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Mycorrhizal weathering: A true case of mineral plant nutrition?

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Abstract. Weatherable minerals in all podzol surface soils and shallow granitic rock under European coniferous forests studied hitherto are criss-crossed by numerous open, tubular pores, 3–10 μm in width. We hypothesize that these pores were formed by complex-forming, low-molecular weight organic acids exuded by or formed in association with mycorrhizal fungi. It is well known that ectomycorrhizal mycelium represents a greatly extended, and better distributed, surface area for the absorption of nutrients. However, there have been few investigations of how the whereabouts of individual hypha affect nutrient uptake. The results presented here provide direct evidence that the mycelium is able to penetrate, and most probably create, microsites which are inaccessible to plant roots and isolated from bulk soil solution phenomena. Dissolved products could be translocated to the host plant roots, bypassing the soil solution with often toxic concentration of Al^{3+} from acid rain, and bypassing competition for nutrient uptake by other organisms. Furthermore, there is strong evidence that "rock-eating" mycorrhizal fungi play a role in the formation of podzol E horizons. The partly speculative interpretations presented here challenge conventional ideas about (1) the importance of nutrient uptake from the bulk soil solution (2) criteria for critical loads of acid atmospheric deposition for forests, and (3) the process of podzolization.

Abbreviations: ICP-AES – Inductively Coupled Plasma–Atomic Emission Spectroscopy; HPLC – High Pressure Liquid Chromatography; SEM – Scanning Electron Microscopy; EDAX – Energy Dispersive X-ray Analysis; LMW acids – Low Molecular Weight acids

Introduction

Mineral weathering by plants, bacteria, and saprotrophic and mycorrhizal fungi increases supply of plant nutrients (Boyle & Voigt 1973; Cromack et al. 1979; Robert & Berthelin 1986; Griffiths et al. 1994; Leyval & Berthelin 1991; Wickman & Wallander 1996; Wallander et al. 1997). These nutrients are conventionally thought to enter the bulk soil solution where they become available to roots and other organisms competing for their uptake. Earlier we reported the widespread abundance of tubular pores (diameter 3–10 μm), associated with ectomycorrhizal fungi, inside weatherable minerals in podzols and surficial granitic rock (Jongmans et al. 1997). Mycorrhizal hypha apparently penetrate aluminium silicate minerals via strongly complexing organic acid exudates. Minerals released by weathering in these pores can be taken up by the mycorrhiza and translocated to the host plant roots, bypassing competition for uptake by other organisms. Here we discuss more comprehensively how this newly discovered direct pathway between plants and minerals expands the list of phenomena of biogeochemical weathering of silicate minerals (Robert & Berthelin 1986; Barker et al. 1997) and challenges conventional assumptions about (1) nutrient uptake, (2) the chemical criteria used in determining critical loads of acid atmospheric deposition on forests (De Vries et al. 1994) and (3) the formation of the podzol E horizon by low molecular weight organic acids (Lundström 1993; Lundström et al. 1995).

Materials and methods

This study deals mainly with three 8000 to 9000 yr old forested podzols under mixed 40 to 90 year old *Pinus sylvestris*, *Picea abies* forest with *Vaccinium myrtillus* and *V. vitis-idaea* in the undergrowth in Finland and Sweden. All profiles, from Finland (in Hyytiälä, 61°48′N, 29°19′E) and from Sweden, near Heden (64°14′N, 10°46′E) and Nyänget (64°14′N, 10°46′E) were developed in glacial till or glacial sediment, and had a 5–10 cm thick mor layer, over a 5 to 15 cm thick E horizon and a 30–40 cm thick B horizon. We also studied a site with granitic bedrock covered by a 2–5 cm thick organic mor layer near Lunsen 8 km south of Uppsala. Thin sections (8 × 8 cm) of undisturbed soil samples from the O, E, B and C horizon of the three podzols were prepared following the method of Fitzpatrick (1970). Undisturbed soil samples (8 × 8 cm) were taken from the O, E, and B horizon of profile Nyänget for stereomicroscopy. Small (1 × 0.5 cm) undisturbed sub samples were isolated from the E horizons and from pieces of granite chipped off the surface for scanning electron microscopy studies, providing images and qualitative chemical spectra.

