Review

Oxalate production by fungi: significance in geomycology, biodeterioration and bioremediation

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ABSTRACT

Oxalate is a key metabolite that plays a significant role in many metal and mineral transformations mediated by fungi. Metal and mineral transformations are central to geomycological processes including nutrient and element cycling, rock, mineral and metal transformations, bioweathering and mycogenic biomineral formation. Some fungal transformations have potential applications in environmental biotechnology, e.g. metal and radionuclide leaching, biorecovery, detoxification and bioremediation, and in the production or deposition of biominerals or metallic elements with catalytic or other properties. Metal and mineral transformations may also result in adverse effects when these processes result in biodeterioration of natural and synthetic materials, rock and mineral-based building materials (e.g. concrete), biocorrosion of metals, alloys and related substances, and adverse effects on radionuclide speciation, mobility and containment. Oxalate is ubiquitous in all these contexts. This paper seeks to draw together salient information from environmental and applied research to emphasize the importance of oxalate in geomycology, biodeterioration, environmental biotechnology and bioremediation.

1. Introduction

In the biosphere, oxalic acid, $(COOH)_2$, or more commonly its oxalate salts, are found in plants, animals and microbes, as well as in soils and rocks, and in rock and mineral-based cultural artefacts, building materials and structures (e.g. Graustein *et al.*, 1977; Wilson and Jones, 1983; Pinna, 1993; Arnott, 1982, 1995; Dutton and Evans, 1996; Gadd, 1999; Nakata, 2003; Arvaniti *et al.*, 2010; Perez-Rodriguez *et al.*, 2011; Aragno and Verrecchia, 2012). It is a substance that has

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long fascinated scientists in many disciplines. Oxalic acid is the simplest organic di-acid and oxalate is the most oxidized carbon compound after carbon dioxide. Calcium oxalate crystals were among the first objects to be observed using light microscopy (van Leeuwenhoek, 1675) while detection of oxalate may be used as a biosignature for pre-existence of life in extreme environments, cultural heritage and astrobiology (Gorbushina et al., 2002; Frost, 2004; Kolo and Claeys, 2005). Oxalic acid is produced by a wide variety of fungi, including saprotrophic, symbiotic and pathogenic species (Wilson et al., 1980; Arnott, 1982; Wilson and Jones, 1984; Whitney and Arnott, 1987, 1988; Birkby and Preece, 1988; Lapeyrie, 1988; Lapeyrie et al., 1987, 1990; Jones et al., 1992; Horner et al., 1995; Dutton and Evans, 1996; Arvieu et al., 2003; Gadd, 2007; Purvis et al., 2008). Although often regarded as a waste metabolite, it has many functional roles and effects that range from metal detoxification, increasing plant susceptibility to fungal infection, acting as an electron donor in lignocellulose degradation and the reduction of certain metals, e.g. Mn(IV), as well as many other roles in geomycology including bio-weathering and cycling of metals, P, S, and other elements, mineral dissolution and mineral formation (e.g. Dutton and Evans, 1996; Gharieb et al., 1998; Gadd, 1999, 2006, 2007, 2011; Landeweert et al., 2001; Purvis et al., 2008; Rosling et al., 2009; Gadd and Raven, 2011). Oxalate production is also involved in biodeterioration of rock and mineral substrates, lignocellulosic materials, and the alteration and decay of cultural heritage (Pinzari et al., 2010, 2013). This review outlines oxalate production by fungi, surveying its roles in the context of geomycology, the scientific study of the role of fungi in processes of fundamental importance to geology (Sterflinger, 2000; Gadd, 2006, 2007, 2008, 2011), and the applied significance of oxalate in biodeterioration, bioremediation and environmental biotechnology. The significance of oxalate in lignocellulose degradation and plant pathogenesis will not be covered in detail.

2. Metal chemistry of oxalate

Oxalic acid is a relatively strong acid and of central significance to its chemical properties is the ability of the oxalate anion to complex metals, resulting in formation of metal−oxalate complexes and/or precipitation of insoluble metal oxalates depending on the metal and chemical conditions (Arnott, 1995; Gadd, 1999). Most simple oxalates are sparingly soluble in water except alkali metals (e.g. Li, Na, K), NH_4^+ and Fe(III). Divalent metal oxalates are also insoluble, the most soluble being magnesium oxalate and the least soluble being calcium and lead oxalate. Most metals of interest of interest to biological and other scientists form simple and complex oxalates including those of Mg, Ca, Sr, Ba, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ag, Cd, Sn, Hg, Pb as well as actinides and lanthanides (Figs 1−3). Many oxalates are crystalline or amorphous solids, and solubility products for simple metal oxalates generally lie between 10^{-5} and 10^{-15}. It is thought only simple metal oxalates can occur in living organisms as excess oxalate is toxic. Precipitation may follow the simple equation:

$$M_{aq}^{n+} + n/2 C_2O_4{}^{2-} + xH_2O \rightarrow M(C_2O_4)_{n/2} \cdot xH_2O$$
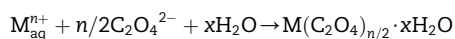
Thus, oxalate production can result in metal mobilization from solid substrates, e.g. rocks and minerals, by acidolysis (proton-mediated dissolution) and complex formation (ligand-promoted dissolution) or metal immobilization by the formation of insoluble oxalate minerals. These properties are central to all the contexts discussed in this article.

