Mineral transformations by mycorrhizal fungi

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Mineral Transformations by Mycorrhizal Fungi

Elena Martino & Silvia Perotto

Abstract

This review addresses the significance and the mechanisms of mineral weathering by mycorrhizal fungi, and the role of this process in plant nutrition and protection from metal toxicity. The fact that mycorrhizal mycelia may actively release nutrients from mineral particles through weathering is raising an increasing interest and the uptake of mineral-derived nutrients by the host plants has been reported. Both chemical dissolution (protonation, chelation) and physical mechanisms (high hyphal pressures) are involved in the weathering process. Mineral solubilization can result in the release of the associated toxic metals. Organic acid exudation and metal complexation may represent a host plant protection mechanism.

Keywords: metal toxicity, mineral weathering, mycorrhizal fungi,

WEATHERING BY MYCORRHIZAL FUNGI: GENERAL INTRODUCTION

About a decade ago, Jongmans et al. (1997) Jongmans, A G, van Breemen, N, Lundström, U S, van Hees, P AW, Finlay, R D, Srinivasan, M, Unestam, T, Giesler, R, Melkerud, P-A and Olsson, M. 1997. Rock-eating fungi. *Nature*, 389: 682–683. found tunnels inside mineral grains that were likely formed by hyphae of ectomycorrhizal (ECM) fungi. This observation implied that mycorrhizal fungi were able to dissolve mineral grains. This finding raised several questions on the ecology of these microorganisms that started to be called "rock-eating" fungi (Van Schöll et al. 2008 Van Schöll, L, Kuyper, T W, Smits, M M, Landeweert, R, Hoffland, E and van Breemen, N. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. *Plant Soil*, 303: 35–47.). Although it is well accepted that mycorrhiza assist plants in the acquisition of mineral nutrients already in the soil solution, the fact that mycorrhizal mycelia, either by themselves, or in association with bacteria or other fungi, may actively release nutrients from mineral particles and rock surfaces through weathering is raising increasing interest (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254. ; Finlay and Rosling 2006 Finlay, R D and Rosling, A. 2006. "Integrated nutrient cycles in forest ecosystems, the role of ectomycorrhizal fungi". In *Fungi in biogeochemical cycles*, Edited by: Gadd, G M. 28–50. Cambridge: Cambridge University Press. ; Wallander 2006 Wallander, H. 2006. "Mineral dissolution by ectomycorrhiza". In *Fungi in biogeochemical cycles*, Edited by: Gadd, G M. 681–717. Cambridge: Cambridge University Press. ; Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.).

Fungi play a central role in many microbiological and ecological processes, influencing soil fertility, cycling of minerals and organic matter, as well as plant health and nutrition (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.

). Fungi are heterotrophs and require external sources of organic carbon for energy and cellular synthesis. They have adopted three different trophic strategies to obtain this carbon, occurring as saprotrophs, necrotrophs, and biotrophs. Mycorrhizal symbiosis is the most ancient and widespread form of fungal symbiosis with plant roots (Smith and Read 2008 Smith, S E and Read, D J. 2008. *Mycorrhizal symbiosis* , 3rd edn, Academic Press.). More than 80% of plant roots form mycorrhiza with soil fungi, and in boreal and temperate regions, as much as 90% of the woody tree root tips are covered by ectomycorrhizal fungal sheaths (as much as 600 km of fungal mycelium per kg of soil) (Ek 1997 Ek, H. 1997. The influence of nitrogen fertilization on the carbon economy of *Paxillus involutus* in ectomycorrhizal association with *Betula pendula*. *New Phytol*, 135: 133–142. ; Read and Perez-Moreno 2003 Read, D J and Perez-Moreno, J. 2003. Mycorrhizas and nutrient cycling in ecosystems—A journey towards relevance?. *New Phytol*, 157: 475–492.). Thus, virtually all nutrients taken up by trees pass through these fungi, and in return, the fungi receive 20%–30% of the carbon fixed during photosynthesis by the host plants (Högberg and Högberg 2002 Högberg, M N and Högberg, P. 2002. Extramatrical ectomycorrhizal mycelium contributes one-third of microbial biomass and produces, together with associated roots, half the dissolved organic carbon in a forest soil. *New Phytol*, 154: 791–795.).

Mycorrhizal fungi are therefore one of the most important ecological groups of soil microorganisms (Jongmans et al. 1997 Jongmans, A G, van Breemen, N, Lundström, U S, van Hees, P AW, Finlay, R D, Srinivasan, M, Unestam, T, Giesler, R, Melkerud, P-A and Olsson, M. 1997. Rock-eating fungi. *Nature*, 389: 682–683. ; Lundström et al. 2000 Lundström, U S, Van Breemen, N and Bain, D. 2000. The podzolization process. A review. *Geoderma*, 94: 91–107.) and they are well-known plant growth promoters (Finlay 2004 Finlay, RD. 2004. Mycorrhizal fungi and their multifunctional roles. *Mycologist*, 18: 91–96.). This characteristic results from the ability of these fungi to efficiently remove organic and inorganic nutrients from soil organic matter and minerals (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254. ; Blum et al. 2002 Blum, J D, Klaue, A, Nezat, C A, Driscoll, C T, Johnson, C E, Siccama, T G, Eagar, C, Fahey, T J and Likens, G E. 2002. Mycorrhizal weathering of apatite as important calcium source in base-poor forest ecosystems. *Nature*, 417: 729–731.). Although rock weathering was classically thought of as an inorganic process, it is now recognized that plants, and especially forests, accelerate weathering rates by a factor of 4 to 10 compared to geologically similar, nonvegetated areas (Moulton et al. 2000 Moulton, K L, West, J and Berner, R A. 2000. Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering. *Am J Sci*, 300: 539–570. ; Bonneville et al. 2009 Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618.). Saprotrophs and also mycorrhizal fungi play a key role in the mineralogical modification that characterizes weathering (Balogh-Brunstad et al. 2008 Balogh-Brunstad, Z, Keller, C K, Gill, R A, Bormann, B T and Li, C Y. 2008. The effect of bacteria and fungi on chemical weathering and chemical denudation fluxes in pine growth experiments. *Biogeochemistry*, 88: 153–167.). Kennedy et al. (2006) Kennedy, M, Droser, M, Mayer, L M, Pevear, D and Mrofka, D. 2006. Late Precambrian oxygenation: Inception of the clay mineral factory. *Science*, 311: 1446–1449. suggested that the expansion of soil biota and especially fungi during the Late Proterozoic helped create conditions suitable for animal life (Bonneville et al. 2009 Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618.).

Seven different types of mycorrhizal symbioses have been distinguished on the basis of morphological characteristics and of the fungal and plant species involved (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional

diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.). *Arbuscular mycorrhiza* is the most ancient and widespread form. Paleobotanical and molecular sequence data suggest that the first land plants formed associations with Glomalean fungi from the Glomeromycota about 460 million years ago (Redecker et al. 2000 Redecker, D, Kodner, R and Graham, L E. 2000. Glomalean fungi from the Ordovician. *Science*, 289: 1920–1921.). *Ericoid mycorrhiza* are formed in three plant families, the Ericaceae, Empetraceae, and Epacridaceae, all belonging to the order Ericales. These plants grow principally as dwarf shrubs in upland and lowland heaths and other nutrient-impoverished areas, suggesting that nutritional, rather than climatic, factors determine their distribution. Around 3400 plant species form this type of mycorrhizal association with various fungi from the Ascomycota (i.e., *Rhizoscyphus ericae, Oidiodendron maius*), which penetrate the cell walls of roots and form coiled structures within each cell without penetrating the host plasma membrane (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.).

Recent evidence suggests that basidiomycetes belonging to clade B Sebacinales are also common ericoid mycorrhizal fungi (Selosse et al. 2007 Selosse, M-A, Setaro, S, Glatard, F, Richard, F, Urcelay, C and Weiss, M. 2007. Sebacinales are common mycorrhizal associates of Ericaceae. *New Phytol*, 174: 864–878.). Many long-lived herbaceous and woody plants form a third type of mycorrhiza, *ectomycorrhiza*. The fungi are predominantly from the Basidiomycota and Ascomycota and as many as 10,000 fungal species and 8000 plant species may be involved, globally (Taylor and Alexander 2005 Taylor, A FS and Alexander, I. 2005. The ectomycorrhizal symbiosis: life in the real world. *Mycologist*, 19: 102–112.). Although this represents only a small fraction of the total number of terrestrial plants, these species often form the dominant components of forest ecosystems and occupy a disproportionately large area.

The plant species involved are usually trees or shrubs from cool, temperate boreal or montane forests, but also include arctic-alpine dwarf shrub communities, Mediterranean/ chaparral vegetation, and many species in the Dipterocarpaceae and leguminous Caesalpinoideae in tropical forests. The fungi do not penetrate the host cells, and the symbiosis is characterized by the presence of a fungal mantle around each of the short roots, as well as a network of intercellular hyphae penetrating between the epidermal and cortical cells, the so-called Hartig net.

Like the arbuscules in arbuscular mycorrhiza, this interface is an effective way of increasing the surface area of contact between the fungus and its host plant. The mantle is usually connected to a more or less well-developed extraradical mycelium, which may extend for many centimetres from the root into the soil (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.). This extraradical mycelium may form a significant fraction of the total microbial biomass in forest soils and estimates of 700–900 kg ha^{-1} have been published (Wallander et al. 2001 Wallander, H, Nilsson, L O, Hagerberg, D and Bååth, E. 2001. Estimation of the biomass and seasonal growth of external mycelium of ectomycorrhizal fungi in the field. *New Phytol*, 151: 752–760.).

The hyphae that grow outward from the mantle into the surrounding soil are very efficient nutrient scavengers, owing to their high surface area:mass ratio and their ability to penetrate microsites that are inaccessible to plant roots. The expanding mycorrhizal mycelium exploits a larger soil volume than do roots alone (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254.). Four other types of mycorrhiza can be recognized: the *orchid mycorrhiza* (Bidartondo et al. 2002 Bidartondo, M I, Redecker, D, Hijri, I, Wiemken, A,

Bruns, T D, Domínguez, L, Sérsic, A, Leake, J R and Read, D J. 2002. Epiparasitic plants specialized on arbuscular mycorrhizal fungi. *Nature*, 419: 389–392. ; Leake 2004 Leake, JR. 2004. Myco-heterotroph/epiparasitic plant interactions with ectomycorrhizal and arbuscular mycorrhizal fungi. *Curr Op Pl Biol*, 7: 422–428. ; Bidartondo 2005 Bidartondo, MI. 2005. The evolutionary ecology of myco-heterotrophy. *New Phytol*, 167: 335–352.); the *monotropoid mycorrhizal*, involving the achlorophyllous Monotropaceae (Leake 2004 Leake, JR. 2004. Myco-heterotroph/epiparasitic plant interactions with ectomycorrhizal and arbuscular mycorrhizal fungi. *Curr Op Pl Biol*, 7: 422–428. ; Bidartondo 2005 Bidartondo, MI. 2005. The evolutionary ecology of myco-heterotrophy. *New Phytol*, 167: 335–352.), the *arbutoid mycorrhiza* formed between fungi that are normally ectomycorrhizal and plants in the genera *Arbutus*, *Arctostaphylos*, and the family Pyrolaceae and finally the *ectendomycorrhiza*, which have features of both ectomycorrhizas and endomycorrhizas (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.).

In terms of mineral weathering and dissolution, mycorrhizal fungi form one of the most prominent groups of soil microorganisms (Devevre et al. 1996 Devevre, O, Garbaye, J and Botton, B. 1996. Release of complexing organic acids by rhizosphere fungi as a factor in Norway Spruce yellowing in acidic soils. *Mycol Res*, 100: 1367–1374. ; Jongmans et al. 1997 Jongmans, A G, van Breemen, N, Lundström, U S, van Hees, P AW, Finlay, R D, Srinivasan, M, Unestam, T, Giesler, R, Melkerud, P-A and Olsson, M. 1997. Rock-eating fungi. *Nature*, 389: 682–683. ; Lundström et al. 2000 Lundström, U S, Van Breemen, N and Bain, D. 2000. The podzolization process. A review. *Geoderma*, 94: 91–107.). The depth and the extension of mycorrhizal fungal attack on the mineral substrate, although controlled by various factors (fungal type, nutrient availability, porosity, mineral composition, temperature and light), can reach tens of centimeters (Jackson et al. 1996 Jackson, R B, Canadell, J, Ehleringer, J R, Mooney, H A, Sala, O E and Schulze, E D. 1996. A global analysis of root distributions for terrestrial biomes. *Oecologia*, 108: 389–411. ; Rosling et al. 2003 Rosling, A, Landeweert, R, Lindahl, B, Larsson, K H, Kuyper, T W, Taylor, A FS and Finlay, R. 2003. Vertical distribution of ectomycorrhizal root tips in a podzol soil profile. *New Phytol*, 159: 775–783. ; Hendricks et al. 2006 Hendricks, J J, Mitchell, R J, Kuehn, K A, Pecot, S D and Sims, S E. 2006. Measuring external mycelia production of ectomycorrhizal fungi in the field: the soil matrix matters. *New Phytol*, 171: 179–186.). For example, a number of experimental studies have shown the ability of ectomycorrhizal fungi (e.g., *Paxillus involutus, Pisolithus tinctorius, Laccaria laccata, L. bicolor, Hebeloma cylindrosporum, H. crustuliniforme, Cenococcum geophilum*) to dissolve Ca-bearing minerals (Callot et al. 1985 Callot, G, Mousain, D and Plassard, C. 1985. Concentration of calcium carbonate on the walls of fungal hyphae. *Agronomie*, 5: 143–150. ; Lapeyrie et al. 1991 Lapeyrie, F, Ranger, J and Vairelles, D. 1991. Phosphate-solubilizing activity of ectomycorrhizal fungi in vitro. *Can J Bot*, 69: 342–346. ; Gharieb and Gadd 1999 Gharieb, M M and Gadd, G M. 1999. Influence of nitrogen source on the solubilization of natural gypsum ($CaSO_4 \cdot 2H_2O$) and the formation of calcium oxalate by different oxalic and citric acid-producing fungi. *Mycol Res*, 103: 473–481.).

The ability of some ericoid mycorrhizal fungi (mycorrhizal endophytes of *Woollsia pungens* (Epacridaceae), *Hymenoscyphus ericae* and *Oidiodendron maius*) to dissolve hydroxyapatite, and Zn oxide and phosphate have also been reported (Van Leerdam et al. 2001 Van Leerdam, D M, Williams, P A and Cairney, J WG. 2001. Phosphate-solubilising abilities of ericoid mycorrhizal endophytes of *Woolsia pungens (Epacridaceae)*. *Austr J Bot*, 49: 75–80. ; Martino et al. 2003a Martino, E, Perotto, S, Parsons, R and Gadd, G M. 2003a. Solubilization of insoluble inorganic zinc compounds by ericoid mycorrhizal fungi derived from heavy metal polluted sites. *Soil Biol Biochem*, 35: 133–141.). For dissolution of Ca sulphate (gypsum) and different forms of Ca phosphate, it was found that solubilization was significantly affected by the nature of the supplied N

source, and greater mineral dissolution has been demonstrated in the presence of NH_4^+ than in the presence of NO_3^- (Lapeyrie et al. 1991 Lapeyrie, F, Ranger, J and Vairelles, D. 1991. Phosphate-solubilizing activity of ectomycorrhizal fungi in vitro. *Can J Bot*, 69: 342–346. ; Gharieb and Gadd 1999 Gharieb, M M and Gadd, G M. 1999. Influence of nitrogen source on the solubilization of natural gypsum ($CaSO_4 \cdot 2H_2O$) and the formation of calcium oxalate by different oxalic and citric acid-producing fungi. *Mycol Res*, 103: 473–481. ; Whitelaw et al. 1999 Whitelaw, M A, Harden, T J and Helyar, K R. 1999. Phosphate solubilization in solution culture by the soil fungus *Penicillium radicum*. *Soil Biol Bioch*, 31: 655–665. ; Van Leerdam et al. 2001 Van Leerdam, D M, Williams, P A and Cairney, J WG. 2001. Phosphate-solubilising abilities of ericoid mycorrhizal endophytes of *Woolsia pungens (Epacridaceae)*. *Austr J Bot*, 49: 75–80.). This is presumed to reflect acidification of the medium as a result of H^+ excretion from hyphae during NH_4^+ uptake. Fomina et al. (2005) Fomina, M, Alexander, I J, Colpaert, J V and Gadd, G M. 2005. Solubilization of toxic metal minerals and metal tolerance of mycorrhizal fungi. *Soil Biol Biochem*, 37: 857–866. clearly indicate that, for the majority of the mycorrhizal fungi they tested grown on solid medium with NH_4^+ as the N source, acidification was the main mechanism of mineral dissolution, which could be enhanced by metal chelation by organic acid anions (see below).

