

# The role of fungi in weathering

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No rock at the Earth's surface escapes weathering. This process is the primary source of all the essential elements for organisms, except nitrogen and carbon. Since the onset of terrestrial life, weathering has been accelerated under the influence of biota. The study of biological weathering started at the end of the 19th century. Although the role of bacteria (Eubacteria, Archaea) has attracted a lot of interest, until recently the role of fungi has largely been neglected. More recently, however, fungal weathering has become an increasingly important focus of biogeochemical research.

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Weathering is the primary source of all essential elements for organisms, except nitrogen and carbon. During the process of physical disintegration and chemical decomposition of rocks at the Earth's surface, elements such as phosphorus, calcium, potassium, magnesium, and many trace elements are released in a form directly available to the biota. Together with atmospheric deposition, weathering provides the major influx of these elements in bioavailable form in most ecosystems. It therefore contributes substantially to soil fertility and ecosystem productivity.

In order to fully understand the process of nutrient cycling in ecosystems it is necessary to understand the role that organisms play in weathering. Various observations

## In a nutshell:

- Saprotrophic and mutualistic (mycorrhizal and lichen-forming) fungi increase rates of mineral weathering, a process that is driven mainly by dissolved CO<sub>2</sub>, protons, and organic anions
- Fungal weathering may be important at ecological and evolutionary time scales, influencing cycles of phosphate, of basic nutrient cations (K, Mg, Ca), and possibly of oxygen and carbon dioxide
- Mutualistic fungi are likely to be most important in weathering because of substantial carbon costs to produce organic anions
- The extent to which fungal weathering feeds back to vegetation development and the biogeochemical implications of this feedback are still largely unknown

point to a major role of fungi in this process.

First, the early terrestrial plants had no true roots and the colonization of land by photosynthetic eukaryotes depended strongly on mycorrhizal fungi. The first plants were associated with arbuscular mycorrhizal fungi. Together with saprotrophic fungi, they must have helped to increase CO<sub>2</sub> concentrations and decrease pH in the root zone, which accelerates weathering.

Secondly, rock is a very hostile environment, where organisms encounter extreme fluctuations of moisture and temperature and limited nutrient availability. Nevertheless, biological activity is abundant in and on rocks that have been exposed to the atmosphere for some time (Gorbushina and Krumbein 2000). Free-living fungi and lichens establish on bare rocks (Figure 1); if they contain a cyanobacterium, as in the species *Stereocaulon vulcani*, both N-fixation and weathering pave the way for subsequent vegetation succession and soil formation. Several studies have shown that lichen-covered rocks weather an order of magnitude faster than bare rocks (Stretch and Viles 2002). Below the rock surface, endolithic fungal communities may also accelerate weathering. Lichens and saprotrophic fungi can accelerate the decay of sandstone and limestone statues, but may also slow down weathering rates (Mottershead *et al.* 2003).

Finally, mineral grains from soils are often completely covered by fungal hyphae, which form grooves as they travel over the grains (Figure 2).

Fungi have fewer geochemical capabilities as a result of redox reactions than bacteria. However, because of their ubiquitous presence and their ability to bridge distances by means of mycelial growth, fungi do have opportunities for weathering as well (Banfield *et al.* 1999; Sterflinger 2000). The growth of fungal hyphal tips is often accompanied by the production of organic anions and protons (Gadd 1999), which helps to break down weak spots in solid rock substrates. The production of weathering agents such as low molecular weight organic anions (LMWOAs) has substantial carbon costs. As a result, symbiotic fungi that

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are provided with organic carbon compounds by a plant have an advantage over saprotrophic organisms. The latter depend on dead organic material, which is rare on bare rock and unweathered soil.