Calcium oxalate is the most abundantly found oxalate, and in living organisms and the environment, main forms are the monohydrate (whewellite) and the dihydrate (weddellite). The monohydrate generally exhibits monoclinic crystals (a rectangular prism with a parallelogram as its base) and the dihydrate tetragonal crystals (rectangular prism with a square base), although a wide variety of other crystalline forms can occur including needles, biconcave disks, dumbbells, and druses (carnation flower shape) (Arnott, 1995). A classic crystal shape of the dihydrate is the eight-face bi-pyramid, often seen in solid fungal growth media (Figs 1 and 4). The monohydrate is the least soluble form but calcium oxalate solubility is increased at pH values <5. Calcium oxalate precipitation can be represented by the simple equation:

$$Ca^{2+} + C_2O_4{}^{2-} + xH_2O \rightarrow Ca(C_2O_4) \cdot xH_2O(s) \downarrow$$
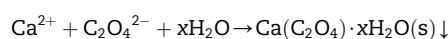
The initial precipitation is the trihydrate which loses water of crystallization to form the monohydrate or dihydrate, depending on environmental conditions. Calcium oxalate is ubiquitously associated with fungi (Cromack et al., 1979; Jones et al., 1992; Arnott, 1995; Dutton and Evans, 1996; Gadd, 1999; Tait et al., 1999; Jarosz-Wilkolazka and Gadd, 2003; Arvieu et al., 2003; Jarosz-Wilkolazka and Graz, 2006; Burford et al., 2006; Pinzari et al., 2010; Guggiari et al., 2011) (Figs 1 and 4), but other metal oxalate complexes and crystals can also be produced, including those of Co, Cd, Cu, Mn, Mg, Ni, Sr, Pb and Zn, according to similar chemical principles (Murphy and Levy, 1983; Sutter et al., 1983; Sayer et al., 1995; Sayer and Gadd, 1997; Magyarosy et al., 2002; Adeyemi and Gadd, 2005; Gadd et al., 2005; Fomina et al., 2005a, 2007a; Gadd, 2011; Wei et al., 2012, 2013) (Figs 2, 3, 5 and 6). It is often stated that metal oxalate formation may confer protection from the potentially toxic effects of such metals (Murphy and Levy, 1983; Sutter et al., 1983; Purvis and Halls, 1996; Clausen et al., 2000; Jarosz-Wilkolazka and Gadd, 2003; Meharg, 2003; Green and Clausen, 2003; Johansson et al., 2008).