THE MECHANISMS INVOLVED IN WEATHERING BY MYCORRHIZAL FUNGI

The rate of *biotic weathering* is fundamentally controlled by the biomass, surface area of contact, and capacity of roots and their mycorrhizal fungal partners to interact physically and chemically with minerals (Taylor et al. 2009 Taylor, L L, Leake, J R, Quirk, J, Hardy, K, Banwart, S A and Beerling, D J. 2009. Biological weathering and the long-term carbon cycle: integrating mycorrhizal evolution and function into the current paradigm. *Geobiology*, 7: 171–191.), which are, with the exception of N and C, the ultimate source for all mineral nutrients required for biotic life. Nutrients become available through weathering of these minerals i.e., physical disintegration and chemical dissolution (Van Hees et al. 2006 Van Hees, P AW, Rosling, A, Lundström, U S and Finlay, R D. 2006. The biogeochemical impact of ectomycorrhizal conifers on major soil elements (Al, Fe, K and Si). *Geoderma*, 136: 364–377.). The weathering rate and the mechanisms controlling it are highly important in relation to issues such as soil fertility and ecosystem productivity (Van Hees et al. 2006 Van Hees, P AW, Rosling, A, Lundström, U S and Finlay, R D. 2006. The biogeochemical impact of ectomycorrhizal conifers on major soil elements (Al, Fe, K and Si). *Geoderma*, 136: 364–377.). Smits et al. (2008) Smits, M M, Bonneville, S, Haward, S and Leake, J R. 2008. Ectomycorrhizal weathering, a matter of scale?. *Mineral Magaz*, 72: 131–134. showed for the first time grain-scale effects of ECM fungi, in symbiosis with a host plant, on mineral weathering under sterile conditions. ECM fungi actively direct their growth and energy flow towards mineral grains containing essential nutrient elements for the tree and fungus.

Two main mechanisms are suspected to be involved in mineral weathering under aerobic conditions: acidification and complexation. Indeed, acidification is generally linked to the production of microbial organic acids and protons, and complexation is generally linked to the production of microbial chelating molecules, like siderophores or organic acids (Uroz et al. 2007 Uroz, S, Calvaruso, C, Turpault, M P, Pierrat, J C, Mustin, C and Frey-Klett, P. 2007. Effect of the mycorrhizosphere on the genotypic and metabolic diversity of the bacterial communities involved in mineral weathering in a forest soil. *Appl Environ Microbiol*, 73: 3019–3027.).

Mycorrhizal fungi, as well as other fungi, can dissolve minerals in the course of the so-called "heterotrophic leaching" by employing several mechanisms, including protonation (acidolysis), chelation (complexolysis) and metal accumulation, where the biomass functions as a metal sink

(Burford et al. 2003 Burford, E P, Fomina, M and Gadd, G M. 2003. Fungal involvement in bioweathering and biotransformation of rocks and minerals. *Mineral Mag*, 67: 1127–1155. ; Fomina et al. 2004 Fomina, M, Alexander, I J, Hillier, S and Gadd, G M. 2004. Zinc phosphate and pyromorphite solubilization by soil plant-symbiotic fungi. *Geomicrobiol J*, 21: 351–366. ; Kraemer 2004 Kraemer, SM. 2004. Iron oxide dissolution and solubility in the presence of siderophores. *Aquatic Sci*, 66: 3–18. ; Adeyemi and Gadd 2005 Adeyemi, A O and Gadd, G M. 2005. Fungal degradation of calcium-, lead and silicon-bearing minerals. *Biometals*, 18: 269–281. ; Gadd 2007 Gadd, GM. 2007. Geomycology: Biogeochemical transformations of rocks, minerals, metals and radionuclides by fungi, bioweathering and bioremediation. *Mycol Res*, 111: 3–49.). Recently, physical mechanisms were also reported for mycorrhizal fungi, which can apply a pressure onto the minerals that can be as high as the pressure in an average car tyre (2.2 bars = 0.22 MPa) (Bonneville et al. 2009 Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618.).

Chemical Dissolution Mechanisms

Among the chemical mechanisms, it has been reported that *acidification* in the mycorrhizosphere soil contributes to increased weathering of micas and K feldspars around the colonized root tips, by increasing cation exchange capacity and concentrations of soluble and exchangeable K^+, Ca^{2+} and Mg^{2+} (Arocena et al. 1999 Arocena, J M, Glowa, K R, Massicotte, H B and Lavkulich, L. 1999. Chemical and mineral composition of ectomycorrhizosphere soils of subalpine fir (*Abies lasiocarpa* (Hook.) Nutt.) in the AE horizon of a Luvisol. *Can J Soil Sci*, 79: 25–35. ; Arocena and Glowa 2000 Arocena, J M and Glowa, K R. 2000. Mineral weathering in ectomycorrhizosphere of subalpine fir (*Abies lasiocarpa* (Hook.) Nutt.) as revealed by soil solution composition. *Forest Ecol Manage*, 133: 61–70.). *Organic anions*, such as oxalate and citrate, are strong ligands (Welch and Ullman 1993 Welch, S A and Ullman, W J. 1993. The effect of organic acids on plagioclase dissolution rates and stoichiometry. *Geoch Cosmoch Acta*, 57: 2725–2736.) and they are assumed to be the most potent biological weathering agents in the soil (Ochs 1996 Ochs, M. 1996. Influence of humified and non-humified natural organic compounds on mineral dissolution. *Chem Geol*, 132: 119–124. ; Barker et al. 1998 Barker, W W, Welch, S A, Chu, S and Banfield, J F. 1998. Experimental observations of the effects of bacteria on aluminosilicate weathering. *Am Mineral*, 83: 1551–1563.) because of their dual acidifying and chelating ability (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254.).

Oxalic acid, and to a lesser extent citric acid, are the most abundant low molecular weight organic acids (LMWOAs) produced by ECM fungi (Lapeyrie et al. 1987 Lapeyrie, F, Chilvers, G A and Bhem, C A. 1987. Oxalic acid synthesis by the mycorrhizal fungus *Paxillus involutus* (Batsch. ex Fr.) Fr. *New Phytol*, 106: 139–146. ; van Hees et al. 2006 Van Hees, P AW, Rosling, A, Lundström, U S and Finlay, R D. 2006. The biogeochemical impact of ectomycorrhizal conifers on major soil elements (Al, Fe, K and Si). *Geoderma*, 136: 364–377.) and can solubilize minerals by protonating or chelating cations (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254.). Organic acids greatly enhance the dissolution of primary silicate minerals, thereby mobilizing essential lithophilic plant nutrients. Silicate minerals such as feldspars, micas, hornblende and pyroxene provide Ca, Mg and K; apatite is the main primary mineral source of P (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254.). Landeweert et al. (2001) Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks:

ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254. proposed that the ectomycorrhizal hyphae exude LMWOAs, such as citrate and oxalate, at their hyphal tips near mineral surfaces, in this way accelerating mineral weathering (Van Schöll et al. 2006b Van Schöll, L, Smits, M M and Hoffland, E. 2006b. Ectomycorrhizal weathering of the soil minerals muscovite and hornblende. *New Phytol*, 171: 805–814.) and mobilizing P, K, Ca and Mg from solid mineral substrates (Wallander and Wickman, 1999 Wallander, H and Wickman, T. 1999. Biotite and microcline as potassium sources in ectomycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Mycorrhiza*, 9: 25–32. ; Wallander 2000a Wallander, H. 2000a. Uptake of P from apatite by *Pinus sylvestris* seedlings colonised by different ectomycorrhizal fungi. *Plant Soil*, 218: 249–256. , 2000b Wallander, H. 2000b. Use of strontium isotopes and foliar K content to estimate weathering of biotite induced by pine seedlings colonised by ectomycorrhizal fungi from two different soils. *Plant Soil*, 222: 215–229.).

In addition, *tunnels* in weatherable minerals enable ectomycorrhizal hyphae to reach the interior of the minerals and access nutrients like P from mineral (i.e., apatite) inclusions (Wallander and Hagerberg 2004 Wallander, H and Hagerberg, D. 2004. Do ectomycorrhizal fungi have a significant role in weathering of minerals in forest soil?. *Symbiosis*, 27: 249–257.). As mentioned above the term "rock-eating fungi" was coined by Jongmans et al. (1997) Jongmans, A G, van Breemen, N, Lundström, U S, van Hees, P AW, Finlay, R D, Srinivasan, M, Unestam, T, Giesler, R, Melkerud, P-A and Olsson, M. 1997. Rock-eating fungi. *Nature*, 389: 682–683. , when they described microscopic tunnels contained within feldspar and hornblende grains in the E horizon of podzol soils (Van Schöll et al. 2008 Van Schöll, L, Kuyper, T W, Smits, M M, Landeweert, R, Hoffland, E and van Breemen, N. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. *Plant Soil*, 303: 35–47.).

Podzols are characterised by four distinct soil horizons: a dark-coloured organic (O) horizon underlain by a white/ash-coloured eluvial (E) horizon, overlying a usually dark-coloured illuvial (B) horizon on top of the unaltered parent (C) material. These tunnels had smooth and parallel-oriented walls with a constant diameter (3–10 μm) and rounded ends, which distinguished them from (coalesced) etch pits and cracks caused by abiotic weathering processes known so far (Hoffland et al. 2002 Hoffland, E, Giesler, R, Jongmans, T and Van Breemen, N. 2002. Increasing feldspar tunneling by fungi across a North Sweden podzol chronosequence. *Ecosystems*, 5: 11–22.).

Because (1) the size and shape of the tunnels perfectly fitted hyphae, (2) some tunnels were actually colonised by hyphae and (3) hyphae were seen to penetrate mineral grains, a fungal role for rock weathering seemed likely (Van Schöll et al. 2008 Van Schöll, L, Kuyper, T W, Smits, M M, Landeweert, R, Hoffland, E and van Breemen, N. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. *Plant Soil*, 303: 35–47.). Jongmans et al. (1997) Jongmans, A G, van Breemen, N, Lundström, U S, van Hees, P AW, Finlay, R D, Srinivasan, M, Unestam, T, Giesler, R, Melkerud, P-A and Olsson, M. 1997. Rock-eating fungi. *Nature*, 389: 682–683. further hypothesised that such tunnels were formed through LMWOAs exuded at hyphal tips. The term rock-eating fungi therefore refers to fungi that have the capacity to exude LMWOAs to an extent that mineral weathering rates are significantly increased. The host trees would provide important sinks for the nutrients released through dissolution in the pores and mycorrhizal hyphae would provide direct conduits for translocation of nutrients to plants from microsites isolated from the bulk soil solution (Van Schöll et al. 2008 Van Schöll, L, Kuyper, T W, Smits, M M, Landeweert, R, Hoffland, E and van Breemen, N. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. *Plant Soil*, 303: 35–47.).

More recently, Van Breemen et al. (2000a) Van Breemen, N, Finlay, R D, Lundström, U, Jongmans, A G, Giesler, R and Olsson, M. 2000a. Mycorrhizal weathering: a true case of mineral

nutrition?. *Biogeochemistry*, 49: 53–67. also hypothesize that these pores were formed by complex-forming LMWOAs exuded by or formed in association with mycorrhizal fungi. They provided 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. Moreover, Van Breemen et al. (2000b) Van Breemen, N, Lundström, U S and Jongmans, A G. 2000b. Do plants drive podzolization via rock-eating mycorrhizal fungi?. *Geoderma*, 94: 163–171. presented evidence that such rock-eating mycorrhizal fungi help to mobilize Al and Si from weatherable minerals of the E horizon, and transport these elements into the O horizon from where they may percolate downwards.

They hypothesized that weathering products mobilized by ectomycorrhizal fungai in the E horizon are transported through hyphae towards the hyphal mantles of mycorrhizal roots, most of which are probably in the O horizon. Most of the P and an appreciable part of other nutrients derived by mineral weathering (notably K, Mg and Ca) are probably transferred to the plant, bypassing the soil solution with often toxic concentration of Al^{3+} from acid rain, and bypassing competition for nutrient uptake by other organisms. It is highly unlikely, however, that much of the Si and the (organically complexed) Al and Fe is taken up by the tree roots. These elements will therefore be either exuded from the hypha near the root, or stored inside the hypha, to be released when the hypha die. Part of the soluble complexes may percolate downward, causing relatively high fluxes of Al, Fe and Si from the O into the E horizon. Mean annual fluxes of Al, Fe and Si at the O/E boundary and the E/B boundary, estimated from hydrological data and soil solution concentrations (Giesler et al. 2000 Giesler, R, Ilvesniemi, H, Nyberg, L, Van Hees, P AW, Starr, M, Bishop, K, Kareinen, T and Lundström, U S. 2000. Distribution and mobilization of Al, Fe and Si in three podzolic soil profiles in relation to the humus layer. *Geoderma*, 94: 249–263.) confirm this hypothesis.

In this hypothesis, the release of dissolved Si and (organically complexed) Al in the O horizon is an integral part of the process of podzolization itself, which in this case appears to be driven by plant-ectomycorrhizal associations in search of nutrients (Van Breemen et al. 2000b Van Breemen, N, Lundström, U S and Jongmans, A G. 2000b. Do plants drive podzolization via rock-eating mycorrhizal fungi?. *Geoderma*, 94: 163–171.).

An extensive survey of 75 soils from Europe, Asia, North America and Australia revealed that tunnelled minerals occur almost exclusively in podzols in temperate and boreal zones, and also sometimes in acid brown forest soils (Hoffland et al. 2005 Hoffland, E, Smits, M M, Van Schöll, L and Landeweert, R. 2005. "Rock-eating mycorrhizas: mobilizing nutrients from minerals?". In *Plant nutrition for food security, human health and environmental protection* Edited by: Li, C J, Zhang, F S, Doberman, A, Hinsinger, P, Lambers, H, Li, X L, Marschner, P, Maene, L, McGrath, S, Oenema, O, Peng, S B, Rengel, Z, Shen, Q R and Welch, R. 802–803. Beijing). No tunnelled minerals were observed in podzol soils that had developed under the arbuscular mycorrhizal kauri (*Agathis australis*) in New Zealand. Northern temperate and boreal podzols typically develop under a vegetation of ECM coniferous trees, with an undergrowth of ericaceous shrubs, and develop in a time-scale of several hundred to thousand years (Lundström et al. 2000 Lundström, U S, Van Breemen, N and Bain, D. 2000. The podzolization process. A review. *Geoderma*, 94: 91–107.). These northern temperate and boreal podzols are therefore indicative for the long-term presence of ECM fungi.