In addition, we studied all archived thin sections of podzol E-horizons available to us for the presence of micro pores in weatherable minerals. These included podzols under *Pinus sylvestris* in the Netherlands (2×) , and under

Pinus sylvestris and *Picea abies* forest in Sweden (1×), Denmark (1 ×) and Switzerland (3×).

We estimated mineral weathering from the distribution of major and trace elements throughout the soil profile, using Zr as an internal standard, because of its resistance to low-temperature weathering (Schützel et al. 1963; Nickel 1973), according to: $X^l = (X^c * Zr^w/Zr^c) - X^w$, where X^l: loss of the element X, g m^{-2}. X^c: concentration of the element X, % of soil material <2 mm, in parent material. X^w: present amount of the element X, g m^{-2}, in a weathered horizon.

We selected the Nyänget soil to quantify weathering because it is located at an altitude of 250 m a.s.l., higher than any Baltic Sea precursors following deglaciation, so that the soil mineral material was not stratified by any wave washing. Area-weighted samples were taken with a core sampler from 10 sub sites to about 1.5–2 m depth. From each horizon sub-samples were put together in a composite sample. After air-drying, the fraction <2 mm (matrix) was separated for chemical analyses.

For total elemental soil analysis about 15 g of split samples were homogenised by grinding in an agate mortar and ignited. 0.125 g of each sample was fused with 0.375 g lithium metaborate at 1000 °C and subsequently dissolved in HNO_3 and analysed by plasma emission spectrometry (ICP–AES). Amorphous Si, Al and Fe phases were extracted by NH_4 oxalate at pH 3 (Van Reeuwijk 1995).

Soil solutions were obtained 5 or 6 times over the growing season (May to October, 1996) by centrifugation of field-moist samples for 30 min at 14000 rpm, filtered through a 0.45 μm filter (Giesler & Lundström 1993), and frozen immediately until analysis. Low-molecular weight organic acids were assayed by HPLC using a Supelcogel C610-H ion exclusion column after ultrafiltering samples twice through a 1000-D filter (Van Hees et al. 1999).

Results

Microscopic characterization

Petrographic microscope observations in thin sections of the E horizons in the soils from Hyytiäla, Heden and Nyänget suggested the common presence of elongated pores, 3–10 μm in grains of feldspar and hornblende. Rounded (circular to ellipsoidal) ulterior boundings of confined stretches of pores in thin sections suggested a tubular pore shape. This was confirmed by scanning electron microscopy (SEM) of the interior of crushed grains (Figure 1(D)), which revealed smooth tubular pores of 3–10 μm in diameter. Less than 1%