3. Oxalate biosynthesis

Biosynthesis of oxalic acid and the formation of oxalates, especially those of calcium, is a property found in a wide variety of free-living and symbiotic fungi. Calcium oxalate can be associated with hyphae, as well as strands, cords and rhizomorphs, fruiting bodies, lichen thalli, and mycorrhizal systems in soil, decomposing plant biomass, and rocks as well as in the built environment and rock and mineral-based or mineral-containing cultural heritage (Graustein et al., 1977; Arnott, 1982; Whitney and Arnott, 1987, 1988; Wilson and Jones, 1983; Birkby and Preece, 1988; Ascaso et al., 1990; Lapeyrie et al., 1990; Jones et al., 1992; Yang et al., 1993; Horner et al., 1995; Wilson, 1995; Oyarbide et al., 2001; Landeweert et al., 2001; Bjelland et al., 2002; Arvieu et al., 2003; Burford et al., 2006; Schilling and Jellison, 2007; Courty
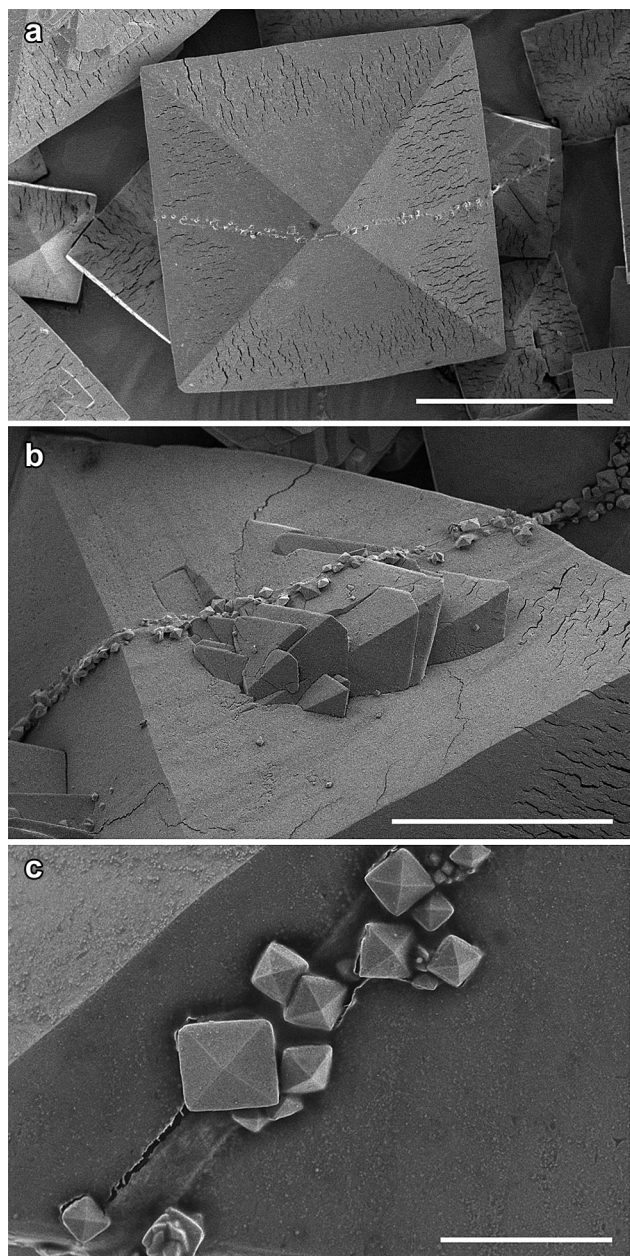
Fig. 1 — Calcium oxalate crystals produced after growth of *Beauveria caledonica* on 0.5 % (w/v) CaCO$_3$-containing medium for 24 d at 25 °C. Some very large crystals resulted as well as smaller crystals that have nucleated around fungal hyphae. Bar markers = (a) 100 μm (b) 50 μm (c) 10 μm (Li Q and Gadd GM, unpublished data).

et al., 2010; Pinzari *et al.*, 2013) (Figs 1, 4, 5, 7−9). Oxalate formation has been suggested as a taxonomically-useful character although this is highly debatable given its ubiquity and dependence on growth and environmental conditions. Earlier reports of intracellular deposition of calcium oxalate appear dubious, with many observations likely to be the result of artefacts of preparation for microscopy. Some misinterpretations may have arisen due to dehydration and shrinkage of extracellular polysaccharide or other mucilaginous material containing deposited oxalate, interwoven

hyphae, or precipitation reactions occurring within dead biomass (Connolly and Jellison, 1995; Connolly *et al.*, 1995; Gadd, 1999). The hydrated extracellular matrix of fungal mycelium also provides a good microenvironment for geochemical reactions, such as oxalate precipitation, to occur (Fomina *et al.*, 2005a).

In *Aspergillus niger*, oxalic acid biosynthesis occurs exclusively by conversion of oxaloacetate (arising from the action of pyruvate carboxylase on pyruvate produced by glycolysis) to oxalate and acetate by a cytoplasmic Mn^{2+}-dependent oxaloacetate acetylhydrolyase (OAH), with optimal production in the pH range of 5−8 (Kubicek *et al.*, 1988; Pedersen *et al.*, 2000a). This tricarboxylic acid (TCA) cycle independent pathway was confirmed using an *A. niger* mutant lacking OAH that did not produce any oxalate (Ruijter *et al.*, 1999; Pedersen *et al.*, 2000a,b), and also in *Botrytis cinerea* by disruption of the oahA gene encoding OAH (Han *et al.*, 2007). This pathway may be widely distributed in fungi (Magnusson and Lasure, 2004). As well as the cytoplasmic route of oxalate formation *via* OAH, oxalate can also be formed in other fungi, e.g. the wood-rot *Fomitopsis palustris*, *via* the glyoxylate (GLOX) cycle by the action of glyoxysomal glyoxylate dehydrogenase on glyoxylate, and this can be coupled to the TCA cycle and coordinated with acetate recycling routes (Munir *et al.*, 2001a,b; Sakai *et al.*, 2006; Hattori *et al.*, 2007). Oxaloacetate cannot pass across the membranes of mitochondria and glyoxysomes, and malate may flow out from the TCA or GLOX to be oxidized to form oxaloacetate. The TCA and GLOX cycles are replenished with succinate and glyoxylate, respectively meaning the GLOX and TCA cycles are anaplerotic to each other to keep both cycles coupled (Munir *et al.*, 2001a; Sakai *et al.*, 2006). This metabolic coupling system may serve for oxalate biosynthesis accompanied by energy production. Therefore it has been proposed that *F. palustris* acquires energy for growth by oxidizing glucose to oxalate, and this may be a general feature of both brown- and white-rot fungi during wood degradation (Munir *et al.*, 2001a). This therefore means a direct link between oxalate biosynthesis and the biogeochemical cycling of carbon, and indeed all other elements in wood. Oxalate production can be affected by many factors including carbon and nitrogen source, and environmental pH (Akamatsu *et al.*, 1994; Dutton and Evans, 1996). Oxalate is potentially toxic and so needs to efflux from cells or be broken down. A novel oxalate transporter (FpOAR) has been identified in *F. palustris* (Watanabe *et al.*, 2010). The other means of oxalate detoxification is by degradation and this is a common property, especially in wood-degrading fungi (Watanabe *et al.*, 2010).