It is not clear if ericoid endomycorrhiza play a role in the podzolization commonly found under ericaceous plants. Ericoid fungi can also produce high amounts of LMWOAs (Martino et al. 2003a Martino, E, Perotto, S, Parsons, R and Gadd, G M. 2003a. Solubilization of insoluble inorganic zinc compounds by ericoid mycorrhizal fungi derived from heavy metal polluted sites. *Soil Biol*

Biochem, 35: 133–141.), and may thereby contribute to tunnel formation. It seems unlikely, however, that ericoid mycorrhizal fungi are (solely) responsible for tunnel formation, as tunnels were found in sites with no ericoid mycorrhizal plants, and where they are unlikely to have grown, considering the rapid establishment of the productivity gradient following deglaciation (Giesler et al. 1998 Giesler, R, Högberg, M and Högberg, P. 1998. Soil chemistry and plants in Fennoscandian boreal forest as exemplified by a local gradient. *Ecology*, 79: 119–137.). ECM fungi could therefore have been responsible or co-responsible for tunnel formation.

The contribution of ECM mineral tunnelling to total weathering was quantified via image analysis in soil thin sections (Smits et al. 2005 Smits, M M, Hoffland, E and Van Breemen, N. 2005. Contribution of mineral tunneling to total feldspar weathering. *Geoderma*, 125: 59–69.) which were taken from a North Michigan dune chronosequence.

Although it was initially postulated that mineral tunnelling by fungal hyphae might contribute substantially to weathering, measurements by Smits and colleagues (2005) Smits, M M, Hoffland, E and Van Breemen, N. 2005. Contribution of mineral tunneling to total feldspar weathering. *Geoderma*, 125: 59–69. showed that the contribution to total feldspar weathering is less than 1%, suggesting that the weathering of mineral surfaces is quantitatively more important. Output from an improved version of the model (Smits et al. 2008 Smits, M M, Bonneville, S, Haward, S and Leake, J R. 2008. Ectomycorrhizal weathering, a matter of scale?. *Mineral Magaz*, 72: 131–134.) indicated that surface weathering is an order of magnitude higher than weathering through tunnelling.

In chronosequences, tunnelled minerals only emerged when easily weatherable base cation-containing minerals had disappeared (biotite) or were strongly weathered (hornblende), suggesting that ECM fungal weathering is driven by the (reduced) bioavailability of K, Ca and Mg (Hoffland et al. 2002 Hoffland, E, Giesler, R, Jongmans, T and Van Breemen, N. 2002. Increasing feldspar tunneling by fungi across a North Sweden podzol chronosequence. *Ecosystems*, 5: 11–22. ; Smits et al. 2005 Smits, M M, Hoffland, E and Van Breemen, N. 2005. Contribution of mineral tunneling to total feldspar weathering. *Geoderma*, 125: 59–69.). Tunnelling is therefore only one aspect of ECM weathering. *Surface weathering* by ECM fungi is likely to be quantitatively more important, as also proposed by Van Hees et al. (2004) Van Hees, P AW, Jones, D L, Jentschke, G and Godbold, D L. 2004. Mobilization of aluminium, iron and silicon by *Picea abies* and ectomycorrhizas in a forest soil. *Eur J Soil Sci*, 55: 101–111. based on a scanning electron microscope study. Most mycorrhizal fungi grow in unsaturated soils and are intolerant of waterlogging.

Their mycelial networks strongly attach to mineral surfaces, and weathering processes are likely to be initiated and to proceed directly at the mineral-fungal interface. This interface may therefore play a far greater role in initiating and controlling the weathering rates than previously thought. There is clearly a large potential for interaction between mycorrhizal hyphae and mineral surfaces and researches by Rosling et al. (2003) Rosling, A, Landeweert, R, Lindahl, B, Larsson, K H, Kuyper, T W, Taylor, A FS and Finlay, R. 2003. Vertical distribution of ectomycorrhizal root tips in a podzol soil profile. *New Phytol*, 159: 775–783. revealed that at least 50% of the mycorrhizal fungal taxa found in a podzol soil in the North of Sweden were exclusively associated with the mineral soil horizons.

Surprisingly, this was the first detailed study to consider ectomycorrhizal taxa throughout the soil profile since almost all studies are confined to the upper organic horizons. In a soil column study by van Hees et al. (2004) Van Hees, P AW, Jones, D L, Jentschke, G and Godbold, D L. 2004. Mobilization of aluminium, iron and silicon by *Picea abies* and ectomycorrhizas in a forest soil. *Eur J Soil Sci*, 55: 101–111. , the presence of young *Picea abies* trees and the ectomycorrhizal fungus *P. involutus* increased Al and Si mobilization 1.5–2 times as compared to non-planted

controls, despite similar pH values. The possible enhancement of Al and Si mobilization by hyphae was mainly attributed to surface dissolution.

In soil, hyphae tightly enclose mineral particles (Robert and Berthelin 1986 Robert, M and Berthelin, J. 1986. "Role of biological and biochemical factors in soil mineral weathering". In *Interactions of Soil Minerals with Natural Organics and Microbes*, Edited by: Huang, P M and Schnitzer, M. 453–495. SSSA special publication. 17. ; Van Breemen et al. 2000a Van Breemen, N, Finlay, R D, Lundström, U, Jongmans, A G, Giesler, R and Olsson, M. 2000a. Mycorrhizal weathering: a true case of mineral nutrition?. *Biogeochemistry*, 49: 53–67.) and penetrate mineral interlayer spaces (Robert and Berthelin 1986 Robert, M and Berthelin, J. 1986. "Role of biological and biochemical factors in soil mineral weathering". In *Interactions of Soil Minerals with Natural Organics and Microbes*, Edited by: Huang, P M and Schnitzer, M. 453–495. SSSA special publication. 17.). Mat-forming fungi provide a clear example of ectomycorrhizal surface mineral weathering. In forest soil, certain species of ectomycorrhizal fungi (*Hysterangium* spp., *Hydnellum* spp. and *Gautieria* spp.) form mat-like structures at the interface of the surface humus layer and upper mineral soil. These fungal mats can cover several m^2 of forest floor (Entry et al. 1992 Entry, J A, Rose, C L and Cromack, K. 1992. Microbial biomass and nutrient concentrations in hyphal mats of the ectomycorrhizal fungus *Hysterangium setchellii* in a coniferous forest soil. *Soil Biol Biochem*, 24: 447–453.). The mineral soil within this concentrated mass of hyphae is often weathered more strongly than the surrounding soil and this has been attributed to the excretion of oxalic acid by the mat-forming ectomycorrhizal fungus. Within the mats, calcium oxalate crystals are abundant and decomposition rates and nutrient availability are increased relative to the adjacent soil (Entry et al. 1992 Entry, J A, Rose, C L and Cromack, K. 1992. Microbial biomass and nutrient concentrations in hyphal mats of the ectomycorrhizal fungus *Hysterangium setchellii* in a coniferous forest soil. *Soil Biol Biochem*, 24: 447–453.).

LMWOAs production by ECM can increase in *nutrient deficiency conditions*. ECM fungi might increase mineral weathering by exuding LMWOAs in response to P or Mg and K deficiencies (Hoffland et al. 2004 Hoffland, E, Kuyper, T W, Wallander, H, Plassard, C, Gorbushina, A A, Haselwandter, K, Holmström, S, Landeweert, R, Lundström, U, Rosling, A, Sen, R, Smits, M, van Hees, P and Van Breemen, N. 2004. The role of fungi in weathering. *Front Ecol Environ*, 2: 258–264.). Enhanced oxalate exudation in response to Mg and K deficiency has been shown for ectomycorrhizal fungi *in vitro* (Paris et al. 1996 Paris, F, Botton, B and Lapeyrie, F. 1996. *In vitro* weathering of phlogopite by ectomycorrhizal fungi. II. Effect of K$^+$ and Mg^{2+} deficiency and N sources on accumulation of oxalate and H$^+$. *Plant Soil*, 179: 141–50.) and in symbiosis with a host tree (Van Schöll et al. 2006a Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163.). Van Schöll et al. (2006a) Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163. tested the hypothesis that ECM fungi enhance the exudation of LMWOAs when Mg, K and P are in low supply to increase the mobilization of these base cations from mineral grains. The response of tree seedlings and ECM fungi grown in pure culture can be different from the response when grown in symbiosis. Ectomycorrhizal fungi and *Pinus sylvestris* seedlings were cultured in symbiosis and in isolation with a complete nutrient supply or with Mg, K, P or N in low supply.

The fungal species used were *P. involutus*, which is commonly associated with organic soil horizons; *Piloderma croceum* (also known as *Piloderma fallax*), which has been found in both organic and mineral horizons; and *Hebeloma longicaudum* which has been found in the mineral horizon (Laiho 1970 Laiho, O. 1970. *Paxillus involutus* as a mycorrhizal symbiont of forest trees. *Acta For Fenn*, 106: 5–72. ; Landeweert et al. 2003 Landeweert, R, Leeflang, P, Kuyper, T W,

Hoffland, E, Rosling, A, Wernars, K and Smit, E. 2003. Molecular identification of ectomycorrhizal mycelium in soil horizons. *Appl Environ Microbiol*, 69: 327–333.). Concentrations of all dicarboxylic LMWOA in the rooting medium were measured. Nonmycorrhizal seedlings released predominantly malonate. Colonization with *Hebeloma longicaudum* decreased the amount of organic anions exuded, whereas *P. involutus* and *P. croceum* increased the concentration of oxalate but not the total amount of LMWOA. Phosphorus deficiency increased the concentration of LMWOA by nonmycorrhizal and ECM seedlings. Magnesium deficiency increased the concentration of oxalate by nonmycorrhizal and ECM seedlings, but not the concentration of total LMWOA. K limitation did not influence the exudation of LMWOAs by nonmycorrhizal and ECM seedlings.

The authors concluded that ectomycorrhizal fungi did not increase the total concentration of LMWOA compared with nonmycorrhizal seedlings but, depending on the fungal species, they affected the type of LMWOA found. The fact that P limitation significantly increased the total concentrations of LMWOAs is in contrast with the results reported by Van Hees et al. (2003) Van Hees, P AW, Godbold, D L, Jentschke, G and Jones, D L. 2003. Impact of ectomycorhizas on the concentration and biodegradation of simple organic acids in a forest soil. *Eur J Soil Sci*, 54: 697–706. , who did not find any effect of omitting P from the nutrient solution. In the latter study anyway there was a very high turnover of organic anions, as evidenced from the low concentrations found, and this may have obscured treatment effects.

Van Schöll et al. (2006a) Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163. also showed that *P. involutus* grown in pure culture responded differently to low nutrient supply compared with symbiotic growth. Under P deficiency, the concentration of malonate, but not oxalate, exuded by *P. involutus* in pure culture was significantly increased compared with complete nutrition or limited N, Mg or K. Also, acidification was stronger with low P supply than with low N, Mg K or complete nutrient supply. These findings can explain the high phosphate-solubilizing activity of *P. involutus* found by Lapeyrie et al. (1991) Lapeyrie, F, Ranger, J and Vairelles, D. 1991. Phosphate-solubilizing activity of ectomycorrhizal fungi in vitro. *Can J Bot*, 69: 342–346. .

These results show the potential of trees and ECM fungi to manipulate their environment and to respond to nutrient deficiencies by increasing the exudation of LMWOAs with high weathering ability.

Among the micronutrients derived from soil minerals, iron is essential for various cellular processes (Neilands 1995 Neilands, JB. 1995. Siderophores. Structure and function of microbial iron transport compounds. *J Biol Chem*, 270: 26723–26726. ; Rineau et al. 2008 Rineau, F, Courty, P E, Uroz, S, Buée, M and Garbaye, J. 2008. Simple microplate assays to measure iron mobilization and oxalate secretion by ectomycorrhizal tree roots. *Soil Biol Biochem*, 40: 2460–2463.). It is abundant in soils but, in the aerobic conditions and at the most frequent soil pH values (6–8), it is mostly present as insoluble ferric iron hydroxides, a form unaccessible for living organisms (Dancis et al. 1990 Dancis, A, Klausner, R D, Hinnesbuch, A G and Barriocanal, J G. 1990. Genetic evidence that ferric reductase is required for iron uptake in *Saccharomyces cerevisiae*. *Mol Cell Biol*, 10: 2294–2301.).

All plants except the grasses use the Strategy I response to solubilize and transport iron into roots when iron is limiting: a proton pump acidifies the rhizosphere, a ferric chelate reductase converts Fe(III)-chelates to Fe(II) and a Fe(II) transporter moves iron into cells. Grasses produce small molecules with high affinity for ferric iron called phytosiderophores (PSs): PS are secreted into the

rhizosphere where they chelate and help to solubilize Fe(III). The Fe(III)–PS complex is then taken up into root cells through the action of Yellow Stripe1 (YS1) proteins (Walker and Connolly 2008 Walker, E L and Connolly, E L. 2008. Time to pump iron: iron-deficiency-signaling mechanisms of higher plants. *Current Op Pl Biol*, 11: 530–535.).

To have access to the soil iron reservoir, also ECM fungi produce *siderophore* (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254. ; Howard 2004 Howard, DH. 2004. Iron gathering by zoopathogenic fungi. *FEMS Immunol Med Microbiol*, 40: 95–100. ; Kraemer 2004 Kraemer, SM. 2004. Iron oxide dissolution and solubility in the presence of siderophores. *Aquatic Sci*, 66: 3–18.). Ericoid mycorrhizal fungi release ferricrocin or fusigen as the main siderophores. Ferricrocin was also shown to be produced by the ectomycorrhizal fungi *Cenococcum geophilum* and *Hebeloma crustuliniforme*. Arbuscular mycorrhizal fungi are reported to enhance Fe-uptake rates of associated host plants, which can be taken as an indication that mycorrhizal siderophores of a yet unknown structure may be involved. Mycorrhizal fungi of orchids were shown to produce as the main siderophores, both well known ferrichrome-type siderophores or the novel linear trishydroxamate basidiochrome (Haselwandter 2008 Haselwandter, K. 2008. Structure and function of siderophores produced by mycorrhizal fungi. *Mineral Mag*, 72: 61–64.).

Physical Disintegration Mechanisms

A very interestingly work was recently published by Bonneville and collaborators (2009) Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618. . Their findings indicate that fungal weathering is predominantly occurring at the hypha-mineral interface with an early mechanical forcing acting in concert with later chemical alteration of micaceous minerals. They reported for the first time, *in situ* observations at the nanometer scale of the early stages of weathering of biotite by an ectomycorrhizal fungus, *P. involutus*, grown under axenic and controlled temperature, humidity, and photoperiod conditions in symbiosis with a boreal pine tree, *P. sylvestris*.

This approach recreates the essential symbiotic relationship between the tree and the mycorrhizal fungus under the typical unsaturated conditions found in soils, while excluding all other potential weathering pathways (i.e., soil pore water and other soil microorganisms). Ultramicroscopic and spectroscopic analysis of the fungus-biotite interfaces revealed intimate fungal-mineral attachment, biomechanical forcing, altered interlayer spacings, substantial depletion of potassium (~50 nm depth), oxidation of the biotite Fe(II), and the formation of vermiculite and clusters of Fe(III) oxides. The study by Bonneville and collaborators (2009) Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618. demonstrated the biomechanical-chemical alteration interplay at the fungus-biotite interface at the nanometer scale.

They specifically observed that the weathering process was initiated by physical distortion of the lattice structure of biotite within 1 μm of the attached fungal hypha. Only subsequently did the distorted volume become chemically altered through dissolution and oxidation reactions that lead to mineral neoformation. The lattice distortion at the hyphae-biotite contact was likely a consequence of fungal attachment and growth across the biotite surface. Fungal attachment to mineral surfaces usually occurs via class I hydrophobins, which are ubiquitous hyphal surface proteins of basidiomycete fungi (Wosten et al. 1993 Wosten, H AB, De Vries, O MH and Wessels, J GH. 1993. Interfacial self-assembly of a fungal hydrophobin into a hydrophobic rodlet layer. *The Plant Cell*, 5:

1567–1574. , Tagu et al. 2002 Tagu, D, Marmeisse, R, Baillet, Y, Riviere, S, Palin, B, Bernardini, F, Mereau, A, Gay, G, Balestrini, R, Bonfante, P and Martin, F. 2002. Hydrophobins in ectomycorrhizas: heterologous transcription of the *Pisolithus* HydPt-1 gene in yeast and *Hebeloma cylindrosporum*. *Europ J Histochem*, 46: 23–29.) such as *P. involutus*, and which allow hyphae to bind strongly to virtually all mineral surfaces.