#### ■ The major fungi involved in weathering – taxonomic and ecological perspectives

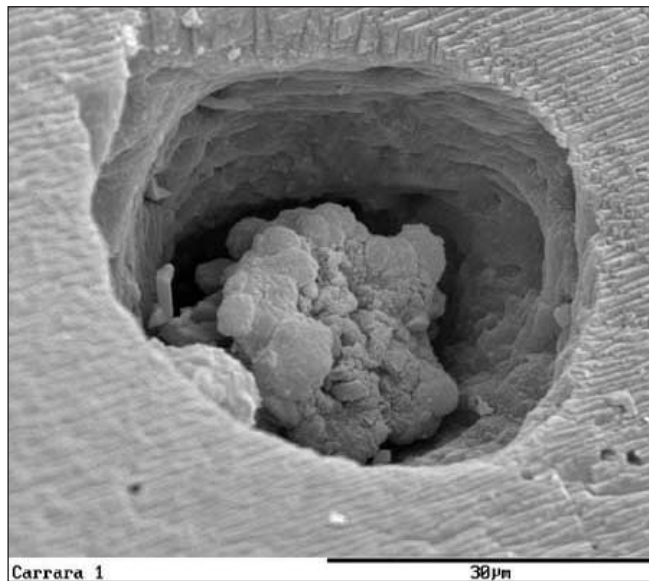
In the fungal phyla Ascomycota, Basidiomycota, and Zygomycota, five important functional groups of fungi with potential weathering capabilities can be recognized:

- (1) Lichen-forming fungi. Lichens, associations between fungi and algae or cyanobacteria, date at least from the early Devonian (400 million years ago). While younger, in evolutionary terms, than the oldest mycorrhizal fungi, lichens have played an important role in rock weathering and soil development (Chen *et al.* 2000). Because the associated fungus is closer to the mineral interface than the plant, the weathering ability of lichens is most probably due mainly to the fungus.
- (2) Mycorrhizal fungi, especially ectomycorrhizal (sheathing mycorrhizal) and ericoid mycorrhizal fungi, which were recognized recently as potentially important for mineral weathering (for a review, see Landeweert *et al.* 2001).
- (3) Saprotrophic fungi, such as *Aspergillus niger* (the major industrial source of citric acid), which use relatively simple carbohydrate sources and quickly proliferate under favorable conditions, like weeds.
- (4) Meristematic black yeasts and other stress-tolerant saprotrophic ascomycetes that use a range of carbohydrate sources (Sterflinger and Krumbein 1997).
- (5) Saprotrophic organisms that use the lignocellulose complex. White rot and brown rot fungi produce large amounts of organic anions (especially oxalate) that they use for generating hydrogen peroxide and for the production of Mn chelates that can oxidize a range of phenolic compounds (Dutton and Evans 1996) and may therefore be potential weathering agents.

This review will focus on groups 1 and 2. Through their mutualistic association with a photosynthetic organism, these fungi are likely to possess sufficient carbohydrate sources to be responsible for appreciable amounts of weathering. Species in group 3 and 4 are restricted to a few habitats and their contribution to weathering is limited by the scarcity of assimilable carbon or by their very slow growth. Species in group 5 have the potential to weather rock, but are normally active on dead organic matter, where weatherable minerals are absent or very scarce.

#### ■ How do fungi weather rocks and minerals?

Fungi can penetrate solid materials using both physical and chemical tools. The mycelial growth form allows fungi to exploit weak spots on the rock or grain surface.



**Figure 1.** Scanning electron micrograph of a marble-inhabiting fungal colony within a pit, which has steep walls caused by biochemical and partially biophysical mechanisms. The marble was taken directly from a quarry.

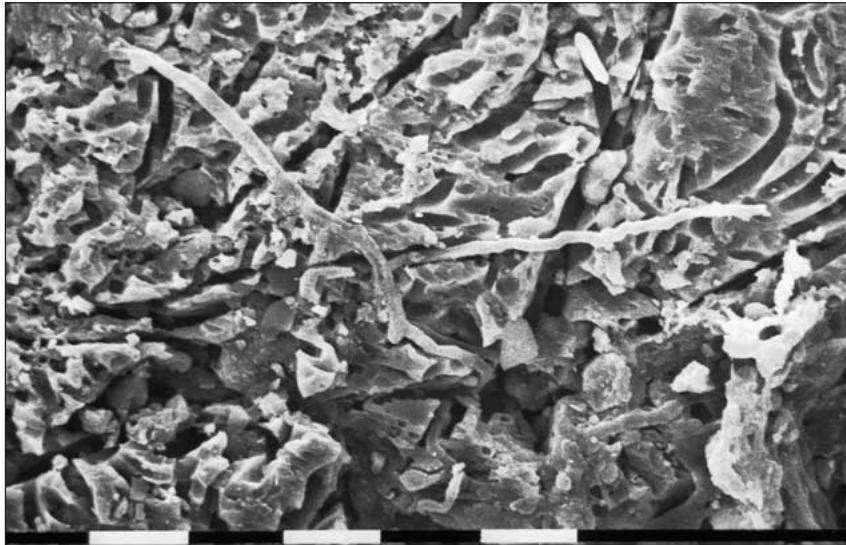
The hyphae responds to surface contours (thigmotropism, or contact guidance) by following scratches, ridges, and grooves, and by penetrating pores or tunnels. These irregularities may result from previous abiotic weathering. At such spots, the fungi may further weather the mineral surface using an array of physical and chemical tools. By preventing rapid diffusion of exudates into the soil solution, these irregularities may help increase fungus-mediated weathering, and may lead to the formation of tunnels (Figure 2; Hoffland *et al.* 2002).

