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Research paper

# Effect of lichen colonization on chemical weathering of hornblende granite as estimated by aqueous elemental flux

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ABSTRACT

It has long been suspected that lichens increase the rate of physical and chemical weathering of rock surfaces, thus playing a role in biogeochemical cycles. However, the relative weathering flux of elements from lichen-colonized rock versus bare rock has been minimally studied; previous attempts to quantify the effect of lichen-cover on weathering have focused disproportionately on evidence from altered weathering rinds on basalt. Here, in a field experiment on hornblende granite in New Jersey (USA), we measured the cumulative waterborne net efflux of five elements over 31 days and six rain events, from multiple constructed miniature watersheds consisting of either lichen-covered or exposed bare rock. On average, lichen-covered watersheds showed approximately double the silicon flux, and three times the calcium and magnesium flux compared to bare-rock. Additionally, efflux of these elements was higher in lichen-covered watersheds across all six rain events. This suggests that lichens do indeed promote increased chemical weathering compared to bare rock, thus likely increasing sequestration of atmospheric $CO_2$ under equal conditions of atmospheric $pCO_2$, temperature, and rainfall. It was also observed that lichen-covered watersheds showed a 50% reduction in iron flux, and had a greater ratio of calcium and magnesium to silicon flux compared to bare-rock watersheds. The possible causes of these patterns are discussed.



## 1. Introduction

The dissolution of rock through weathering processes at the Earth's surface is thought to be a key component of the global long term carbon cycle, in that chemical dissolution of Ca and Mg silicate rocks and subsequent formation of Ca and Mg carbonates in the ocean can act as a long term sink (over millions of years) of atmospheric carbon (Berner et al., 1983). Models and evidence of past global temperatures suggest that this weathering sink has had a major impact on atmospheric $CO_2$ levels and temperature over geological time scales — and that weathering increases brought on by the establishment of vegetated terrestrial ecosystems led to a major drop in global temperature (Berner, 1998). While the enhancement of weathering through the influence of biotic land cover is generally accepted, there is debate as to the magnitude of the effect of lichens and mosses (i.e. relatively thin biotic surface communities) versus that of the later-evolved vascular plants (Drever, 1994; Jackson, 1996). For example, it has been suggested that the effect of lichen communities is negligible to non-existent compared to the effect of vascular plants (Cochran and Berner, 1996), and lichen and/or moss-colonized rocks have been used as a contrast to trees in several weathering studies (e.g. Bormann et al., 1998; Moulton and Berner, 1998; Balogh-Brunstad et al., 2008). While the contribution of lichens may be relatively small today, in the geological past before the development of more deeply-rooted vascular plant-dominated ecosystems, both lichens and other microbial land cover may have been relatively more important to biogeochemical cycles and global temperature, through their biotic enhancement of weathering (Schwartzman and Volk, 1989; Schwartzman, 1999).

A number of mechanisms have been proposed by which lichens might effect an increase in physical and chemical weathering. Fry (1924, 1927) argued for a physical mechanism in which the wetting and subsequent drying of gelatinous secretions from lichen thalli on rock surfaces could be responsible for lifting fragments of material — and this is supported by experimental evidence (Moses and Smith, 1993). In addition, lichen hyphae have been widely demonstrated

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to penetrate surfaces on a variety of rock types, and have been found to be associated with greater spacing between mineral grains (Cooks and Otto, 1990; Barker and Banfield, 1996; Lee and Parsons, 1999). Cooks and Otto (1990) reasoned that the expansion and contraction of such penetrating hyphae should generate sufficient tensile stresses to break loose fragments of material that might otherwise have remained intact.

Theorized mechanisms for biochemical weathering have often been focused upon the action of oxalic acid (Adamo and Violante, 2000; Chen et al., 2000), along with other partially water soluble lichen acids and compounds (Iskandar and Syers, 1971) capable of forming complexes with rock forming metals (Iskandar and Syers, 1972). These molecules, containing anionic groups, are suggested to enhance weathering rate through some combination of chelation and/or chemisorption to the mineral surface, resulting in alteration of electron density to a state favoring hydrolysis (Chen et al., 2000). As evidence, calcium oxalate (Wilson and Jones, 1983) and other lichen acid–metal complexes (Purvis et al., 1990; Adamo et al., 1993; Adamo and Violante, 2000) have been repeatedly found associated with lichen-colonized rock. Another potential weathering agent, organic polymers (suggested to be acid mucopolysaccharides), were observed by Barker and Banfield (1996) to coat silicate mineral grains in amphibole syenite at all lichen mineral interfaces, and to contain secondary weathering products. Such high molecular weight polymers generated by lichens or the associated microbial community may enhance weathering through the action of acid functional groups (Barker and Banfield, 1996), and by moisture retention (Banfield et al., 1999).

In addition to the above mentioned alterations of colonized rock, lichens have been associated with poorly ordered iron oxide crystals (Jackson and Keller, 1970), and the formation of siliceous relicts (Wilson and Jones, 1983; Lee and Parsons, 1999). Yet qualitative alteration of rock by lichens, and theorized weathering mechanisms, are not by themselves entirely convincing evidence of a lichen mediated increase in weathering rate, as the net effects of the various physical and chemical alterations introduced by lichens are poorly quantified.