In addition to their adhesion abilities, the internal hyphal pressures can vary between 0.4 and 1 MPa (Harold 2002 Harold, FM. 2002. Force and compliance: Rethinking morphogenesis in walled cells. *Fungal Gen Biol*, 37: 271–282.) (one or two orders of magnitudes higher than other soil microorganisms can achieve but of the same magnitude order of the root turgor pressure—0.2–0.9 MPa (Palta et al. 1987 Palta, J A, Wyn-Jones, R G and Deri Tomos, A. 1987. Leaf Diffusive Conductance and Tap Root Cell Turgor Pressure of Sugarbeet. *Plant Cell Environm*, 10: 735–740. ; Atwell and Newsome 1990 Atwell, B J and Newsome, J C. 1990. Turgor Pressure in Mechanically Impeded Lupin Roots. *Aust J Plant Physiol*, 17: 49–56. ; Clark et al. 2001 Clark, L J, Whalley, W R and Barraclough, B P. 2001. Partial mechanical impedance can increase the turgor of seedling pea roots. *J Exp Bot*, 52: 167–171.) and reach as high as 8 MPa (or 80 bars) in specialized penetrative structures (appressoria) (Bechinger et al. 1999 Bechinger, C, Giebel, K-F, Schnell, M, Leiderer, P, Deising, H B and Bastmeyer, M. 1999. Optical measurements of invasive forces exerted by appressoria of a plant pathogenic fungus. *Science*, 285: 1896–1899.).

This high internal pressure is believed both to drive hyphal growth (Bastmeyer et al. 2002 Bastmeyer, M, Deising, H B and Bechinger, C. 2002. Force exertion in fungal infection. *Ann Rev Bioph Biom Struct*, 31: 321–341.) and to be an evolutionary adaptation to penetrate plant tissue and rock surfaces (Jongmans et al. 1997 Jongmans, A G, van Breemen, N, Lundström, U S, van Hees, P AW, Finlay, R D, Srinivasan, M, Unestam, T, Giesler, R, Melkerud, P-A and Olsson, M. 1997. Rock-eating fungi. *Nature*, 389: 682–683. ; Money 1999 Money, PN. 1999. Fungus punches its way in. *Science*, 201: 332–333.). These observations suggest that the high internal pressure of the hyphal tip, especially during growth, combined with the firm adhesion of the growing hyphae to the biotite surface, may create a downward component of force and/or stress large enough to mechanically affect the biotite crystal structure orientation. The increase in size of the potassium depletion zone suggests a progressive potassium transfer from the biotite to the hypha and probably to the tree root system.

Cation uptake by fungi is usually achieved by proton pumps, which acidify their near environment (Lian et al. 2007 Lian, B, Wang, B, Pan, M, Liu, C and Teng, H H. 2007. Microbial release of potassium from K-bearing minerals by thermophilic fungus *Aspergillus fumigatus*. *Geoch Cosmoch Acta*, 72: 87–98.). Protons diffusing into the biotite substitute the potassium in the interlayer and ultimately cause the partial transformation of biotite into potassium-free vermiculite adjacent to the hypha. The role of the fungi in the oxidation of Fe(II), and especially whether this is an active biological process or a secondary effect of the fungal weathering of biotite, is unclear. Microcavities formed during the very early stages of contact may facilitate the penetration of oxidizing compounds or exudates into the biotite structure, possibly causing Fe(II) oxidation. The formation of vermiculite and/or Fe(III) oxide subdomains is commonly reported to be the first step in biotite weathering under abiotic acidic conditions in liquid media (Murakami et al. 2003 Murakami, T, Utsunomiya, S, Yokoyama, T and Kasama, T. 2003. Biotite dissolution processes and mechanisms in the laboratory and in nature: Early stage weathering environment and vermiculitization. *Am Mineral*, 88: 377–386.).

Bonneville et al. (2009) Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618. demonstrated, under close to natural conditions and in a

liquid-free medium, that such secondary minerals can also be formed in relatively short periods at the interface between living fungal hyphae and biotite. The mechanism documented in their study is a significant advance on previous simplistic concepts of biotic weathering relying solely on the effects of fungal exudates (i.e., organic acids, ligands, and siderophores) released into the soil pore water. Those exudates are thought to consist of aqueous ligands for elements of biological interest, for example oxalic acid, which strongly binds iron in solution; hence, thermodynamically favoring the dissolution of iron-bearing minerals.

Through weakening of the biotite lattice structure and the formation of microcavities (increase of mineral surface area), the mechanical forcing of the mineral surface by the hypha greatly enhances the chemical weathering rates, which in turn will promote further physical breakdown of the mineral. This mechanical-chemical weathering interplay at the hypha-mineral interface therefore provides the ECM fungus with a hitherto unsuspected means to weather rocks and to actively acquire essential nutrients for plant growth in return for photosynthate carbon. Ultimately these processes form soils. Given the ubiquitous occurrence of ECM fungi in symbiotic association in boreal and temperate forests, these findings have major implications for our understanding of the link between biologically induced rock weathering and the carbon cycle at the global scale (Bonneville et al. 2009 Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618.).

MYCORRHIZAL FUNGAL WEATHERING AND PLANT NUTRITION

Minerals are a reservoir of nutrients in the soil. Evidence which indicates that mineral weathering by soil microorganisms affects ion cycling and plant nutrition is accumulating (Toro et al. 1997 Toro, M, Azcon, R and Barea, J. 1997. Improvement of arbuscular mycorrhizal development by inoculation of soil with phosphate-solubilizing rhizobacteria to improve rock phosphate bioavailability (32P) and nutrient cycling. *Appl Environ Microbiol*, 63: 4408–4412. ; Wallander 2000a Wallander, H. 2000a. Uptake of P from apatite by *Pinus sylvestris* seedlings colonised by different ectomycorrhizal fungi. *Plant Soil*, 218: 249–256. , 2000b Wallander, H. 2000b. Use of strontium isotopes and foliar K content to estimate weathering of biotite induced by pine seedlings colonised by ectomycorrhizal fungi from two different soils. *Plant Soil*, 222: 215–229. ; Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254. ; Calvaruso et al. 2006 Calvaruso, C, Turpault, M P and Frey-Klett, P. 2006. Root-associated bacteria contribute to mineral weathering and to mineral nutrition in trees: a budgeting analysis. *Appl Environ Microbiol*, 72: 1258–1266.), as already mentioned in the previous paragraph. The physical, chemical and biological weathering of minerals play in fact a major role in forest ecosystems as these processes release numerous nutrients required for tree growth (e.g., phosphorus, potassium, magnesium, calcium, and iron) (Uroz et al. 2007 Uroz, S, Calvaruso, C, Turpault, M P, Pierrat, J C, Mustin, C and Frey-Klett, P. 2007. Effect of the mycorrhizosphere on the genotypic and metabolic diversity of the bacterial communities involved in mineral weathering in a forest soil. *Appl Environ Microbiol*, 73: 3019–3027.). Several studies have shown an increased uptake of mineral-derived nutrients by trees when in symbiosis with ECM fungi (Leyval and Berthelin 1993 Leyval, C and Berthelin, J. 1993. Rhizodeposition and net release of soluble organic compounds by pine and beech seedlings inoculated with rhizobacteria and ectomycorrhizal fungi. *Biol Fertil Soils*, 15: 259–267. ; Olsson and Wallander 1998 Olsson, P A and Wallander, H. 1998. Interactions between ectomycorrhizal fungi and the bacterial community in soil amended with various primary minerals. *FEMS Microbiol Ecol*, 27: 195–205. ; Wallander and Wickman 1999

Wallander, H and Wickman, T. 1999. Biotite and microcline as potassium sources in ectomycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Mycorrhiza*, 9: 25–32. ; Wallander 2000a Wallander, H. 2000a. Uptake of P from apatite by *Pinus sylvestris* seedlings colonised by different ectomycorrhizal fungi. *Plant Soil*, 218: 249–256. , 2000b Wallander, H. 2000b. Use of strontium isotopes and foliar K content to estimate weathering of biotite induced by pine seedlings colonised by ectomycorrhizal fungi from two different soils. *Plant Soil*, 222: 215–229. ; Van Schöll et al. 2006a Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163.).

The hypothesis that ECM fungi contribute to the uptake and subsequent transport to the tree of base cations through the enhanced weathering of soil mineral grains implied a new role of ECM in plant nutrition (Van Schöll et al. 2008 Van Schöll, L, Kuyper, T W, Smits, M M, Landeweert, R, Hoffland, E and van Breemen, N. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. *Plant Soil*, 303: 35–47.). The role of ECM fungi in the uptake of N and P is well established (Smith and Read 2008 Smith, S E and Read, D J. 2008. *Mycorrhizal symbiosis* , 3rd edn, Academic Press.). The role of ECM fungi in weathering and subsequent uptake of base cations is potentially increasingly important in situations where acid rain and intensive biomass harvesting increase losses and decrease storage of K, Mg and Ca.

Under the present conditions, forest growth in some stands may become limited by K and/or Mg rather than N (Landman et al. 1997 Landmann, G, Hunter, I R and Hendershot, W. 1997. "Temporal and spatial development of magnesium deficiency in forest stands in Europe, North America and New Zealand". In *Magnesium deficiency in forest ecosystems*, Edited by: Hüttl, R F and Schaaf, W. Dordrecht: Kluwer. ; Übel and Heinsdorf 1997 Übel, E and Heinsdorf, D. 1997. Results of long-term K and Mg fertilizer experiments in afforestation. *For Ecol Manag*, 91: 47–52. ; Thelin 2000 Thelin, G. 2000. "Nutrient imbalance in Norway spruce". Ph.D. thesis, Lund University.). An increased uptake of mineral-derived nutrients by tree seedlings when grown in symbiosis with ECM fungi has been found in several pot experiments (Wallander 2006 Wallander, H. 2006. "Mineral dissolution by ectomycorrhiza". In *Fungi in biogeochemical cycles*, Edited by: Gadd, G M. 681–717. Cambridge: Cambridge University Press.).

Phosphorus is an essential element for plant and microbial nutrition and can only be assimilated as soluble phosphate species. However, in the soil, a large proportion of the phosphorus pool is poorly soluble, which means that the mechanisms by which fungi and plants obtain phosphate are of major significance. Plants have evolved a range of adaptive morphological, biochemical and symbiotic strategies that increase the acquisition of Pi and/or improve the efficiency of internal utilization of Pi. Among these adaptations is an increase of root hair formation and the formation of cluster roots by some species (López-Bucio et al. 2003 López-Bucio, J, Cruz-Ramírez, A and Herrera-Estrella, L. 2003. The role of nutrient availability in regulating root architecture. *Current Op Pl Biol*, 6: 280–287.). Cluster roots comprise bottlebrush-like clusters of rootlets of determinate development arising along the lateral roots. They have been found in a range of plant species adapted to habitats of extremely low soil fertility (members of the Proteaceae, Cyperaceae and Restionaceae families).

These combine a high density of determinate lateral roots in a localised soil volume for gathering Pi, with a synchronised release of organic acids and acid phosphatases that increase the availability of Pi in the immediate vicinity of these roots. Most agricultural, heath and forest species that form cluster roots do not appear to become colonised by mycorrhizal fungi. Formation of cluster roots or mycorrhizal colonisation therefore appears to be alternative strategies for improving Pi acquisition in most species (López-Bucio et al. 2003 López-Bucio, J, Cruz-Ramírez, A and Herrera-Estrella, L. 2003. The role of nutrient availability in regulating root architecture. *Current Op Pl Biol*, 6: 280–

287. ; Lambers et al. 2008 Lambers, H, Raven, J A, Shaver, G R and Smith, S E. 2008. Plant nutrient-acquisition strategies change with soil age. *Trends Ecol Evol*, 23: 95–103.).

The important role of mycorrhizal fungi in improving plant phosphorus nutrition has been reported by numerous studies, emphasizing the phosphate-solubilizing ability of mycorrhizal fungi (i.e. calcium and iron phosphates) (Leyval and Berthelin 1986 Leyval, C and Berthelin, J. 1986. "Comparison between the utilization of phosphorus from insoluble mineral phosphates by ectomycorrhizal fungi and rhizobacteria". In *Physiological and genetical aspects of mycorrhizae: Proceedings of the 1st European Symposium on Mycorrhizae*, Edited by: Gianinazzi Pearson, V and Gianinazzi, S. 345–349. Dijon. Paris, , France: INRA. ; Lapeyrie et al. 1991 Lapeyrie, F, Ranger, J and Vairelles, D. 1991. Phosphate-solubilizing activity of ectomycorrhizal fungi in vitro. *Can J Bot*, 69: 342–346. ; Wallander et al. 1997 Wallander, H, Wickman, T and Jacks, G. 1997. Apatite as a P source in mycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Plant Soil*, 196: 123–131. ; Whitelaw 2000 Whitelaw, MA. 2000. Growth promotion of plants inoculated with phosphate-solubilizing fungi. *Adv Agron*, 69: 99–151.). The ability to solubilize poorly soluble calcium phosphates, such as hydroxyapatite, has been described for a range of ECM fungi (*Pisolithus, Paxillus, Trichoderma*, and *Suillus*) (Paris et al. 1996 Paris, F, Botton, B and Lapeyrie, F. 1996. *In vitro* weathering of phlogopite by ectomycorrhizal fungi. II. Effect of K^+ and Mg^{2+} deficiency and N sources on accumulation of oxalate and H^+. *Plant Soil*, 179: 141–50. , Altomare et al. 1999 Altomare, C, Norvell, W A, Bjorkman, T and Harman, G E. 1999. Solubilization of phosphates and micronutrients by the plant-growth-promoting and biocontrol fungus *Trichoderma harzianum rifai* 1295–22. *Appl Environ Microbiol*, 65: 2926–2933. , Wallander 2000a Wallander, H. 2000a. Uptake of P from apatite by *Pinus sylvestris* seedlings colonised by different ectomycorrhizal fungi. *Plant Soil*, 218: 249–256. , 2000b Wallander, H. 2000b. Use of strontium isotopes and foliar K content to estimate weathering of biotite induced by pine seedlings colonised by ectomycorrhizal fungi from two different soils. *Plant Soil*, 222: 215–229.). The same fungi proved to be able to weather silicates as well (Altomare et al. 1999 Altomare, C, Norvell, W A, Bjorkman, T and Harman, G E. 1999. Solubilization of phosphates and micronutrients by the plant-growth-promoting and biocontrol fungus *Trichoderma harzianum rifai* 1295–22. *Appl Environ Microbiol*, 65: 2926–2933. , Wallander 2000a Wallander, H. 2000a. Uptake of P from apatite by *Pinus sylvestris* seedlings colonised by different ectomycorrhizal fungi. *Plant Soil*, 218: 249–256. , 2000b Wallander, H. 2000b. Use of strontium isotopes and foliar K content to estimate weathering of biotite induced by pine seedlings colonised by ectomycorrhizal fungi from two different soils. *Plant Soil*, 222: 215–229.). Concerning arbuscular mycorrhizal (AM) fungi, AM plants utilize more soluble phosphorus from soil mineral phosphate than non-inoculated plants (Duponnois et al. 2005 Duponnois, R, Colombet, A, Hien, V and Thioulouse, J. 2005. The mycorrhizal fungus *Glomus intraradices* and rock phosphate amendment influence plant growth and microbial activity in the rhizosphere of *Acacia holosericea*. *Soil Biol Biochem*, 37: 1460–1468.).

Duponnois et al. (2005) Duponnois, R, Colombet, A, Hien, V and Thioulouse, J. 2005. The mycorrhizal fungus *Glomus intraradices* and rock phosphate amendment influence plant growth and microbial activity in the rhizosphere of *Acacia holosericea*. *Soil Biol Biochem*, 37: 1460–1468. examined the AM fungus, *Glomus intraradices* for its effect on the growth of *Acacia holosericea* and on the plant-available phosphate. *G. intraradices* inoculation was highly beneficial to the growth of *A. holosericea* plants in controlled conditions, optimising P solubilization from the mineral phosphate.