#### Biogeophysical mechanisms

Using osmotic pressure, fungal appressoria (infection organs) produce pressures of up to 10–20  $\mu\text{N}/\mu\text{m}^2$ , sufficient to penetrate inert, bullet-proof material (Howard *et al.* 1991). However, such forces alone are probably not great enough to allow the hyphal tip to penetrate a rock, making chemical tools essential. Fungi most likely do accelerate physical weathering, however, by sending hyphae penetrating into cracks, spaces, and mineral cleavage planes, by incorporating mineral fragments in the lichen thallus, by forming secondary minerals that further disrupt the rocks, and by expanding and contracting hyphae during cycles of wetting and drying and freezing and thawing. Simultaneously, fungi can decelerate physical weathering where thallus or mycelium provides a cover that reduces temperature fluctuations, wind abrasion, or raindrop impact (Ariño *et al.* 1995).

#### Biogeochemical mechanisms

Two categories of chemical weathering agents are produced by fungi: proton-based and ligand-based agents.



**Figure 2.** Scanning electron micrograph of the surface of a mineral grain covered by grooves that may have been created by fungal hyphae. Two hyphae are visible. The feldspar grain originates from the E horizon of a 5400-year-old sand dune along Lake Michigan (Scale bar size: 10  $\mu\text{m}$ ).

Proton-based agents include respiratory  $\text{CO}_2$ /carbonic acid and other acids produced in the areas directly surrounding the tips of the fungal hyphae or the ectomycorrhizal roots. Ligand-based weathering agents include organic anions, siderophores, lichen acids, and other polyphenolic acids and acid polysaccharides. Low molecular weight organic acids, the most important group of weathering agents, belong to both groups.

*Low molecular weight organic acids.* These important weathering agents combine a high (relative to  $\text{CO}_2$ ) acid strength with metal-binding capacities. They are exuded as anions such as oxalate and citrate because oxalic and citric acid are strong acids that are dissociated at the fungal cytosolic pH (around 7). A linear correlation between  $\text{H}^+$  and oxalate concentrations has been found in the rhizosphere soil of ectomycorrhizal plants, indicating that protons and oxalate anions are released simultaneously (Casarin *et al.* 2003). Oxalate and citrate have a strong tendency to bind to tri- and divalent metal cations such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cu}^{2+}$ . This binding (complexation) lowers the activity of free cations in the soil solution, lowering the saturation state and promoting their further dissolution from minerals and thus promoting mineral weathering. For lichens, oxalate is quantitatively by far the most important LMWOA. Ectomycorrhizal fungi show a larger array of LMWOAs, including citrate and malate (Landeweert *et al.* 2001). Ericoid mycorrhizal fungi also produce oxalate, especially strains that are tolerant to heavy metals (Martino *et al.* 2003). So far, there have been no reports that arbuscular mycorrhizal fungi produce LMWOAs.

*Respiratory carbon dioxide.* The dissolution of respiratory  $\text{CO}_2$  in water generates carbonic acid, which lowers the local pH and thereby enhances solubilization of minerals. The relative importance of  $\text{CO}_2$  and LMWOAs is difficult

to establish, because of the short lifetime of organic acids once they are exuded. Most geochemists assume that  $\text{CO}_2$  is the dominant weathering agent because its conjugate base,  $\text{HCO}_3^-$ , is the major anion accompanying weathering-derived cations in continental drainage waters. However, initial weathering could have been brought about by LMWOAs, followed by respiration of the organic anion to  $\text{CO}_2$ . Respiration by ectomycorrhizal roots and the mycelia of mycorrhizal fungi accounts for more than 50% of total respiration (Bhupinderpal-Singh *et al.* 2003).