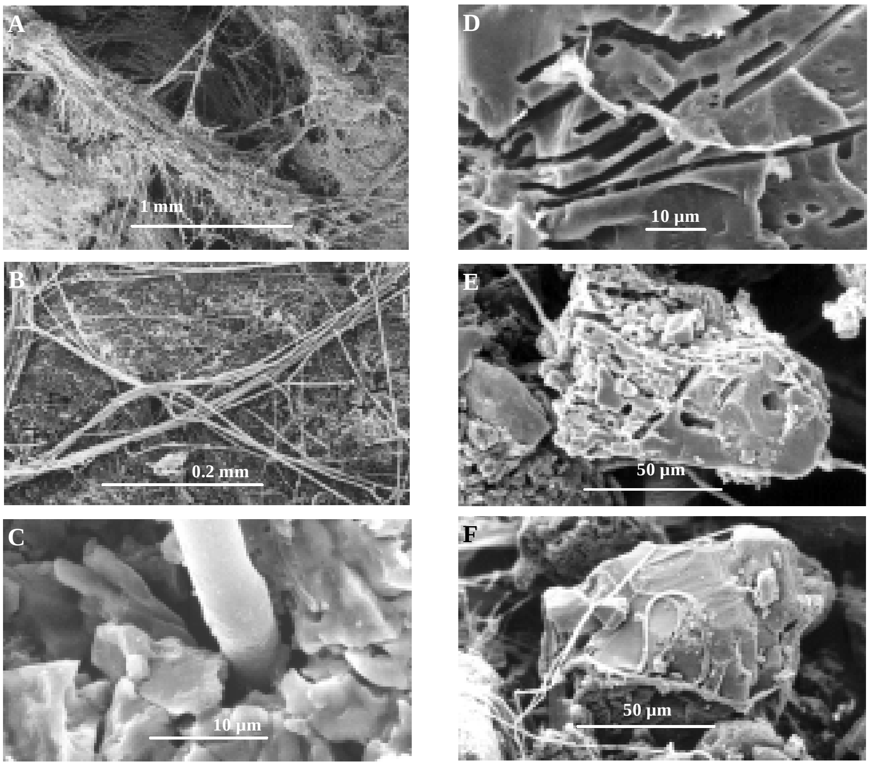

Figure 1. Scanning electron micrographs. Mineral chemistry was determined by in-situ EDAX analysis using a JEOL SEM Apparatus. A–D: Granitic rock, Uppsala; D-F-E horizon of Nyänget podzol (A) mycorrhizal root and associated mycelial mat on granitic rock, Uppsala. (B) Hypha overgrowing and entering a weathered surface of the Uppsala granite. (C) Do, Hyphen entering feldspar from the same granite surface. (D) Interior of crushed feldspar grain with interconnected tubular pores and associated fungal hypha. (E) Hypha associated with grain of Ca feldspar. (F) Do., with grain of quartz.

of the pores contained hypha (in thin sections) or were associated with hypha that appeared partly dislodged from the pores when crushing the grains (in SEM, Figure 1(D)). The number of occupied pores was probably underestimated because sample preparation for thin sections and SEM must have destroyed or disrupted hypha inside pores. The Lunsen granite had a strongly corroded surface with numerous hypha penetrating strongly corroded feldspars (Figure 1(B, C)). In thin sections most pore tracks were curved and appeared to be unrelated to directions of cleavage- and twinning planes, but some were straight and oriented crystallographically.

Most mineral grains from the Nyänget E horizon were enveloped by networks of hypha, regardless of their mineralogy (Figure 1(E, F)). The exterior of most feldspar grains, but not of quartz grains, was scarred by numerous rounded furrows and holes. Feldspars (Figure 1(B, C, E)) but not quartz (Figure 1(F)), were seen to be entered by hypha. Many weatherable minerals (but none of the quartz grains) showed pores in thin sections.

The Nyänget podzol E horizon contained abundant ectomycorrhizal fungal hypha and roots colonised by *Piloderma* and *Cenococcum* species as well as an unidentified white mycorrhizal fungus. The granite surface had closely adhering mycorrhizal roots attached to a dense mycelial mat (Figure 1(A)) dominated by *Suillus bovinus*, with some *Piloderma croceum* and *Cenococcum geophilum*. Ectomycorrhizal hyphal cords and hypha extended from ectomycorrhizal roots into fissures in strongly weathered granite.

Similar pores associated with hypha were found to be abundant in weatherable minerals in all other thin sections from podzol E horizons. Tubular pores were rare in acid brown forest soils (Cambisols) under broadleaved forest (*Quercus, Fagus*) from the Netherlands (2×) and Denmark (1×).

Of the LMW organic acids, citrate (20–250 μM), shikimate (1–40 μM), and fumarate (1–10 μM), were observed in practically all samples from Nyänget. Oxalate (3–15 μM), malate (30–120 μM), lactate (8–80 μM), acetate (50–330 μM), malonate (20–50 μM), formate (23–450 μM), and *t*-aconitate (5–7 μM) were observed less frequently (Van Hees et al. in press). The highest concentrations occurred mostly in the mor layer. Total LMW concentrations were 2 to 15 times lower in the E horizon (pH 3.5). LMW organic acids (oxalate and citrate) were observed occasionally in the B horizon. Soil solution obtained by centrifugation of the mor layer covering the Lunsen granitic bedrock, as well as deionized water placed in contact with the granite for a few minutes contained the same LMW organic acids in similar concentrations as the podzol soil solutions. The geochemical composition of all soil profiles had a characteristic vertical pattern with increasing concentrations of Si, Ca, Mg and K from A to C horizons and decreasing levels of Zr , and Fe and Al concentration that were very low in the E horizon but peaked in the B horizon. Assuming that the parent material was vertically homogenous, these patterns can be interpreted as losses by weathering in the E horizon, especially for Fe (76% of the original amount lost), Mg (73%), Ca (57%), Na (39%) and Al (39%). The small relative loss of Si is due to the large amount of quartz (about 60% in the parent material) that accumulates residually during weathering.