Most forest ecosystems are considered to be *N-limited*. For a wide range of fungi, oxalate production is stimulated by low N availability (Dutton and Evans 1996 Dutton, M V and Evans, C S. 1996. Oxalate production by fungi: Its role in pathogenicity and ecology in the soil environment. *Can J Microbio*, 42: 881–895.). *P. involutus* increased the concentration of oxalate in response to N

limitation when grown in pure culture (Van Schöll et al. 2006a Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163.). On the other hand, in areas with high levels of N deposition, Mg, K and P can become limiting (Tamm et al. 1999 Tamm, C O, Aronsson, A, Popovic, B and Flower Ellis, J. 1999. Optimum nutrition and nitrogen saturation in Scots pine stands. *Studia Forest Sue*, 1999: 1–126.), and enhanced weathering of mineral grains by increased exudation of LMWOAs can become an important mechanism for nutrient supply and forest growth. It is broadly held that mycorrhizas are relatively unimportant in disturbed and N-limited soils dominated by fast-growing species (e.g., many species belonging to Brassicaceae and Chenopodiaceae), which flourish on disturbed sites and complete their life cycle rapidly; these species exhibit no special strategies other than rapid growth of roots, and formation of root hairs (Lambers et al. 2008 Lambers, H, Raven, J A, Shaver, G R and Smith, S E. 2008. Plant nutrient-acquisition strategies change with soil age. *Trends Ecol Evol*, 23: 95–103.).

Although phosphorus becomes increasingly limiting in ancient soils, as it gradually disappears through leaching and erosion, nitrogen tends to limit plant productivity on young soils. As already discussed, adaptations to N- and P-limited conditions include mycorrhizas and cluster roots. Mycorrhizas 'scavenge' P from solution or 'mine' insoluble organic N. Cluster roots function in severely P-impoverished landscapes, 'mining' P fixed as insoluble inorganic phosphates. The 'scavenging' and 'mining' strategies of mycorrhizal species without and non-mycorrhizal species with cluster roots, respectively, allow functioning on soils that differ markedly in P availability (Lambers et al. 2008 Lambers, H, Raven, J A, Shaver, G R and Smith, S E. 2008. Plant nutrient-acquisition strategies change with soil age. *Trends Ecol Evol*, 23: 95–103.). Anyway, the cluster root strategy is not restricted to ancient landscapes, but also occurs in many species in North America and Europe, where it tends to increase in importance in either relatively acidic or calcareous soils, where P is immobilized. There are thus many ecosystems where plants with all the possible N- and P-acquisition strategies coexist.

Long-term pot experiments showed that ECM seedlings are able to mobilize and take up phosphorus but also *potassium*, *magnesium* and *iron* from rock phosphate, phlogopite (mica), biotite, apatite or vermiculite (Leyval and Berthelin 1989 Leyval, C and Berthelin, J. 1989. Interactions between Laccaria laccata, *Agrobacterium radiobacter* and beech roots: influence on P, K, Mg, and Fe mobilization from minerals and plant growth. *Plant Soil*, 117: 103–110. ; Paris et al. 1995a Paris, F, Bonnaud, P, Ranger, J and Lapeyrie, F. 1995a. *In vitro* weathering of phlogopite by ectomycorrhizal fungi. I. Effect of K^+ and Mg^{2+} deficiency on phyllosilicate evolution. *Plant Soil*, 177: 191–201. , 1995b Paris, F, Bonnaud, P, Ranger, J, Robert, M and Lapeyrie, F. 1995b. Weathering of ammonium- or calcium-saturated 2:1 phyllosilicates by ectomycorrhizal fungi in vitro. *Soil Biol Biochem*, 27: 1237–1244. ; Wallander et al. 1997 Wallander, H, Wickman, T and Jacks, G. 1997. Apatite as a P source in mycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Plant Soil*, 196: 123–131. ; Wallander and Wickman 1999 Wallander, H and Wickman, T. 1999. Biotite and microcline as potassium sources in ectomycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Mycorrhiza*, 9: 25–32. ; Wallander 2000b Wallander, H. 2000b. Use of strontium isotopes and foliar K content to estimate weathering of biotite induced by pine seedlings colonised by ectomycorrhizal fungi from two different soils. *Plant Soil*, 222: 215–229. ; Glowa et al. 2003 Glowa, K R, Arocena, J M and Masssicotte, H B. 2003. Extraction of potassium and/or magnesium from selected soil minerals by *Piloderma*. *Geomicrobiol J*, 20: 99–111.).

Van Schöll et al. (2006b) Van Schöll, L, Smits, M M and Hoffland, E. 2006b. Ectomycorrhizal weathering of the soil minerals muscovite and hornblende. *New Phytol*, 171: 805–814. determined the effect of ECM fungi on K and Mg availability through mineral weathering. Non-mycorrhizal and ECM tree seedlings were grown in pots with muscovite as the only K source or hornblende as

the only Mg source. Weathering of muscovite was increased by tree seedlings by a factor 1.7, and was increased even further to a factor of 3.3 when tree seedlings were colonised by *P. involutus*. However, colonisation of the tree seedlings by the ECM fungi *Suillus bovinus* or *P. croceum* did not have an additional effect. Only seedlings colonised by *P. involutus* significantly increased oxalate exudation under K deficiency.

This K deficiency-induced oxalate exudation could explain the enhanced weathering of muscovite. Therefore, the increased ECM mineral weathering in response to nutrient deficiency could be a species specific response. The *P. involutus*-mediated mobilization of K from muscovite resulted in increased K content of root plus adhering hyphae, but not of shoots. Under natural conditions, ectomycorrhizal fungi generally enhance shoot growth of their host tree, and it may be expected that mobilized K will be transported to the shoot. By retaining K in the hyphae, the K is protected against leaching (Van Schöll et al. 2006b).

Decreased leaching of K and other base cations under ectomycorrhizal seedlings compared with nonmycorrhizal seedlings has been shown by Jonnarth et al. (2003). After decomposition, the K retained in the roots and hyphae will become available for uptake. The ecosystem influx of bioavailable K will be especially important in forests where K is growth-limiting, because of a combination of high biomass removal and decreasing concentrations of K in the soil solution as a result of continuous acidification and leaching (Übel and Heinsdorf 1997 Übel, E and Heinsdorf, D. 1997. Results of long-term K and Mg fertilizer experiments in afforestation. *For Ecol Manag*, 91: 47–52. ; Jönsson et al. 2003 Jönsson, U, Rosengren, U, Thelin, G and Nihlgard, B. 2003. Acidification-induced chemical changes in coniferous forest soils in southern Sweden 1988–99. *Environ Poll*, 123: 75–83.).

The depletion of *calcium* in forest ecosystems is thought to be a consequence of acidic deposition and to be at present restricting the recovery of forest and aquatic systems (Huntington 2000 Huntington, TG. 2000. The potential for calcium depletion in forest ecosystems of southeastern United States: Review and analysis. *Glob Biogeochem Cycles*, 14: 623–638.) now that acidic deposition itself is declining (Blum et al. 2002 Blum, J D, Klaue, A, Nezat, C A, Driscoll, C T, Johnson, C E, Siccama, T G, Eagar, C, Fahey, T J and Likens, G E. 2002. Mycorrhizal weathering of apatite as important calcium source in base-poor forest ecosystems. *Nature*, 417: 729–731.). This depletion of calcium has been inferred from studies (Likens et al. 1996 Likens, G E, Driscoll, C T and Buso, D C. 1996. Long-term effects of acid rain: Response and recovery of a forest ecosystem. *Science*, 272: 244–246.) showing that sources of calcium in forest ecosystems—namely, atmospheric deposition and mineral weathering of silicate rocks such as plagioclase, a calcium-sodium silicate—do not match calcium outputs observed in forest streams. It is therefore thought that calcium is being lost from exchangeable and organically bound calcium in forest soils (Blum et al. 2002).

Blum et al. (2002) Blum, J D, Klaue, A, Nezat, C A, Driscoll, C T, Johnson, C E, Siccama, T G, Eagar, C, Fahey, T J and Likens, G E. 2002. Mycorrhizal weathering of apatite as important calcium source in base-poor forest ecosystems. *Nature*, 417: 729–731. showed that the dissolution of apatite (calcium phosphate) represents a source of calcium that is comparable in size to known inputs from atmospheric sources and silicate weathering. Moreover, apatite-derived calcium was utilized largely by ECM tree species, suggesting that mycorrhiza may weather apatite and absorb the released ions directly, without the ions entering the exchangeable soil pool. Therefore, it seems that apatite weathering can compensate for some of the calcium lost from base-poor ecosystems, and should be considered when estimating soil acidification impacts and calcium cycling (Blum et al. 2002 Blum, J D, Klaue, A, Nezat, C A, Driscoll, C T, Johnson, C E, Siccama, T G, Eagar, C,

Fahey, T J and Likens, G E. 2002. Mycorrhizal weathering of apatite as important calcium source in base-poor forest ecosystems. *Nature*, 417: 729–731.).

In most studies the effect on mineral weathering was determined via nutrient uptake into the tree seedlings (Leyval and Berthelin 1989 Leyval, C and Berthelin, J. 1989. Interactions between Laccaria laccata, *Agrobacterium radiobacter* and beech roots: influence on P, K, Mg, and Fe mobilization from minerals and plant growth. *Plant Soil*, 117: 103–110. ; Wallander et al. 1997 Wallander, H, Wickman, T and Jacks, G. 1997. Apatite as a P source in mycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Plant Soil*, 196: 123–131. ; Wallander and Wickman 1999 Wallander, H and Wickman, T. 1999. Biotite and microcline as potassium sources in ectomycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Mycorrhiza*, 9: 25–32. ; Wallander 2000a Wallander, H. 2000a. Uptake of P from apatite by *Pinus sylvestris* seedlings colonised by different ectomycorrhizal fungi. *Plant Soil*, 218: 249–256. , 2000b Wallander, H. 2000b. Use of strontium isotopes and foliar K content to estimate weathering of biotite induced by pine seedlings colonised by ectomycorrhizal fungi from two different soils. *Plant Soil*, 222: 215–229. ; Casarin et al. 2004 Casarin, V, Plassard, C, Hinsinger, P and Arvieu, J C. 2004. Quantification of ectomycorrhizal fungal effects on the bioavailability and mobilization of soil P in the rhizosphere of *Pinus pinaster*. *New Phytol*, 163: 177–185.). Interpretation of these experiments is complicated by the fact that ECM fungi can enhance growth and nutrient uptake through factors other than increased weathering: (1) ECM fungi can enhance uptake of nutrients through better soil exploration by hyphae compared with roots; (2) ECM fungi can take up N and P from organic sources largely unavailable to nonmycorrhizal roots; (3) ECM and nonmycorrhizal seedlings may be affected differently by changes in the rooting medium caused by the addition of mineral grains (e.g. changes in water availability or pH) (Van Schöll et al. 2006b Van Schöll, L, Smits, M M and Hoffland, E. 2006b. Ectomycorrhizal weathering of the soil minerals muscovite and hornblende. *New Phytol*, 171: 805–814.). These problems can be overcome by making a complete mineral budget in which all pools of mobile minerals are quantified (Van Schöll et al. 2006b Van Schöll, L, Smits, M M and Hoffland, E. 2006b. Ectomycorrhizal weathering of the soil minerals muscovite and hornblende. *New Phytol*, 171: 805–814.). In this way, Van Hees et al. (2004) Van Hees, P AW, Jones, D L, Jentschke, G and Godbold, D L. 2004. Mobilization of aluminium, iron and silicon by *Picea abies* and ectomycorrhizas in a forest soil. *Eur J Soil Sci*, 55: 101–111. showed that tree seedlings can enhance mineral weathering, as indicated by increased leaching of Al, Si and Fe, and that ECM colonization doubles mineral weathering.

In the same way, Bakker et al. (2004) Bakker, M R, George, E, Turpault, M P, Zhang, J L and Zeller, B. 2004. Impact of Douglas-fir and Scots pine seedlings on plagioclase weathering under acidic conditions. *Plant Soil*, 266: 247–259. showed that ECM seedlings of Scots pine (*P. sylvestris*) and Douglas-fir (*Pseudotsuga menziesii*) increased plagioclase weathering, but they did not distinguish between effects of trees and ECM fungi. From these and other results (Jentschke et al. 2001 Jentschke, G, Brandes, B, Kuhn, A J, Schröder, W H and Godbold, D L. 2001. Interdependence of phosphorus, nitrogen, potassium and magnesium translocation by the ectomycorrhizal fungus *Paxillus involutus*. *New Phytol*, 149: 327–337. ; Heinonsalo et al. 2004 Heinonsalo, J, Hurme, K R and Sen, R. 2004. Recent C-14-labelled assimilate allocation to Scots pine seedling root and mycorrhizosphere compartments developed on reconstructed podzol humus, E- and B-mineral horizons. *Plant Soil*, 259: 111–121. ; Rosling et al. 2004 Rosling, A, Lindahl, B D and Finlay, R D. 2004. Carbon allocation to ectomycorrhizal roots and mycelium colonising different mineral substrates. *New Phytol*, 162: 795–802. ; Van Schöll et al. 2006a Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163.) it seems clear that ECM fungi and tree seedlings can adapt to base cation deficiencies by increased proliferation and by increased mineral weathering through enhanced exudation of LMWOAs.

It remains, however, uncertain if this response is regulated by plant exudation or by fungal exudation when both organisms are grown in symbiosis. The exudation of oxalate and malonate by *P. sylvestris* seedlings and *P. involutus* in response to nutrient deficiencies differed strongly when grown either in pure culture or in symbiosis (Van Schöll et al. 2006a Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163.). Therefore only experiments with both symbiotic partners can yield ecological realism (Van Schöll et al. 2008).

ECOLOGICAL IMPORTANCE OF WEATHERING BY MYCORRHIZAL FUNGI: WEATHERING IN THE MYCORRHIZOSPHERE

Symbiotic mycorrhizal associations between plants and fungi occur, almost ubiquitously, in a wide range of terrestrial ecosystems (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.). Historically, mycorrhizal research has mainly been focused within the rather narrow perspective of the effects of the symbiosis on individual plants, in particular, the improved acquisition of dissolved mineral nutrients such as P. It is well accepted that mycorrhizal fungi improve the acquisition of mineral nutrients which are already in solution and that they do so by means of an extraradical mycelium which is a physical extension of the root system (Smith and Read 2008 Smith, S E and Read, D J. 2008. *Mycorrhizal symbiosis* , 3rd edn, Academic Press.).

By virtue of their small diameter the hyphae are also able to penetrate soil microsites which are inaccessible to plant roots. Examples of improved vegetative growth and nutrient status of individual plants following mycorrhizal inoculation abound (Smith and Read 2008 Smith, S E and Read, D J. 2008. *Mycorrhizal symbiosis* , 3rd edn, Academic Press.), especially in pot experiments, but the effects of mycorrhizal fungi on plant *fitness* are more difficult to demonstrate. More recent research has widened the context in which mycorrhizal symbiosis is viewed and placed greater emphasis on the effects of mycorrhizal symbiosis on plant communities and ecosystems (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.).