*Acidification due to nitrogen uptake.* As with plants,  $\text{NH}_4^+$  uptake by fungi results in excess cation uptake, compensated for by an efflux of  $\text{H}^+$  and subsequent acidification. Ectomycorrhizal fungi preferentially take up ammonium over nitrate, and the uptake of  $\text{NH}_4^+$  usually represents

80–90% of cation uptake. The resulting proton release was thought to be responsible for the dissolution of mineral phosphates in agar medium by ten ectomycorrhizal fungi, belonging to seven species, and grown *in vitro* with  $\text{NH}_4^+$  as the sole N source (Lapeyrie *et al.* 1991). With  $\text{NO}_3^-$  supply, only one isolate of *Paxillus involutus*, which was characterized by a high oxalate production, was able to dissolve the phosphate minerals.

*Lichen compounds.* “Lichen acids”, produced by the fungal partner in the lichen symbiosis, have for a long time been recognized as the major weathering components of lichens growing on rocks (Chen *et al.* 2000). However, because of their low solubility in water, these polyphenolic compounds (not all of them being acids) are probably far less important than oxalate and other LMWOAs. Furthermore, lichen compounds are usually concentrated in the upper thallus, at the fungal–algal or cyanobacterial interface, not at the mineral interface. In the field, metal–lichen–acid complexes have very rarely been reported, suggesting they play a limited role in weathering.

*Siderophores.* Siderophores are low molecular weight molecules producing highly stable complexes with iron ( $\text{Fe}^{3+}$ ). Many mycorrhizal fungal species produce siderophores (Haselwandter 1995). The solubilization of iron from the mineral goethite (ferric oxyhydroxide) by the ectomycorrhizal fungus *Suillus granulatus* was attributed to the release of siderophores (Watteau and Berthelin 1994). Ericoid mycorrhizal fungi produce the siderophores ferricrocin and fusigen. Ferricrocin is the main siderophore of the ectomycorrhizal fungus *Cenococcum geophilum* (Haselwandter and Winkelmann 2002), some E-strain fungi forming ectendomycorrhizae, and *Phialocephala fortinii*, a dark septate root endophyte (Bartholdy *et al.* 2001). The siderophores ferricrocin and ferricrocin have been identified in coniferous forest soil

solution from Scandinavia (Moberg *et al.* 2003).

*Acidic mucopolysaccharides.* In vivo observations of the lichen–mineral interface suggest that the fungal cell wall is separated from the mineral interface by a coating of extracellular organic polymers, such as mucopolysaccharides (Barker and Banfield 1996). These polymers can accelerate mineral dissolution by forming a ring structure around metal ions such as aluminum and calcium.

### ■ Formation of secondary minerals

Another aspect of weathering is the formation of secondary minerals. Metal oxalates are formed by lichens, ectomycorrhizal, and ericoid mycorrhizal fungi, iron (hydr)oxides by lichens, clay minerals by lichens, and ectomycorrhizal fungi and carbonates in mycorrhizal fungi and lichens (Gadd 1999; Adamo and Violante 2000; Arocena and Glowa 2000). The abundance of metal oxalates, coupled with their insolubility, is consistent with the hypothesis that oxalate primarily functions to immobilize excess calcium and toxic heavy metals. Support for this hypothesis comes from the link between oxalate production and tolerance to high levels of heavy metals (Gadd 1999). Hyphae of a large number of ectomycorrhizal fungi contain crystals of calcium oxalate on their outer surfaces. Formation of minerals by lichens has been recently reviewed by Adamo and Violante (2000) and will not be discussed further here.

Biogenetic calcium oxalate and calcium carbonate may be present in the patina (“scialbatura”) often found on monuments (Del Monte *et al.* 1987). This patina may decelerate weathering under humid conditions because it reduces the impact of rain. In arid conditions, lichens may accelerate weathering because they protect the rock against dehydration (Viles 1995; Stretch and Viles 2002). The balance between enhanced and reduced weathering is a function of the species composition of the weathering community, rock type, and prevailing environmental conditions.