Table 1. Element losses from primary minerals in the E horizon (0–10 cm depth) and the B horizon (1–30 cm) in the Nyänget profile expressed either in kg m^{-2}, or in% of the original amount in the respective horizons. The total losses of Si, Al and Fe from the B horizon were somewhat lower due to secondary amorphous precipitates of Si (1.3 kg m^{-2}) , Al (2.4 kg m^{-2}) and Fe (1.7 kg m^{-2}) as quantified by extraction with ammonium oxalate.

		Si	Al	Fe	Ca	Mg	K	Na
E	kg/m^2	7.4	3.5	1.8	1.01	0.49	0.90	1.28
B		6.6	1.5	0.2	0.65	0.17	0.78	0.58
E	%	15.5	39.2	76.4	56.6	73.4	23.1	39.4
B		6.6	8.1	3.2	17.5	12.3	9.8	8.6

Discussion

Formation of micro pores

The morphological observations can only be explained by fungal hypha creating the tubular pores. Fungi, including mycorrhizal fungi are known to exude low molecular weight (LMW) organic acids at their hyphal tips (Lapeyrie et al. 1987). Alternatively, bacteria may produce LMW acids from organic acid precursors exuded by mycorrhizal hypha (Sun et al, in press). These acids form complexes with dissolved Al and Fe, thereby greatly enhancing mineral weathering (Leyal & Berthelin 1991; Blum & Stillings 1995). The fact that seemingly infinite numbers of hyphal cords and hypha extend from ectomycorrhizal roots into fissures in strongly weathered granite as well as into podzol E horizons, strongly suggests that the “rock-eating” fungi are dominantly or wholly (ecto)mycorrhizal. High concentrations of LMW organic acids associated with ectomycorrhizal mats in and just below coniferous forest floors provide strong evidence for formation of such acids in the presence of these fungi (Graustein et al. 1977; Cromack et al. 1979; Entry et al. 1991; Griffiths et al. 1994). Because it is virtually impossible to track an individual rock-penetrating hypha back to an ectomycorrhizal root due to differences in scale between the mycorrhiza (mm) and the single hypha entering pores in minerals (μm), and to the very dense tangle of hypha, it cannot be excluded that other fungi are also involved. The alternative argument, however, that these are only saprotrophic fungi, and that mycorrhizal fungi are not an essential component, is extremely unlikely. Saprotrophic fungi are able to produce LMW acids (Devêvre et al. 1996), but of course depend on soil organic matter, plant litter and perhaps on ectomycorrhizal fungi for their energy supply. The podzol E horizon is very low in organic matter, and the granite is completely devoid of it, yet virtually all sand grains appear enmeshed with fungal hypha. The only substrates that could be of use to fungi in the granite and the E horizon are nutrients from minerals. That saprotrophic fungi would send down carbon wrested under competition from other saprotrophs in the organic surface horizon into the E horizon to extract nutrients from minerals, appears very unlikely. Furthermore, in the sites we have been investigating the biomass of ectomycorrhizal fungal hypha is known to be high. An ectomycorrhizal origin of the fungi eating their way through weatherable minerals in podzol E horizons is further supported by the fact that ectomycorrhizal mushrooms are more common on podzolic than on non-podzolic soils, and that ectomycorrhizal conifers (particularly *Pinus* spp) are commonly associated with podzols throughout the world. Finally, weathering of microcline and biotite is known to be stimulated by ectomycorrhizal trees such as *Pinus sylvestris* (Wickman & Wallander 1996; Wallander et al. 1997).

In conlusion, while complex associations of different fungi and bacteria may well be involved in the weathering phenomenon we describe, mycorrhizal hypha appear to be essential in providing carbon (energy) to other microbes and their hypha represent the dominant pathway for return of nutrients released from any dissolution of minerals by bacteria and other microbes. These ideas are supported by the recent work of Frey et al. (1997) and Frey-Klett et al. (1997). In the remainder of the paper, therefor, the term “rock-eating” mycorrhizal activity should be considered in the context of a possible microbial association driven by symbiotic mycorrhizal fungi.