Increasing attention has been paid to the role of the extraradical mycelial phase of the symbiosis (Finlay 2005 Finlay, RD. 2005. "Action and interaction in the mycorrhizal hyphosphere: a re-evaluation of the role of mycorrhizal symbiosis in nutrient acquisition and plant ecology". In *Nutrient acquisition by plants: an ecological perspective*, Edited by: BassiriRad, H. 221–276. Heidelberg: Springer-Verlag. ; Anderson and Cairney 2007 Anderson, I C and Cairney, J WG. 2007. Ectomycorrhizal fungi: exploring the mycelial frontier. *FEMS Microbiol Rev*, 31: 388–406.) and the importance of using realistic substrates to answer relevant, ecological questions (Read and Perez-Moreno 2003 Read, D J and Perez-Moreno, J. 2003. Mycorrhizas and nutrient cycling in ecosystems—A journey towards relevance?. *New Phytol*, 157: 475–492.). Many authors have highlighted the multifunctional nature of mycorrhizal effects (Newsham et al. 1995 Newsham, K K, Fitter, A H and Watkinson, A R. 1995. Multi-functionality and biodiversity in arbuscular mycorrhizas. *Trends Ecol Evol*, 10: 407–411. ; Finlay 2004 Finlay, RD. 2004. Mycorrhizal fungi and their multifunctional roles. *Mycologist*, 18: 91–96.), including interactions with bacteria (Johansson et al. 2004 Johansson, J F, Paul, L R and Finlay, R D. 2004. Microbial interactions in the mycorrhizosphere and their significance for sustainable agriculture. *FEMS Microbiol Ecol*, 48: 1–13. ; Frey-Klett et al. 2007 Frey-Klett, J, Garbaye, J and Tarkka, M. 2007. The mycorrhiza helper

bacteria revisited. *New Phytol*, 176: 22–36.), weathering of minerals (Landeweert et al. 2001 Landeweert, R, Hoffland, E, Finlay, R D, Kuyper, T W and Van Breemen, N. 2001. Linking plants to rocks: ectomycorrhizal fungi mobilize nutrients from minerals. *Trends Ecol Evol*, 16: 248–254. ; Finlay and Rosling 2006 Finlay, R D and Rosling, A. 2006. "Integrated nutrient cycles in forest ecosystems, the role of ectomycorrhizal fungi". In *Fungi in biogeochemical cycles*, Edited by: Gadd, G M. 28–50. Cambridge: Cambridge University Press. ; Wallander 2006 Wallander, H. 2006. "Mineral dissolution by ectomycorrhiza". In *Fungi in biogeochemical cycles*, Edited by: Gadd, G M. 681–717. Cambridge: Cambridge University Press.), carbon cycling (Johnson et al. 2002 Johnson, D, Leake, J R, Ostle, N, Ineson, P and Read, D J. 2002. *In situ* $^{13}CO_2$ pulse-labelling of upland grassland demonstrates that a rapid pathway of carbon flux from arbuscular mycorrhizal mycelia to the soil. *New Phytol*, 153: 327–334.), effects on plant communities (Van der Heijden et al. 1998 Van Der Heijden, M GA, Klironomos, J N, Ursic, M, Moutoglis, P, Streitwolf-Engel, R, Boller, T, Wiemken, A and Sanders, I R. 1998. Mycorrhizal fungal diversity determines plant biodiversity, ecosystem variability and productivity. *Nature*, 396: 69–72.), tripartite syntheses with mycoheterotrophs (Leake 2004 Leake, JR. 2004. Myco-heterotroph/epiparasitic plant interactions with ectomycorrhizal and arbuscular mycorrhizal fungi. *Curr Op Pl Biol*, 7: 422–428. ; Bidartondo 2005 Bidartondo, MI. 2005. The evolutionary ecology of myco-heterotrophy. *New Phytol*, 167: 335–352.), and mediation of plant responses to stress (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.).

In the rhizosphere of forest trees, ECM fungi, microfungi, and bacteria physically interact and form multitrophic complexes that contribute to tree nutrition (Frey-Klett et al. 2005 Frey-Klett, P, Chavatte, M, Clausse, M L, Courrier, S, Le Roux, C, Raaijmakers, J, Martinotti, M G, Pierrat, J C and Garbaye, J. 2005. Ectomycorrhizal symbiosis affects functional diversity of rhizosphere fluorescent pseudomonads. *New Phytol*, 165: 317–328.). Frey et al. (1997) Frey, P, Frey-Klett, P, Garbaye, J, Berge, O and Heulin, T. 1997. Metabolic and genotypic fingerprinting of fluorescent pseudomonads associated with the Douglas fir-*Laccaria bicolor* mycorrhizosphere. *Appl Environ Microbiol*, 63: 1852–1860. and Frey-Klett et al. (2005) Frey-Klett, P, Chavatte, M, Clausse, M L, Courrier, S, Le Roux, C, Raaijmakers, J, Martinotti, M G, Pierrat, J C and Garbaye, J. 2005. Ectomycorrhizal symbiosis affects functional diversity of rhizosphere fluorescent pseudomonads. *New Phytol*, 165: 317–328. studied the genotypic and functional diversity of fluorescent pseudomonads in a forest nursery soil and demonstrated that the Douglas fir-*Laccaria bicolor* ECM symbiosis is responsible for the genotypic and functional structure of the fluorescent pseudomonad communities. This probably results from the biochemical impact of the symbiosis on the surrounding soil, the so-called mycorrhizosphere effect (Rambelli 1973 Rambelli, A. 1973. "The rhizosphere of mycorrhizae". In *Ectomycorrhizae, their ecology and physiology*, Edited by: Marks, G C and Kozlowski, T T. 299–349. New York, NY: Academic Press. ; Barea et al. 2002 Barea, J M, Azcon, R and Azcon-Aguilar, C. 2002. Mycorrhizosphere interactions to improve plant fitness and soil quality. *Anton van Leeuw*, 81: 343–351. ; Johansson et al. 2004 Johansson, J F, Paul, L R and Finlay, R D. 2004. Microbial interactions in the mycorrhizosphere and their significance for sustainable agriculture. *FEMS Microbiol Ecol*, 48: 1–13. ; De Boer et al. 2005 De Boer, W, Folman, L B, Summerbell, R C and Boddy, L. 2005. Living in a fungal world: impact of fungi on soil bacterial niche development. *FEMS Microbiol Rev*, 29: 795–811.). As the mycorrhizosphere selected strains that were able to solubilize inorganic phosphate and efficiently mobilize iron in comparison with the fluorescent pseudomonad communities in the bulk soil, Frey-Klett et al. (2005) Frey-Klett, P, Chavatte, M, Clausse, M L, Courrier, S, Le Roux, C, Raaijmakers, J, Martinotti, M G, Pierrat, J C and Garbaye, J. 2005. Ectomycorrhizal symbiosis affects functional diversity of rhizosphere fluorescent pseudomonads. *New Phytol*, 165: 317–328. suggested that the symbiosis has an indirect effect on plant nutrition via its selective pressure on bacterial communities.

Uroz et al. ([2007](#) [Uroz, S](#), [Calvaruso, C](#), [Turpault, M P](#), [Pierrat, J C](#), [Mustin, C](#) and [Frey-Klett, P](#). 2007. Effect of the mycorrhizosphere on the genotypic and metabolic diversity of the bacterial communities involved in mineral weathering in a forest soil. *Appl Environ Microbiol*, 73: 3019–3027. , [2009](#) [Uroz, S](#), [Calvaruso, C](#), [Turpault, M P](#) and [Frey-Klett, P](#). 2009. Mineral weathering by bacteria: ecology, actors and mechanisms. *Trends Microbiol*, 17: 378–387.) confirmed that the ectomycorrhizosphere determines the structure of the functional diversity of culturable bacterial communities related to the mineral-weathering process. Similar results were obtained by [Frey et al. (1997)](#) [Frey, P](#), [Frey-Klett, P](#), [Garbaye, J](#), [Berge, O](#) and [Heulin, T](#). 1997. Metabolic and genotypic fingerprinting of fluorescent pseudomonads associated with the Douglas fir-*Laccaria bicolor* mycorrhizosphere. *Appl Environ Microbiol*, 63: 1852–1860. and [Calvaruso et al. (2007)](#) [Calvaruso, C](#), [Turpault, M P](#), [Leclerc, E](#) and [Frey-Klett, P](#). 2007. Impact of ectomycorrhizosphere on the functional diversity of soil bacterial and fungal communities from a forest stand in relation to nutrient mobilization processes. *Microb Ecol*, 54: 567–577. . In nature, mycorrhizal fungi live in close association with bacterial communities. [Uroz et al. (2007)](#) [Uroz, S](#), [Calvaruso, C](#), [Turpault, M P](#), [Pierrat, J C](#), [Mustin, C](#) and [Frey-Klett, P](#). 2007. Effect of the mycorrhizosphere on the genotypic and metabolic diversity of the bacterial communities involved in mineral weathering in a forest soil. *Appl Environ Microbiol*, 73: 3019–3027. demonstrated that the mineral-weathering potential of the bacterial isolates living in the vicinity of *Scleroderma* mycelium was greater than the mineral-weathering potential of the isolates living in the surrounding bulk soil.

Therefore, they hypothesised that some of the functional activities, like mineral weathering, that have classically been attributed to ECM fungi could result at least partially from the activity of the associated exo- or even endobacterial communities ([Bertaux et al. 2005](#) [Bertaux, J](#), [Schmid, M](#), [Hutzler, P](#), [Hartmann, A](#), [Garbaye, J](#) and [Frey-Klett, P](#). 2005. Occurrence and distribution of endobacteria in the plant-associated mycelium of the ectomycorrhizal fungus *Laccaria bicolor* S238N. *Environ Microbiol*, 7: 1786–1795.) that have been selected by the ECM symbiosis. Functional complementation between the ECM fungi and the associated bacterial communities would improve the mineral-weathering efficacy of the ECM complexes ([Uroz et al. 2007](#) [Uroz, S](#), [Calvaruso, C](#), [Turpault, M P](#), [Pierrat, J C](#), [Mustin, C](#) and [Frey-Klett, P](#). 2007. Effect of the mycorrhizosphere on the genotypic and metabolic diversity of the bacterial communities involved in mineral weathering in a forest soil. *Appl Environ Microbiol*, 73: 3019–3027.).

MYCORRHIZAL FUNGAL WEATHERING AND METAL CONTAMINATION

The extent of metal and radionuclide contamination in the world is immense ([Fomina et al. 2005](#) [Fomina, M](#), [Alexander, I J](#), [Colpaert, J V](#) and [Gadd, G M](#). 2005. Solubilization of toxic metal minerals and metal tolerance of mycorrhizal fungi. *Soil Biol Biochem*, 37: 857–866.). In the soil environment, metals and radionuclides can be dissolved in solution, held on inorganic soil constituents through various sorption or ion exchange reactions, complexed with soil organic materials, or precipitated as pure or mixed solids ([Knox et al. 2000](#) [Knox, A S](#), [Seaman, J C](#), [Mench, M J](#) and [Vangronsveld, J](#). 2000. "Remediation of metal- and radionuclide-contaminated soils by in situ stabilization techniques". In *Environmental Restoration of Metals-Contaminated Soil*, Edited by: [Iskandar, I K](#). 21–61. BocaRaton, FL: Lewis Publishers.). Unlike degradable organic contaminants and even short-lived radionuclides that can become less toxic over time, metals can be considered conservative because they are not decomposed in the environment. The influence of microbiological processes on contamination of the environment by toxic metals and radionuclides is of economic and environmental significance ([Gadd 1993](#) [Gadd, GM.](#) 1993. Interactions of fungi with toxic metals. *New Phytol*, 124: 25–60. , [2001](#) [Gadd, GM.](#) 2001. "Metal

transformations". In *Fungi in Bioremediation*, Edited by: Gadd, G M. 359–382. Cambridge: Cambridge University Press.).

However, the potential of microbial processes for bioremediation may be dependent on the physical and chemical nature of the site which influences the form in which metals occur. Furthermore, mineral components contain considerable quantities of metals which are biologically unavailable. Certain microbial processes dissolve metal minerals thereby increasing metal bioavailability and potential toxicity, whereas others immobilize them and reduce bioavailability (Fomina et al. 2005 Fomina, M, Alexander, I J, Colpaert, J V and Gadd, G M. 2005. Solubilization of toxic metal minerals and metal tolerance of mycorrhizal fungi. *Soil Biol Biochem*, 37: 857–866.).

Ecto- and endomycorrhizal symbioses can play a crucial role in protecting plants from toxic metals (Meharg and Cairney 2000 Meharg, A A and Cairney, J WG. 2000. Co-evolution of mycorrhizal symbionts and their hosts to metal-contaminated environments. *Adv Ecol Res*, 30: 69–112. ; Meharg 2003 Meharg, AA. 2003. The mechanistic basis of interactions between mycorrhizal associations and toxic metal cations. *Mycol Res*, 107: 1253–1265.). The ability of mycorrhizal associations to ameliorate metal toxicity to higher plants has been shown for ericoid mycorrhizas (Bradley et al. 1981 Bradley, R, Burt, A J and Read, D J. 1981. Mycorrhizal infection and resistance to heavy metal toxicity in *Calluna vulgaris*. *Nature*, 292: 335–337.), ectomycorrhizas (Brown and Wilkins 1985a Brown, M T and Wilkins, D A. 1985a. Zinc tolerance of *Amanita* and *Paxillus*. *Trans Brit Mycol Soc*, 84: 367–369. ,b Brown, M T and Wilkins, D A. 1985b. Zinc tolerance of mycorrhizal *Betula*. *New Phytol*, 99: 101–106. ; Denny and Wilkins 1987a Denny, H J and Wilkins, D A. 1987a. Zinc tolerance in *Betula* spp. III. Variation in response to zinc among ectomycorrhizal associates. *New Phytol*, 106: 535–544. ,b Denny, H J and Wilkins, D A. 1987b. Zinc tolerance in *Betula* ssp. IV. The mechanism of ectomycorrhizal amelioration of zinc toxicity. *New Phytol*, 106: 545–553. ; Van Tichelen et al. 2001 Van Tichelen, K K, Colpaert, J V and Vangronsveld, J. 2001. Ectomycorrhizal protection of *Pinus sylvestris* against copper toxicity. *New Phytol*, 150: 203–213. ; Adriaensen et al. 2003 Adriaensen, K, Van Der Lelie, D, Van Laere, A, Vangrosveld, J and Colpaert, J V. 2003. A zinc-adapted fungus protects pines from zinc stress. *New Phytol*, 161: 549–555. ; Colpaert et al. 2004 Colpaert, J V, Muller, L AH, Lambaerts, M, Andriaensen, K and Vangronsveld, J. 2004. Evolutionary adaptation to Zn toxicity in populations of Suilloid fungi. *New Phytol*, 162: 549–559.) and arbuscular mycorrhizas (Gildon and Tinker 1983 Gildon, A and Tinker, P B. 1983. Interactions of vesicular arbuscular mycorrhizal infection and heavy metals on the development of vesicular–arbuscular micorrhizas. *New Phytol*, 95: 247–261. ; Heggo and Angle 1990 Heggo, A and Angle, J S. 1990. Effects of vesicular–arbuscular mycorrhizal fungi on heavy metal uptake by soybeans. *Soil Biol Biochem*, 22: 856–869.).

The efficiency of protection, however, differs between distinct isolates of mycorrhizal fungi and different toxic metals and protective effects cannot be demonstrated for all associations in all circumstances (Meharg and Cairney 2000 Meharg, A A and Cairney, J WG. 2000. Co-evolution of mycorrhizal symbionts and their hosts to metal-contaminated environments. *Adv Ecol Res*, 30: 69–112.). What is clear is that plant roots and their associated free-living and symbiotic microbial populations significantly alter the physico-chemical characteristics of the rhizosphere by metabolic activities, resulting in a geochemical environment that can be very different from the bulk soil (Olsson and Wallander 1998 Olsson, P A and Wallander, H. 1998. Interactions between ectomycorrhizal fungi and the bacterial community in soil amended with various primary minerals. *FEMS Microbiol Ecol*, 27: 195–205. ; Whitelaw et al. 1999 Whitelaw, M A, Harden, T J and Helyar, K R. 1999. Phosphate solubilization in solution culture by the soil fungus *Penicillium radicum*. *Soil Biol Bioch*, 31: 655–665.). This will have significant consequences for the biogeochemical mobility of metals and associated elements in such an environment.

