.

- ☐ Opening remarks
- ☐ Meeting other students
- ☐ Meeting scientists
- ☐ Keynote speaker
- ☐ Evening activities
- ☐ Research presentations to the reviewers
- ☐ Research presentations to other students
- ☐ Peer review from students
- ☐ Review from scientists
- ☐ Closing ceremony
- ☐ Other activity entitled ________
- ☐ Other activity entitled ________

Why did you choose those events?

19. What part of the SRS did you enjoy the least? You may choose more than one.

- ☐ Opening remarks
- ☐ Meeting other students
- ☐ Meeting scientists
- ☐ Keynote speaker
- ☐ Evening activities
- ☐ Research presentations to the reviewers
- ☐ Research presentations to other students
- ☐ Peer review from students
- ☐ Review from scientists
- ☐ Closing ceremony
- ☐ Other activity entitled ________
- ☐ Other activity entitled ________

Why did you choose those events?

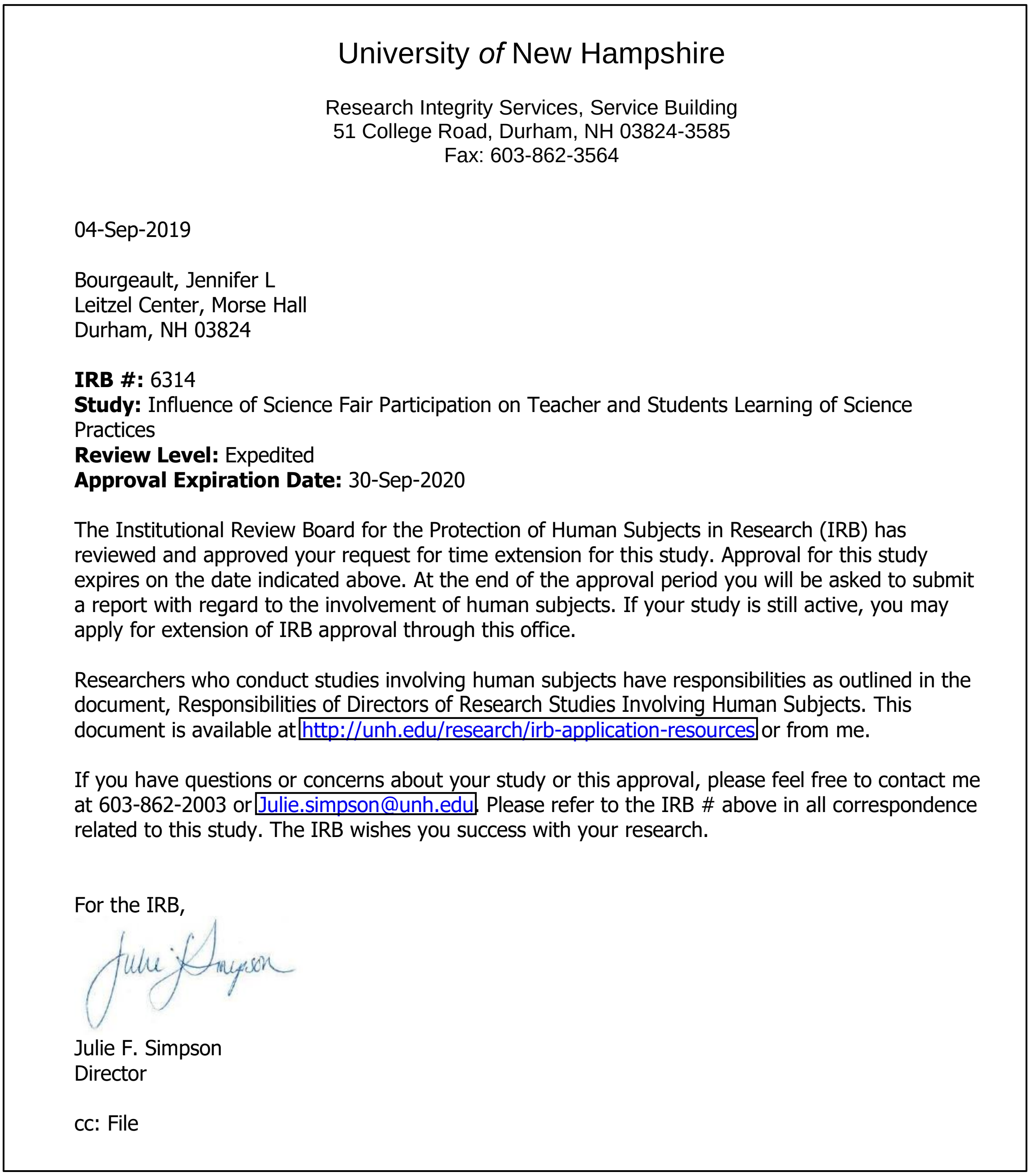
20. Did participating in the research symposium impact your understanding of the scientific process and what it's like to do science research? Explain your answer.

21. Before the student research symposium I thought:

But now I know:

Figure D.3 IRB for the NASA GLOBE Student Research Symposium

Institutional Review Board (IRB) approval was obtained for the 2019 Student Research Symposium. IRB #6314 was extended for the 2019-2020 season. Letter of extension approval included below.



University *of* New Hampshire

Research Integrity Services, Service Building
51 College Road, Durham, NH 03824-3585
Fax: 603-862-3564

04-Sep-2019

Bourgeault, Jennifer L
Leitzel Center, Morse Hall
Durham, NH 03824

IRB #: 6314
Study: Influence of Science Fair Participation on Teacher and Students Learning of Science Practices
Review Level: Expedited
Approval Expiration Date: 30-Sep-2020

The Institutional Review Board for the Protection of Human Subjects in Research (IRB) has reviewed and approved your request for time extension for this study. Approval for this study expires on the date indicated above. At the end of the approval period you will be asked to submit a report with regard to the involvement of human subjects. If your study is still active, you may apply for extension of IRB approval through this office.

Researchers who conduct studies involving human subjects have responsibilities as outlined in the document, Responsibilities of Directors of Research Studies Involving Human Subjects. This document is available at http://unh.edu/research/irb-application-resources or from me.

If you have questions or concerns about your study or this approval, please feel free to contact me at 603-862-2003 or Julie.simpson@unh.edu. Please refer to the IRB # above in all correspondence related to this study. The IRB wishes you success with your research.

For the IRB,

Julie F. Simpson
Director

cc: File