Demand for nutrients of growing trees may well drive “rock-eating” mycorrhizal activity. An important question is what nutrients the fungi are after (which nutrients are most limiting for the fungi), and so, demand for which nutrient steers weathering via plant-mycorrhizal associations. The minerals weathered in the Nyänget E horizon, released P, K Ca and Mg at mass ratios (P:K:Ca:Mg) of 1: 11: 17: 10. During growth of new spruce shoots, these nutrients are taken up at mass ratios of 1:7:13:3 (net uptake) or 1:4:5:1 (total uptake) (Kubin 1983). When minerals are the dominant source of those nutrients, P is in short supply relative to the other nutrients, and plant uptake of base cations is low relative to their release during weathering. This indicates that, at least early during primary succession, when biotic cycling of P is relatively unimportant, P is the most limiting nutrient absorbed by mycorrhizal fungi during their growth inside weatherable aluminium silicates. Phosphorus is commonly solubilized by mycorrhiza, and is typically present as inclusion in feldspars. In one Dutch podzol, we observed feldspars

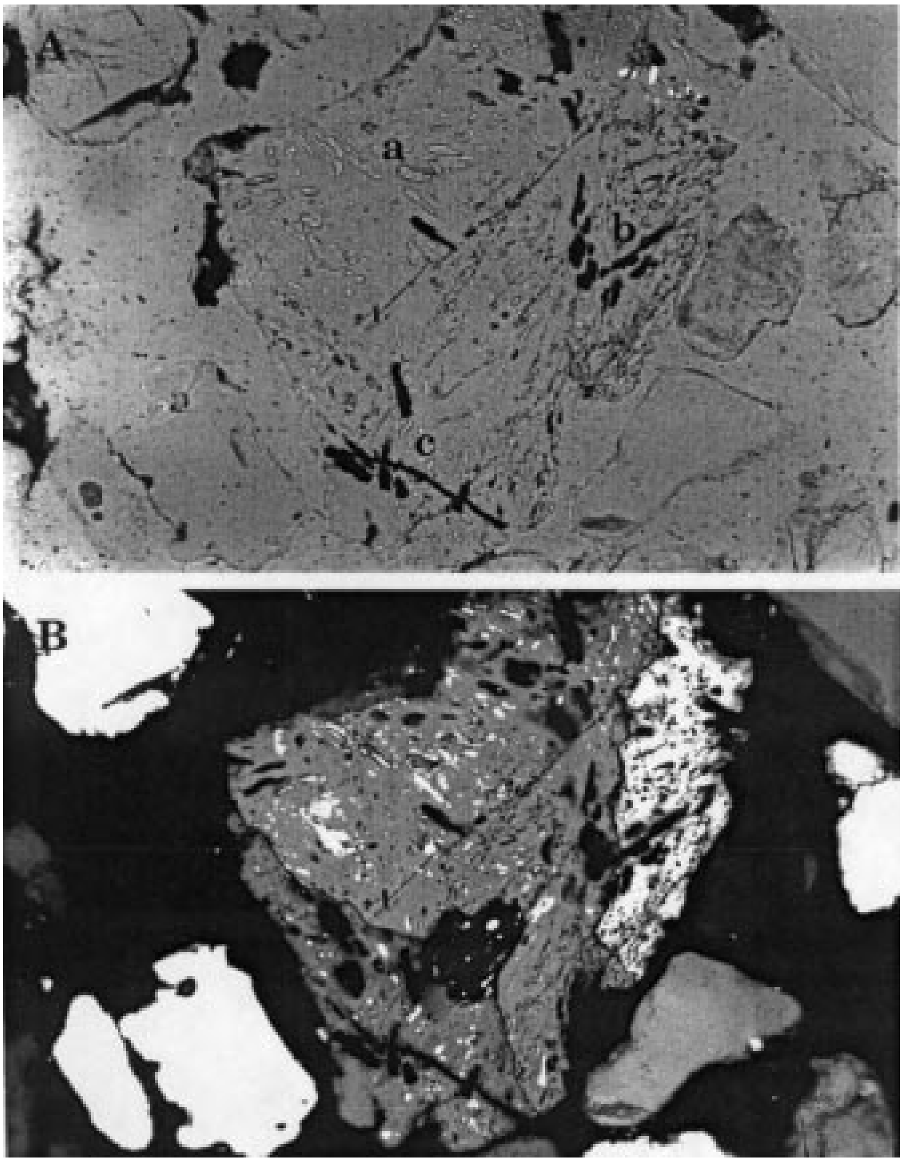

Figure 2. Thin section microphotograph of a Ca-feldspar with apatite inclusions (a); sample from a podzol E horizon near Blitterswijk, the Netherlands, 2(A) normal visible light; 2(B) cross-polarized. Voids in the shape of apatite inclusions (b) were probably created by fungal hypha accessing and dissolving apatite through micropores formed by dissolution of feldspar (c). The greatest dimension of the feldspar grain is about 1 mm.