Two main mechanisms of metal mineral dissolution by fungi are proton-promoted and ligand-promoted (Gadd 2001 Gadd, GM. 2001. "Metal transformations". In *Fungi in Bioremediation*, Edited by: Gadd, G M. 359–382. Cambridge: Cambridge University Press.). Organic acids provide both source of protons for solubilization and metal-chelating anion to complex the metal cation with complexation being dependent on such factors as relative concentrations of the anions and metals, pH, and the stability constants of the various complexes (Devevre et al. 1996 Devevre, O, Garbaye, J and Botton, B. 1996. Release of complexing organic acids by rhizosphere fungi as a factor in Norway Spruce yellowing in acidic soils. *Mycol Res*, 100: 1367–1374.). Conversely, immobilization can result from sorption to cell components or exopolymers, transport and intracellular sequestration or precipitation as insoluble compounds, e.g., oxalates (Gadd 1993 Gadd, GM. 1993. Interactions of fungi with toxic metals. *New Phytol*, 124: 25–60. , 2001 Gadd, GM. 2001. "Metal transformations". In *Fungi in Bioremediation*, Edited by: Gadd, G M. 359–382. Cambridge: Cambridge University Press. ; Sayer and Gadd 1997 Sayer, J A and Gadd, G M. 1997. Solubilisation and transformation of insoluble metal compounds to insoluble metal oxalates by *Aspergillus niger*. *Mycol Res*, 101: 653–661.).

Of special interest are the mechanisms by which fungi and plants obtain phosphate since solubilization of inorganic phosphates can result in release of the associated toxic metals (Gadd 1986 Gadd, GM. 1986. "Fungal responses towards heavy metals". In *Microbes in Extreme Environments*, Edited by: Herbert, R A and Codd, G A. 83–110. London: Academic Press.). Conversely, formation of insoluble metal phosphates will reduce both metal and phosphate bioavailability. For other insoluble metal compounds and minerals (e.g. various sulphates, oxides, carbonates), solubilization can also result in release of anionic species.

The ECM fungi *Suillus granulatus* and *P. tinctorius* promoted the release of cadmium and phosphorus from rock phosphate (Lapeyrie et al. 1991 Lapeyrie, F, Ranger, J and Vairelles, D. 1991. Phosphate-solubilizing activity of ectomycorrhizal fungi in vitro. *Can J Bot*, 69: 342–346.), whereas zinc phosphate was found to be the most easily solubilized compound by the ectomycorrhizal fungi *P. involutus*, *S. bovinus*, *S. luteus*, and *Thelephora terrestris* compared to cadmium, copper, and lead phosphates (Fomina et al. 2004 Fomina, M, Alexander, I J, Hillier, S and Gadd, G M. 2004. Zinc phosphate and pyromorphite solubilization by soil plant-symbiotic fungi. *Geomicrobiol J*, 21: 351–366.). Fomina et al. (2005) Fomina, M, Alexander, I J, Colpaert, J V and Gadd, G M. 2005. Solubilization of toxic metal minerals and metal tolerance of mycorrhizal fungi. *Soil Biol Biochem*, 37: 857–866. investigated the ability of ericoid mycorrhizal and ECM fungi to solubilize different toxic metal (Cd, Cu, Pb, Zn)-containing minerals.

Metal tolerance and solubilizing ability varied widely between different mineral and fungal species, and strains derived from sites differing in the degrees of metal pollution. Zinc phosphate exhibited the least toxicity and was the easiest to solubilize by the majority of tested fungal isolates. Solubilization of toxic metal minerals was connected with both the pH of the medium and growth and tolerance of fungi and it seemed that acidification of the medium was the main mechanism of mineral dissolution for most of the mycorrhizal fungi studied. A very strong lethal effect was observed for ECM isolates in the presence of Pb phosphate, carbonate, sulphide and tetraoxide. In contrast, ericoid mycorrhizal isolates were able to grow on Pb-mineral-amended media.

A significant proportion of ericoid mycorrhizal cultures solubilized Cd and Cu phosphates and cuprite. None of the ericoid mycorrhizal and ECM fungi were able to produce a clear zone in Pb mineral-containing agar. However, many fungi were able to accumulate mobilized Pb in their mycelia. Differences in toxic metal mineral tolerance, mineral solubilization and metal uptake between populations isolated from metal-polluted and uncontaminated sites were related to the toxic metal which was the main pollutant in the original contaminated environment. In general, metal-

tolerant fungi grew and solubilized toxic metal minerals better than non-tolerant isolates (Fomina et al. 2005).

Martino et al. (2003a) Martino, E, Perotto, S, Parsons, R and Gadd, G M. 2003a. Solubilization of insoluble inorganic zinc compounds by ericoid mycorrhizal fungi derived from heavy metal polluted sites. *Soil Biol Biochem*, 35: 133–141. demonstrated that ericoid fungal strains belonging to the species *Oidiodendron maius* and derived from polluted and unpolluted soils mobilize insoluble inorganic zinc compounds to different extents. They found that strains from polluted soils showed little ability to solubilize Zn from both ZnO and $Zn_3(PO_4)_2$, whereas strains from unpolluted soils showed a higher solubilization potential. Martino and colleagues (2003a) Martino, E, Perotto, S, Parsons, R and Gadd, G M. 2003a. Solubilization of insoluble inorganic zinc compounds by ericoid mycorrhizal fungi derived from heavy metal polluted sites. *Soil Biol Biochem*, 35: 133–141. speculated that this may reflect specific strategies to maintain homeostasis of essential metals under different soil conditions. Induction of organic acids (malate and citrate) by the metal compounds was shown to be at least in part responsible for metal solubilization. Zinc precipitation was demonstrated for one of the ericoid strains tested by Martino et al. (2003a) Martino, E, Perotto, S, Parsons, R and Gadd, G M. 2003a. Solubilization of insoluble inorganic zinc compounds by ericoid mycorrhizal fungi derived from heavy metal polluted sites. *Soil Biol Biochem*, 35: 133–141. who observed zinc crystals formation underneath the fungal colony after growing in the presence of insoluble zinc oxide. The insoluble metal compounds was firstly solubilized by the ericoid strain and then precipitated in an insoluble form (Figures 1 and 2).

FIG 1 Crystals formed by *Oidiodendron maius* in the agar medium underneath the fungal colony. (a) Solubilization activity on solid 2% (w/v) malt medium containing 0.12% (w/v) ZnO. The photograph shows the clear zone of solubilization halo around the colony of an *Oidiodendron maius* strain from unpolluted soils. The photograph was taken after 30 d incubation at 25°C. (b) A SEM micrograph showing the morphology of the crystals formed in the medium in correspondence to the solubilization halo. Bar is 20 μm. When these crystals were purified and analysed by SEM and X-ray microanalysis, a strong Zn peak was identified, indicating that they actually represent a form of metal insolubilization (see Martino et al. 2003a Martino, E, Perotto, S, Parsons, R and Gadd, G M. 2003a. Solubilization of insoluble inorganic zinc compounds by ericoid mycorrhizal fungi derived from heavy metal polluted sites. *Soil Biol Biochem*, 35: 133–141.).
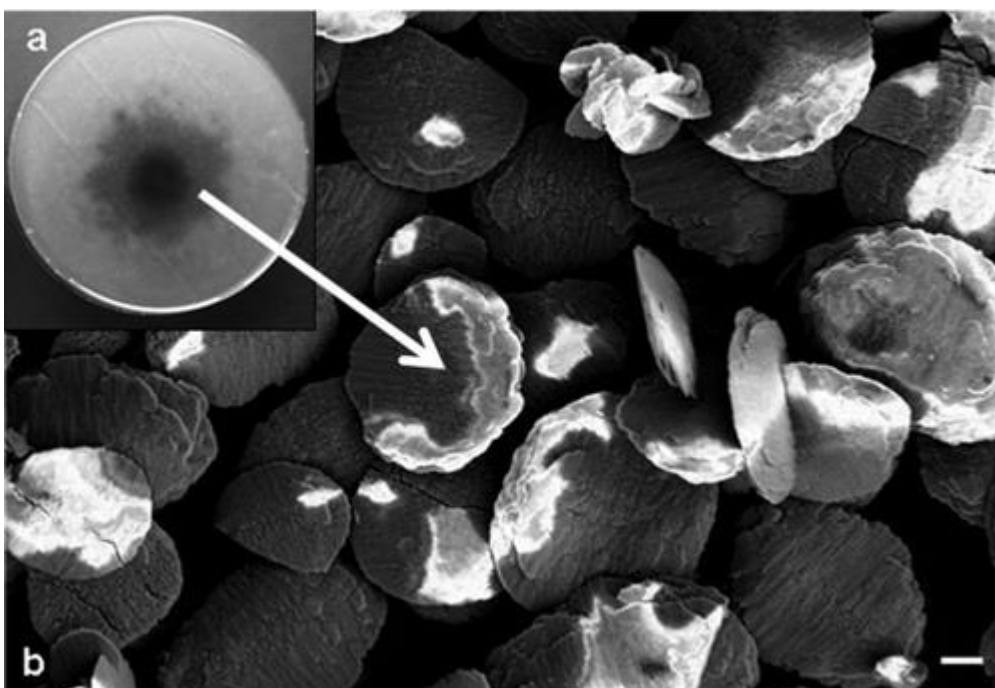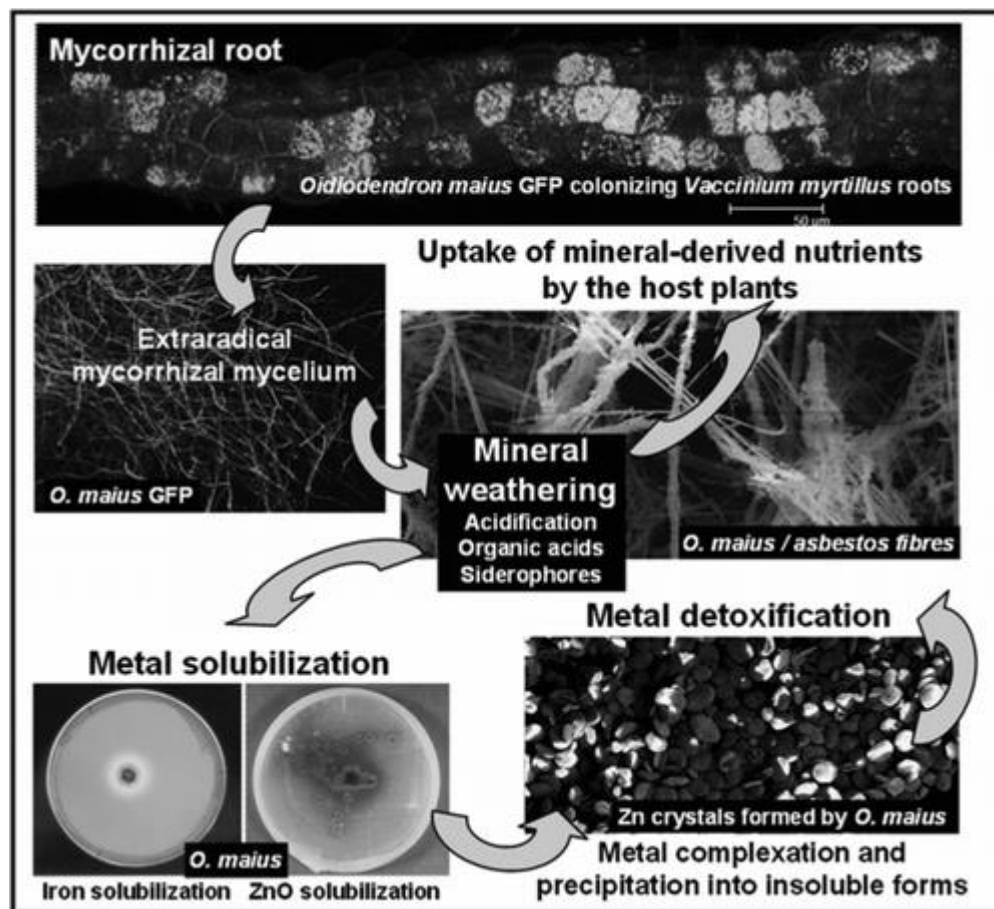
FIG 2 Schematic representation indicating some of the possible interactions between mycorrhizal fungi and insoluble mineral compounds.

Ericoid fungi were also shown to be able to solubilize iron from a very particular substrate, asbestos fibres (Figure 3) (Martino et al. 2003b Martino, E, Prandi, L, Fenoglio, I, Bonfante, P, Perotto, S and Fubini, B. 2003b. Soil fungal hyphae bind and attack asbestos fibres. *Angewandte Chemie-International Edition*, 42: 219–222. , 2004 Martino, E, Cerminara, S, Prandi, L, Fubini, B and Perotto, S. 2004. Physical and biochemical interactions of soil fungi with asbestos fibers. *Environ Toxicol Chem*, 23: 938–944.). Iron, a structural component of most asbestos, is thought to play a crucial role in asbestos toxicity. Surface iron favors fibres uptake by mammalian cells and promotes the generation of free radicals with consequent DNA and lipid damage. In some cases, chemical removal of iron from asbestos fibres has reduced several cellular responses to asbestos. As previously mentioned, microorganisms have developed mechanisms to scavenge iron from poorly soluble forms (Haselwandter et al. 2008).

FIG 3 Effects of an ericoid strain on a suspension of asbestos fibres. (a) *Oidiodendron maius* control culture, without asbestos fibres. (c) Fine asbestos fibres (1.5–4 μm mean diameter) form a turbid suspension when dispersed in the Czapek glucose medium. (b) When the fungal mycelium was grown in the medium containing asbestos fibres, it removed the fibres from the suspension, thus leaving a clear supernatant. This phenomenon indicates that the fungal hyphae can bind or entrap the asbestos material. (d) Scanning electron micrograph showing the fungal hyphae of *O. maius* (arrow) intertwined with asbestos fibres. A large fibre is clearly visible in the center of the photograph (arrowhead), whereas smaller fibres (double arrowhead) can be found associated with the surface of the fungal hyphae (scale bar corresponds to 50 μm). A large fibre is clearly visible in the center of the inset photograph surrounded by fungal hyphae. Scale bar is 20 μm. (e) A specific plate assays shows the release of siderophores by *O. maius*, detected as a clear halo. Highly