Attempts to quantify the effect of lichens on weathering rate have been made in several studies that examined differences in weathering rind under lichen-covered versus bare rock. Jackson and Keller (1970) compared the thickness of weathering rind under bare rock and rock colonized by the lichen *Stereocaulon vulcani*, on recent lava flows in Hawaii, concluding that lichens enhance weathering in the range of 15–71×. Stretch and Viles (2002) using a similar methodology, and focusing on volcanic rock colonized by a variety of lichen species in a significantly drier environment (the Canary Islands), estimated an average weathering enhancement of 16× across all lichen species studied. Brady et al. (1999), in another study on Hawaiin lava flows colonized by *S. vulcani*, used back scattered electron microscopy to measure the porosity of olivine and plagioclase grains found in basaltic rock. They found a weathering enhancement of 2–16× depending on the degree of rainfall.

Using a quite different methodology, McCarroll and Viles (1995) also attempted to quantify the effect of lichen weathering in the field by measuring the hardness and density of rock of moraine ridges colonized by the endolithic lichen, *Lecidea auriculata*, vs. that of similar uncolonized rock. Measurements of hardness validated that lichen colonization made the rock softer which may imply greater weathering rate, and they estimated a 25–50× increase in weathering, by calculating the surface lowering based on measured density, and comparing it to rock of similar composition.

While the results from a variety of methodologies described above support the conclusion that lichens enhance the weathering rate, it would be useful to corroborate these findings by measuring differences in waterborne elemental flux from lichen-colonized versus bare surfaces. Also, unlike studies on weathering rinds, measurement of the degree to which Ca and Mg efflux is increased from lichen-covered rock surfaces reflects not physical but chemical weathering only, and is more directly applicable to models of global biogeochemistry. Finally, it would be useful to quantify the weathering effect of lichens on granitic rock, as granite covers far more of the continental surfaces than basalt, which has been most extensively studied.

To our knowledge only one previous published study on lichen weathering has attempted to measure weathering flux of elements in the field. This was done using a “miniature watershed” technique first devised in that study, conducted in New Hampshire, USA (Aghamiri and Schwartzman, 2002). This study showed a four-fold increase in silicon flux, and 16 fold enhancement of magnesium flux from lichen-covered rock, along with corroborating evidence of increased weathering under lichen cover from a laboratory experiment. The present study is designed to utilize essentially the same method in the field, though testing a different site, lichen species, and rock composition — and employing a test of statistical significance across multiple experimental plots. The objectives of the study were first to test the hypothesis that lichen cover would increase the net flux of elements leaving the measured plots, which presumably reflects increased weathering, and waterborne weathering product. A second objective was to attain a good estimate of weathering enhancement by lichen cover on the granitic rock of the site by averaging across multiple plots.

## 2. Materials and methods

### 2.1. Study site

The study site was a treeless hilltop area with a surface of exposed bedrock, an area of about 50 $m^2$, surrounded by forest, at an altitude of 780 ft, located at the Weis Ecology Center at Ringwood, NJ, USA (41°4′ N, −74°19′ W). The bedrock slopes gently (ca. 16–17%) facing east over the area where study plots were designated, then drops off sharply beyond the edges of the study area. Mean annual temperature at the site is 10.5 °C, and mean temperature for July is 23.1 °C. The mean annual precipitation is 125.0 cm, and the mean precipitation for July is 11.0 cm (1971–2000, NOAA online weather data, Wanaque Raymond Dam, http://www.nrcc.cornell.edu/page_nowdata.html, accessed Jan 02 2009). Until the 1990s, this area had an open tree cover, mainly of wild cherry (*Prunus sp.*) and chestnut oak (*Quercus montana)*, but repeated droughts and defoliating insect outbreaks have killed most of the trees. At the time of the study, mostly only bare snags were left standing around the borders of the site, and the rocks were exposed to full sunlight throughout the day.

Much of the exposed rock surface was dominated by the foliose lichen *Xanthoparmelia plittii* (Gyeln.) Hale, with some areas interspersed with an unidentified crustose lichen. The rock of the site was identified using a bedrock geological map (Dalton et al., 1999), as hornblende granite of the Byram intrusive suite of middle Proterozoic age (Drake et al., 1991b). The dominant minerals include microcline, microperthite, quartz, oligoclase, and hornblende, along with some quartz syenite or quartz monzonite, and smaller contribution from pegmatite and amphibolite. (Dalton et al., 1999). The rock of area sampled using the miniature watersheds was of uniform appearance and presumably mineralogy.

### 2.2. Experimental watersheds and other collection apparatus

Two 2 l HDPE bottles, with a plastic funnel placed in the opening, and cellulose fine mesh filter tucked into the funnel, were placed at the site for rain collection to correct for background ion flux, and two rain gauges were attached at the site to measure