grains with intact, elongated apatite (10 × 80 μm) inclusions, as well as voids of the same shape which probably reflected the presence of former apatite inclusions dissolved by weathering (Figure 2(A, B)). The solubility of apatite strongly increases with decreasing pH , and dissolution rates of apatite are increased by LMW acids produced by microbial metabolism (El Gibaly et al. 1977).

Rates of pore formation

The order of magnitude of the rate at which pores could grow can evaluated from the observed LMW organic acid concentrations and kinetic experiments using these acids to dissolve minerals (Blum & Stillings 1995). Assuming that 0.1 to 1 mM of citric acid is representative for LMW organic acids inside the pores (equivalent to the highest concentrations of total LMW organic acids observed in the field) the dissolution rate of Ca-rich plagioclase feldspars would be in the order of 10^{-8}–10^{-10} mol.m^{-2}.sec^{-1} at 25 °C. Exudation of acids at the tip of a hypha under such conditions could cause a pore to grow by 0.3 to 30 μm/yr. Supply of water through the hydrophobic fungal cords and hypha out to tips would ensure continuous activity through dry periods, but at the ambient summer soil temperature of 11 °C (Degermark 1995), the dissolution rate would be about five times slower (Blum & Stillings 1995) than at 25 °C. Therefore, unless removal of weathering products and/or maintenance of organic acid concentrations well over 1mM cause higher dissolution rates in pores with hypha, several generations of hypha may be needed to create the commonly 50–400 μm long pores. Accumulation of humic material observed in occasional strongly perforated minerals with irregular and wide, apparently fused, pores may reflect repeated colonisation by different generations of hypha.

Assuming that (i) soil formation started 9000 years ago (Melkerud 1989), (ii) the weathering rate was constant over those 9000 years, and (iii) half of total weathering in the E horizon (22 kg.m^{-2}) took place by formation of pores (diameter 6 μm), pore growth in the E horizon averaged 166 m per year per dm^3 of soil. Actual rates would be higher if other substances, e.g., siderophores, would be involved in fungal weathering, as proposed by Callot et al. (1987). At an extension rate of 10 μm per pore per year, $1.66 * 10^7$ hypha tips would eat their way through weatherable minerals per dm^3 at any time. In a homogenous fine sand (particle size 200 μm) with 40% feldspars, this would imply that there are on average 7.2 hypha tips per individual grain. If an individual pore is 200 μm long, 0.2% of all pores would contain hypha. The order of magnitude of these values are in line with micromorphological observations.

Implications of "rock-eating" mycorrhiza

If mineral weathering in podzols takes would indeed place largely in narrow channels inside mineral sand and silt grains, or in bedrock, this would have important potential implications and would raise a number of intriguing questions.

Because mycorrhizal hypha can take up nutrients released by weathering and serve as conduits that supply nutrients to plants roots (Smith & Read 1997; Finlay 1993), pores in minerals created by hypha provide a more direct access of plants to mineral nutrients than via the traditionally postulated route through the bulk soil solution. Provision of nutrients from inside mineral grains via symbiotic microflora would involve close control of plants over weathering. Reduced plant growth due to short supply of nutrients could increase allocation of photosynthetic products to symbiotic microflora (Björkman 1949) and formation of LMW organic acids, resulting in increased weathering. There seems to be consensus that relative allocation of C to fine roots increases with decreasing nitrogen availability, but effects of other nutrients and linkages with below-ground microbial communities are not known (Zak & Pregitzer 1998).