solubilizing fungal strains produced significantly higher amounts of siderophores than less solubilizing fungi, so siderophores might be partly responsible for the iron extraction from fibres (see Martino et al. 2004 Martino, E, Cerminara, S, Prandi, L, Fubini, B and Perotto, S. 2004. Physical and biochemical interactions of soil fungi with asbestos fibers. *Environ Toxicol Chem*, 23: 938–944.).
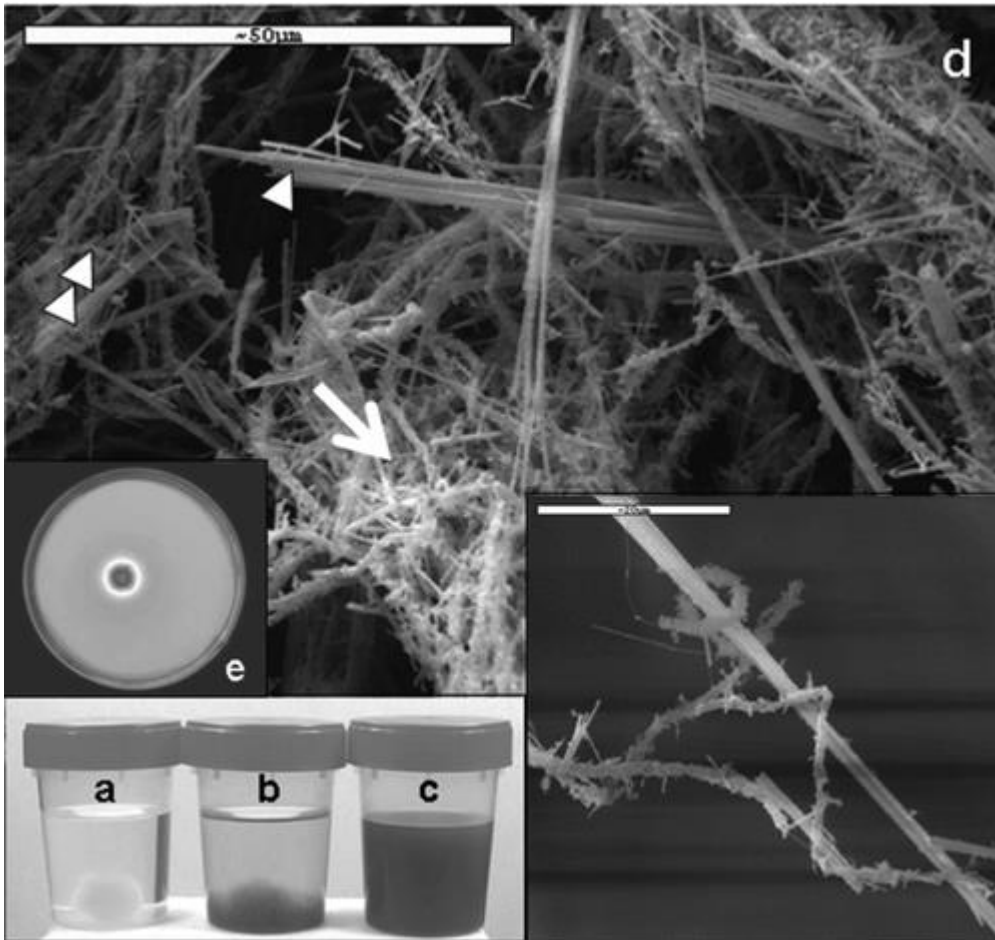
Martino and collaborators (2003b Martino, E, Prandi, L, Fenoglio, I, Bonfante, P, Perotto, S and Fubini, B. 2003b. Soil fungal hyphae bind and attack asbestos fibres. *Angewandte Chemie-International Edition*, 42: 219–222. , 2004 Martino, E, Cerminara, S, Prandi, L, Fubini, B and Perotto, S. 2004. Physical and biochemical interactions of soil fungi with asbestos fibers. *Environ Toxicol Chem*, 23: 938–944.) investigated the ability of some soil fungi to produce iron chelators capable of extracting iron from crocidolite (blue asbestos). Among the species/isolates investigated, also some ericoid mycorrhizal strains could remove iron from crocidolite fibres. A tight interaction between the fungus and the fibres was observed using the scanning electron microscope (SEM) (Figure 3). By binding the fibres and depriving them of iron, selected species/strains of soil fungi might represent interesting tools for the bioremediation of asbestos-contaminated soils.

Processes of toxic metal mineral solubilization by mycorrhizal fungi should therefore be considered in connection with the metal tolerance of these organisms but experiments should also be performed in association with the host plant. Interestingly, Fomina et al. (2006) Fomina, M, Charnock, J M, Hillier, S, Alexander, I J and Gadd, G M. 2006. Zinc phosphate transformations by the *Paxillus involutus*/pine ectomycorrhizal association. *Microb Ecol*, 52: 322–333. investigated zinc phosphate transformations by *Paxillus involutus*/pine ectomycorrhizas using zinc-resistant and zinc-sensitive strains of the ectomycorrhizal fungus under high- and low-phosphorus conditions to further understand fungal roles in the transformation of toxic metal minerals in the mycorrhizosphere. In

the presence of a phosphorus source, an ECM association with a zinc-resistant strain accumulated the least zinc compared to a zinc-sensitive ECM association and non-mycorrhizal plants. Under low-phosphorus conditions, mycorrhizal seedlings infected with the zinc-resistant strain increased the dissolution of zinc phosphate and zinc accumulation by the plant. The Authors concluded that zinc phosphate solubilization and zinc and phosphorus uptake by the association depend on ECM infection, strain of the mycobiont, and the phosphorus status of the matrix.

Aluminium is a major component of most soil mineral grains. Consequently, mineral weathering will release not only base cations but also increase the concentration of Al in the soil solution of the mineral soil layers (Van Schöll et al. 2008 Van Schöll, L, Kuyper, T W, Smits, M M, Landeweert, R, Hoffland, E and van Breemen, N. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. *Plant Soil*, 303: 35–47.). In soils with a pH below 4, a situation typical for podzol soils, dissolved Al is present mainly in the form of the phytotoxic Al^{3+} (Kinraide 1991 Kinraide, TB. 1991. Identity of the rhizotoxic aluminum species. *Plant Soil*, 134: 167–178.), and increased weathering will therefore contribute to Al toxicity. In the debate on the effect of acid deposition, Al toxicity is often seen as the most direct cause of forest deterioration. Under Al toxicity, ECM seedlings maintained higher growth rates than nonmycorrhizal seedlings (Cumming and Weinstein 1990a Cumming, J R and Weinstein, L H. 1990a. Aluminum-mycorrhizal interactions in the physiology of pitch pine seedlings. *Plant Soil*, 125: 7–18. , 1990b Cumming, J R and Weinstein, L H. 1990b. Utilization of aluminum phosphate as a phosphorus source by ectomycorrhizal *Pinus rigida* Mill. seedlings. *New Phytol*, 116: 99–106. ; Hentschel et al. 1993 Hentschel, E, Godbold, D L, Marschner, P, Schlegel, H and Jentschke, G. 1993. The effect of *Paxillus involutus* Fr. on aluminum sensitivity of Norway spruce seedlings. *Tree Physiol*, 12: 379–390. ; Schier and McQuattie 1995 Schier, G A and McQuattie, C J. 1995. Effect of aluminum on the growth, anatomy, and nutrient content of ectomycorrhizal and nonmycorrhizal eastern white pine seedlings. *Can J For Res*, 25: 1252–1262. , 1996 Schier, G A and McQuattie, C J. 1996. Response of ectomycorrhizal and nonmycorrhizal pitch pine (*Pinus rigida*) seedlings to nutrient supply and aluminum: Growth and mineral nutrition. *Can J For Res*, 26: 2145–2152. ; Göransson and Eldhuset 2001 Göransson, A and Eldhuset, T. 2001. Is the Ca + K + Mg/Al ratio in the soil solution a predictive tool for estimating forest damage?. *Water Air Soil Pollut Focus*, 1: 57–74.). These higher growth rates may be due to the fact that ECM fungi generally improve growth of their hosts through better nutrient supply. As shown by Schier and McQuattie (1996) Schier, G A and McQuattie, C J. 1996. Response of ectomycorrhizal and nonmycorrhizal pitch pine (*Pinus rigida*) seedlings to nutrient supply and aluminum: Growth and mineral nutrition. *Can J For Res*, 26: 2145–2152. increased nutrient supply alone can partly mitigate Al toxicity effects on tree seedlings.

The role of ECM fungi in the uptake of Ca and Mg under Al toxicity is especially of interest as Al^{3+} specifically inhibits the uptake of Ca and Mg by kinetic processes at the root cell wall, thereby inducing plant deficiencies of Ca and Mg. ECM fungi ensheath the root apices, which are the main sites for Al toxicity and uptake of Ca and Mg, and it seems likely that ECM fungi affect the uptake Ca and Mg at the root tips (Finlay 1995 Finlay, RD. 1995. Interactions between soil acidification, plant growth and nutrient uptake in ectomycorrhizal associations of forest trees. *Ecol Bull*, 44: 197–214.). Under conditions of sufficient nutrient supply, which avoids differences in growth and biomass between non-mycorrhizal and ECM seedlings (Hobbie 2006 Hobbie, EA. 2006. Carbon allocation to ectomycorrhizal fungi correlates with belowground allocation in culture studies. *Ecology*, 87: 563–569.), uptake of Ca and Mg under Al toxicity was not affected by ECM colonisation (Van Schöll et al. 2005 Van Schöll, L, Keltjens, W G, Hoffland, E and Van Breemen, N. 2005. Effect of ectomycorrhizal colonization on the uptake of Ca, Mg and Al by *Pinus sylvestris* under aluminium toxicity. *For Ecol Manag*, 215: 352–360.).

Mineral tunnelling by ECM hyphae through LMWOA exudation will give the tree direct access to base cations, while at the same time Al^{3+} is detoxified through chelation (Van Breemen et al. 2000a Van Breemen, N, Finlay, R D, Lundström, U, Jongmans, A G, Giesler, R and Olsson, M. 2000a. Mycorrhizal weathering: a true case of mineral nutrition?. *Biogeochemistry*, 49: 53–67. ,b Van Breemen, N, Lundström, U S and Jongmans, A G. 2000b. Do plants drive podzolization via rock-eating mycorrhizal fungi?. *Geoderma*, 94: 163–171.). By directly translocating the weathering products from these protected microsites, uptake is uncoupled from the toxic bulk solution. ECM fungi might play an important role in the Al tolerance of their host trees by the exudation of LMWOAs and subsequent complexation of Al (Ryan et al. 2001 Ryan, P R, Delhaize, E and Jones, D L. 2001. Function and mechanism of organic anion exudation from plant roots. *Ann Rev Plant Physiol Plant Mol Biol*, 52: 527–560.) and dissolution of Ca and Mg (Kinraide 2003 Kinraide, TB. 2003. Toxicity factors in acidic forest soils: attempts to evaluate separately the toxic effects of excessive Al^{3+} and H^+ and insufficient Ca^{2+} and Mg^{2+} upon root elongation. *Eur J Soil Sci*, 54: 323–333.). Exudation of LMWOAs seems a general response mechanism of Al tolerant plants (Ma et al. 2001 Ma, J F, Ryan, P R and Delhaize, E. 2001. Aluminium tolerance in plants and the complexing role of organic acids. *Trends Plant Sci*, 6: 273–278. ; Ryan et al. 2001 Ryan, P R, Delhaize, E and Jones, D L. 2001. Function and mechanism of organic anion exudation from plant roots. *Ann Rev Plant Physiol Plant Mol Biol*, 52: 527–560. ; Barcelo and Poschenrieder 2002 Barcelo, J and Poschenrieder, C. 2002. Fast root growth responses, root exudates, and internal detoxification as clues to the mechanisms of aluminium toxicity and resistance: a review. *Env Exp Bot*, 48: 75–92. ; Kochian et al. 2004 Kochian, L V, Hoekenga, O A and Pinerosa, M A. 2004. How do crop plants tolerate acid soils? Mechanisms of aluminum tolerance and phosphorous efficiency. *Ann Rev Plant Biol*, 55: 459–493.).

Increased exudation of oxalate by tree seedlings under Al toxicity has been shown by Ahonen et al. (2000) Ahonen Jonnarth, U, Van Hees, PAW, Lundstrom, U S and Finlay, R D. 2000. Organic acids produced by mycorrhizal *Pinus sylvestris* exposed to elevated aluminium and heavy metal concentrations. *New Phytol*, 146: 557–567. , and in several cases this was increased further by ECM fungi. Van Schöll (2006a) Van Schöll, L, Hoffland, E and Van Breemen, N. 2006a. Organic anion exudation by ectomycorrhizal fungi and *Pinus sylvestris* in response to nutrient deficiencies. *New Phytol*, 170: 153–163. demonstrated that oxalate exudation by ECM fungi was induced by Al, and exudation was further enhanced by simultaneous Al toxicity and Mg and P deficiency. Arbuscular mycorrhizal fungi can also protect their host plants from Al toxicity. In the eastern United States, broomsedge (*Andropogon virginicus* L.) is found growing on abandoned coal mined lands that have extremely acidic soils with high residual aluminium (Al) concentrations. Broomsedge may be inherently metal-resistant and nutrient-efficient or may rely on the arbuscular mycorrhizal fungal association to overcome limitations on such sites. Cumming and Ning 2003 Cumming, J R and Ning, J. 2003. Arbuscular mycorrhizal fungi enhance aluminium resistance of broomsedge (*Andropogon virginicus* L.). *J Exp Bot*, 54: 1447–1459. showed that an AM fungal consortium conferred Al resistance to broomsedge. They demonstrated that arbuscular mycorrhizal fungi reduced Al uptake and translocation in host plants, potentially reflecting measured reductions in inorganic Al availability in the rhizosphere of mycorrhizal plants.

CONCLUSIONS

On 3 July 2009, *Planet Earth Online* commented on the paper by Bonneville et al. 2009 Bonneville, S, Smits, M M, Brown, A, Harrington, J, Leake, J R, Brydson, R and Benning, L G. 2009. Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale. *Geology*, 37: 615–618. titled: "Root fungi turn rock into soil". Trees help to break down barren rocks into soil, but how does that work exactly? It turns out that mycorrhizal fungi living on the trees' roots do most of the heavy work. The fungi first bend the structure of certain minerals, weaken their crystals

and then remove any useful chemical elements to pass on to their host tree. During the process, the rocks change their chemistry, lose their strength and in the long-run become soil. Different types of mycorrhizal symbioses play fundamental roles in shaping terrestrial ecosystems and the characteristic plant communities that dominate the major terrestrial biomes of the world today do so because selection has favoured symbiotic association functionally adapted to the different environments.

Mycorrhizal fungi connect the primary producers of ecosystems, plants, to the heterogeneously distributed nutrients required for their growth, enabling the flow of energy-rich compounds required for nutrient mobilization whilst simultaneously providing conduits for the translocation of mobilized products back to their hosts (Finlay 2008 Finlay, RD. 2008. Ecological aspects of mycorrhizal symbiosis: with special emphasis on the functional diversity of interactions involving the extraradical mycelium. *J Exp Bot*, 59: 1115–1126.). Elucidating the mechanisms involved, the range of interactions with other organisms, and the ways in which these are regulated remains the goal for understanding the role of these fungi in biogeochemical cycles. New molecular tools have enabled identification of mycorrhizal fungal symbionts with a higher degree of resolution (Buée et al. 2009 Buée, M, Reich, M, Murat, C, Morin, E, Nilsson, R H, Uroz, S and Martin, F. 2009. 454 Pyrosequencing analyses of forest soils reveal an unexpectedly high fungal diversity. *New Phytol*, doi: 10.1111/j.1469–8137.2009.03003.x) revealing a high degree of functional specificity in mycorrhizal associations. Moreover the genome sequencing programmes of mycorrhizal fungi (Martin et al. 2008 Martin, F, Aerts, A, Ahren, D, Brun, A, Danchin, E GJ, Duchaussoy, F, Gibon, J, Kohler, A, Lindquist, E, Pereda, V, Salamov, A, Shapiro, H J, Wuyts, J, Blaudez, D, Buee, M, Brokstein, P, Canback, B, Cohen, D, Courty, P E, Coutinho, P M, Delaruelle, C, Detter, J C, Deveau, A, DiFazio, S, Duplessis, S, Fraissinet-Tachet, L, Lucic, E, Frey-Klett, P, Fourrey, C, Feussner, I, Gay, G, Grimwood, J, Hoegger, P J, Jain, P, Kilaru, S, Labbe, J, Lin, Y C, Legue, V, Le Tacon, F, Marmeisse, R, Melayah, D, Montanini, B, Muratet, M, Nehls, U, Niculita-Hirzel, H, Secq, M PO, Peter, M, Quesneville, H, Rajashekar, B, Reich, M, Rouhier, N, Schmutz, J, Yin, T, Chalot, M, Henrissat, B, Kues, U, Lucas, S, Van de Peer, Y, Podila, G K, Polle, A, Pukkila, P J, Richardson, P M, Rouze, P, Sanders, I R, Stajich, J E, Tunlid, A, Tuskan, G and Grigoriev, I V. 2008. The genome of *Laccaria bicolor* provides insights into mycorrhizal symbiosis. *Nature*, 452: 88–92.) combined with powerful bioinformatics tools will have a major impact on research on mycorrhizas. Comparison of the genomes of various fungi implied in the weathering process will enable functional genomic studies with a focus on the genes responsible for mineral dissolution.

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