### ■ Why do fungi weather minerals?

LMWOAs have a number of ecological functions in addition to their possible role in weathering. The question is whether mineral weathering provides certain fungi with a direct fitness advantage that might result in selection for weathering capacity (Lenton 2001). What nutrients can be made available to fungi in higher amounts through enhanced weathering? What nutrients would help increase their fitness? In symbiotic fungi, weathering may



**Figure 3.** Pure mineral patches of either potassium feldspar (K) or quartz (Q), introduced at the mycelial front in flatbed peat microcosms containing *Pinus sylvestris* seedlings colonized by *Hebeloma crustuliniforme*. Fifteen weeks after introduction, fungal proliferation was more intense in patches of K-feldspar compared to patches of quartz. From Rosling *et al.* (2004).

increase the fitness of the plant, with a positive feedback to the fungus via enhanced carbon availability. In spite of frequent reports of mycorrhizal fungi interacting with minerals (Jongmans *et al.* 1997; Wallander 2000a,b), we do not know if such interactions increase in frequency and/or strength when the host plant becomes more nutrient-limited.

*Basic cations (K, Mg, Ca).* Fungi, with their chitin-containing cell wall, require large amounts of nitrogen, but their need for basic cations may be relatively small. It is therefore unlikely that the ability to release these cations through weathering has been important during evolutionary history. Experiments do not provide support for a hypothesis of fitness effects through basic cations. Relatively high concentrations of such cations in most drainage waters are consistent with the notion that cation supply by weathering – except in old, deeply weathered soils – is likely to exceed plant demand. Primary production is rarely limited by the availability of, for example, K (Hagerberg *et al.* 2003) or Mg (Landmann *et al.* 1997). In

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laboratory experiments, K- and Mg- deficient birch plants allocated less carbon to roots than normal plants (Ericsson 1995). Similarly, Wallander and Wickman (1999) found reduced production of extramatrical mycelium by mycorrhizal fungi on pine seedlings exposed to K deficiency. Hagerberg *et al.* (2003) reported that, even in K-limited forests, addition of the K-containing mineral biotite did not enhance hyphal exploitation of such K-rich patches. In contrast, Rosling *et al.* (2004) showed selective colonization of minerals containing K over minerals that did not (Figure 3). Ectomycorrhizal fungi have been reported to enhance weathering of K- and Mg- containing silicate minerals in the laboratory (Paris *et al.* 1995; Wallander and Wickman 1999; Van Hees *et al.* 2004) and in the field (Arocena and Glowa 2000). Paris *et al.* (1996) suggested that this might be due to increased production of LMWOAs when K and Mg were deficient. Calcium deficiency is probably rare, but may occur in base-poor soils impacted by acid deposition. Blum *et al.* (2002) suggested that ectomycorrhizal trees obtained proportionally more calcium from mineral sources in the soil (apatite) than arbuscular mycorrhizal trees. Many soil fungi do interact with calcium in soil, as can be seen when ectomycorrhizal fungal hyphae are covered with calcium oxalate crystals and large amounts of calcium (Wallander *et al.* 2001). As mentioned earlier, however, producing large amounts of oxalate is more likely to help fungi to decrease dissolved Ca than to increase mineral weathering. Casarin *et al.* (2003) observed a two- to fivefold increase in oxalate after adding calcium carbonate to soils. Although elevated levels of oxalate in solution and the formation of calcium oxalate crystals can be found in mycorrhizal mats (Griffiths *et al.* 1994), the soluble concentrations observed (< 25  $\mu\text{M}$  typically) seem too low to greatly promote weathering (Drever and Stillings 1997). However, in coniferous forests in Sweden, citrate was the most abundant LMWOA (concentrations up to 240  $\mu\text{M}$  in soil solutions of forest floors). Van Hees *et al.* (2002) measured dissolution rates of microcline and labradorite in natural solutions taken from slowly decomposing forest floors layers (citrate concentration 55  $\mu\text{M}$ ) that were 2.4–5.7 times higher than in inorganic solutions.

*Phosphorus.* The role of fungal-mediated weathering in alleviating P-stress may be a more promising candidate for the evolutionary scenario. Next to N, P often limits primary plant productivity, and fungal demand for P is appreciable. Phosphorus deficiency in plants leads to enhanced carbon allocation to roots and to the associated mycorrhizal fungi (Wallander and Nylund 1992; Ericsson 1995). Placing apatite into mesh bags led to a three-fold higher proliferation of ectomycorrhizas around such bags in a P-deficient forest than in a forest with high levels of P. This suggests active foraging for, and dissolution of, P by fungi (Hagerberg *et al.* 2003). Yet, experimental data obtained so far with ectomycorrhizal fungi indicate that a shortage of P did not greatly modify the production of LMWOAs (Lapeyrie *et al.* 1991; Van Hees *et al.* 2003). This discrepancy has not been explained.