So far, we have observed fungal micro pores only in podzol E horizons under coniferous trees, and often with an ericaceous shrub layer. This raises the question of whether this phenomenon is restricted to such environments and if the "rock-eating" mycorrhizal fungi play a major role in podzolization (Van Breemen et al. in press). This is corroborated by (i) the apparent ubiquity of "rock-eating" mycorrhizal fungi in podzol E horizons (ii) the presence of LMW acids in other podzols (Bruckert 1970), (iii) observations of increased podzolization under ectomycorrhizal mats of *Hydnellum scleropdium* (Fisher 1972) and (iv) the role (of microbial decay) of dissolved LMW organic complexes in precipitating secondary Al and Fe compounds in the podzol B horizon (Lundström 1993; Lundström et al. 1995). Concentrations of dissolved Al and Si in podzol O horizons (including the ones studied here, Van Hees et al. in press) are generally high, and not necessarily lower than those in the E horizon (Rustad & Cronan 1995; Lawrence & David 996). Percolation of this (organically complexed) Al plus associated Si from the O into the E horizon is a major, and hitherto unrecognised, part of the podzolization process (Giesler et al. in press). Weathering of minerals incorporated by various physical processes into the organic O can partly explain this phenomenon (Lawrence & David 1996; Giesler et al. in press). Biocycling of Si and Al was invoked to explain the relatively high fluxes of Al and Si from the O horizon from loblolly pine, *Pinus taeda* L. (Markewitz & Richter 1997). Such biocycling might well involve involving "rock-eating" ectomycorrhizal fungi. Weathering products mobilized by "rock-eating" mycorrhizal fungi in the E horizon could be partly transported through hypha towards the hyphal mantles of mycorrhizal roots in the O horizon. The bulk of the Si and (organically complexed) Al are probably not taken up by roots, and would be exuded from the hypha near the root, or stored inside the hypha, to be released when they die. This scenario would require that many of the hypha descend from mycorrhizal roots in the O horizon into the 5–10 cm thick E horizon. While this would not be inconsistent with available published information about the abundance of mycorrhiza Mikola et al. 1966) and hypha (mycorrhizal plus saprotrophic) (Bååth 1980; Bååth et al. 1984; Söderström 1977, 1979) in Scandinavian podzols, we are not aware of direct measurements about how deep hypha penetrate from the O horizon downwards.

Finally, the finding of mycorrhizal pores in weatherable minerals could affect the debate on ecological effects of acidification by acid atmospheric deposition. Increased soil acidification from acid atmospheric deposition in much of Europe has depleted soils of exchangeable base cations (Wesselink 1994; Falkengren-Grerup & Eriksson 1990), and caused strongly elevated concentrations of dissolved inorganic Al^{3+} (Mulder et al. 1989). Inorganic Al^{3+}, in contrast to the organically complexed Al that is released during pore formation in aluminium silicate minerals, is toxic to plants (Rost-Siebert 1985). Low ratios of dissolved $(Ca^{2+} + Mg^{2+})/Al^{3+}$ are particularly detrimental to tree roots, at least for non-mycorrhizal trees growing in nutrient solution. Critical loads of acid atmospheric deposition calculated from critical ratios of dissolved base cations to Al^{3+} from such nutrient solution experiments (Sverdrup & De Vries 1994) are often much lower than actual present-day deposition over a large part of Western Europe (Posch et al. 1997). Such experiments, however, may be irrelevant for uptake of Ca and Mg, and for the functioning of plant roots because actual mycorrhizal trees (1) may take up part of their Ca^{2+} and Mg^{2+} from the inside of mineral and from the mineralized litter in the O horizon, while (2) complexing organic acids exuded by mycorrhizal fungi may inactivate any potentially toxic inorganic Al^{3+} that is accessed by their hypha from the acidified bulk soil solution in the mineral soil. Disregarding the role of mycorrhiza, including nutrient uptake from micro sites inside minerals which are “protected” from competition and less readily affected by acidification, probably invalidates critical acid loads calculated without considering these aspect. This has important consequences for the ongoing debate in Scandinavia about the need to apply lime for sustained forest productivity on soils (almost invariably podzols) affected by acid atmospheric deposition (Staaf et al. 1996). A direct mineral to plant bypass for nutrients via mycorrhizal hyphal tips inside mineral grains and bedrock may also help to explain why forest productivity across Europe has not decreased, in spite of recent excessive soil acidification (Kauppi et al. 1992).

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