Release of cations, P, and silicates should not be considered in isolation. Weathering of apatite releases both P and Ca, and much apatite occurs as inclusions in calcium feldspars.

### ■ Prospects

Fungal weathering has taken place for hundreds of millions of years. How may human impacts on the ecosystem affect fungal-mediated weathering? Inputs of acidifying substances (acid rain) increase the rate of abiotic weathering, both in soils and stone monuments. Do fungi amplify or reduce this effect? For lichens and microcolonial Ascomycota, both amplification and reduction could occur. Cracks and weak spots can become sites for preferential colonization, which then amplify the effect of acid rain. However, the presence of lichens and black yeasts also prevents the entry of diluted sulfuric acid into the interior of such objects, thereby decelerating weathering.

Repeated tree harvesting and anthropogenic acidification may accelerate depletion of basic cations in soils. Hagerberg *et al.* (2003) addressed the question of whether fungal-mediated weathering could compensate for this effect. Hyphal or ectomycorrhizal proliferation of LMWOAs did not change in response to cation shortage, and there has been no decline in forest productivity due to cation shortage, although many calculations had forecast this. This discrepancy between observations and models may suggest some role for ectomycorrhizal weathering processes in slowing down the loss of productivity.

### ■ Novel research questions

To increase our understanding of the ecological implications of fungal weathering we need to know how weathering rates in natural ecosystems respond to nutrient deficiencies and to quantify the fungal contribution to the total weathering budget. An important direction in future research would be to study the production and sinks of LMWOAs. In view of the difficulties of in situ experiments, laboratory experiments in combination with modeling should be used to obtain reasonable estimates. More specifically, the following research questions need to be considered:

- What are accurate production and turnover rates of LMWOAs? Steep concentration gradients may exist from the production source (eg a hypha) into the bulk soil. Protection of LMWOAs against biodegradation may occur at the exuding surfaces and in pores. Also, the role of fungal–bacterial interactions, which may promote or hamper weathering (eg if bacterial consumption of organic acids is rapid) needs quantification.
- What are the carbon costs of LMWOA and other weathering agents? Although seedling carbon allocation to ectomycorrhizal fungi colonizing reconstructed soil horizons has recently been quantified (Figure 4), we do

not have accurate estimates of release rates of LMWOAs and the carbon costs as part of the total carbon budget of the ectomycorrhizal fungus and tree. Carbon costs for citrate release by the cluster roots of (the non-mycorrhizal) *Lupinus albus* in a P-deficient soil have been estimated at 23% of photosynthesis (Dinkelaker *et al.* 1989). While plants invest similar amounts of their carbon to maintain the mycorrhizal symbiosis, it is unlikely that the specific costs for LMWOAs would be that high. Carbon costs must also be related to the additional amounts of P and cations acquired by enhanced weathering. Ultimately, the question of carbon invested and nutrients acquired leads to another question. Which of the organism in the mutualistic symbiosis is in the driver's seat: the mycobiont or the phytobiont?

- How high are fungal weathering rates over time? Estimates are necessary to connect ecological and evolutionary time scales and to understand the nature of the feedback processes that link the various nutrient cycles. Which fraction of total weathering can be attributed solely to fungal activity compared to, for example, plant root and bacterial activity? Sverdrup *et al.* (2002) claimed that mycorrhizal weathering accounts for, at most, 2% of the total weathering. This estimate, however, is attributed by others to ectomycorrhizal fungal tunnelling only (Smits *et al.* 2004), which is just one aspect of fungal weathering. The latter authors suggest that fungal contribution to weathering is much higher than 2%. Surface weathering (Figure 2) is probably quantitatively more important than tunnelling.
- What is the relative importance of various weathering mechanisms as a function of species composition, rock type, and external conditions (moisture, temperature, pollution, climate)?

#### ■ Acknowledgements

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**Figure 4.** (a) Scots pine seedling growing in a reconstructed soil profile (forest floor humus on top of two mineral horizons) and (b) corresponding autoradiography image following  $^{14}\text{CO}_2$  feeding of the seedling shoot. R is a non-mycorrhizal root tip, M1 and M2 are different mycorrhizas, and EM is an external mycelium of an ectomycorrhizal fungus.  $^{14}\text{C}$  allocation to R, EM, and M2 shows up as black spots in the autoradiography image. Since M2 is in the lower mineral horizon, this observation provides further indirect support for a role of mycorrhizal fungi in mineral weathering. (From: Heinonsalo *et al.* 2004).

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