4.   Oxalate degradation

There are a number of enzymes involved in oxalate degradation with the most prevalent in fungi being oxalate decarboxylase (ODC), a manganese-containing cupin family protein (Mehta and Datta, 1991; Dutton et al., 1994; Dutton and Evans, 1996; Micales, 1997; Kathiara *et al.*, 2000; Svedružić *et al.*, 2005; Zhu and Hong, 2010, Makela *et al.*, 2002, 2009, 2010, 2014; Hastrup *et al.*, 2012). This breaks down oxalate to CO$_2$ and formate:
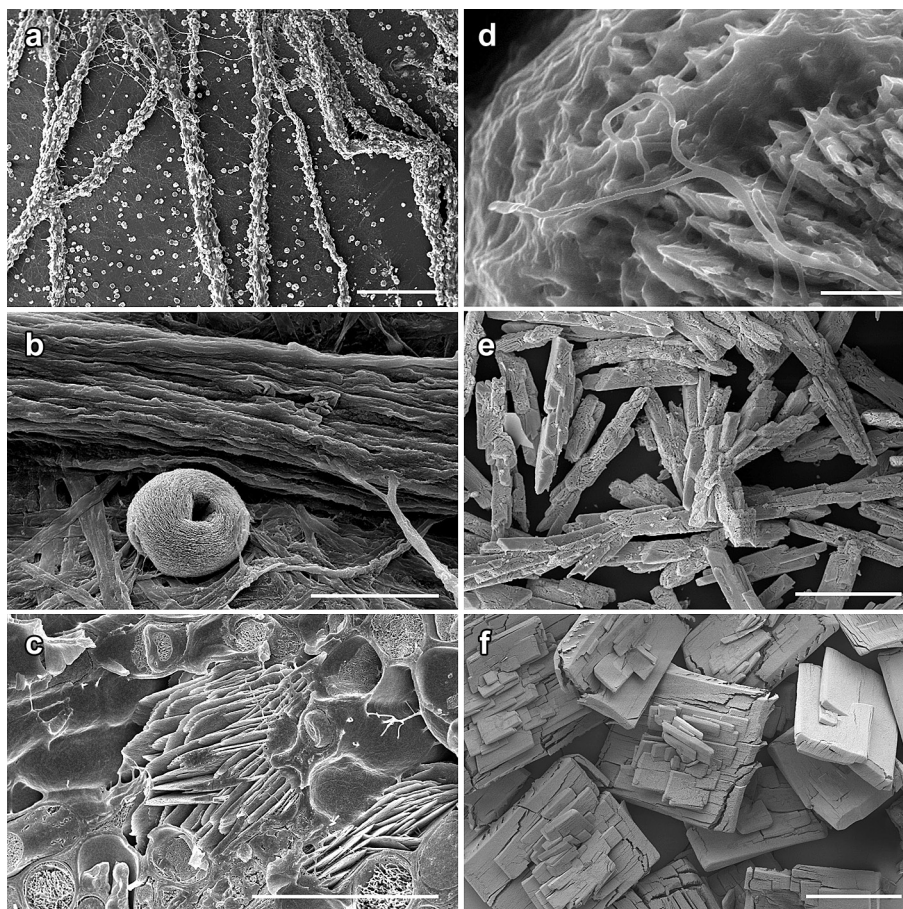
Fig. 2 − **Scanning electron microscopy images of mycogenic metal oxalates. (a) Copper oxalate hydrate (moolooite) precipitation around and associated with hyphal strands of *Beauveria caledonica* after growth in media containing copper phosphate (b) Single moolooite crystal proximal to a hyphal strand of *B. caledonica* grown in presence of copper phosphate (c) hyphal tunnels, some with exopolymeric material, in a large formation of moolooite produced by *B. caledonica* grown in the presence of copper phosphate (d) Hyphae of *B. caledonica* growing across a large formation of zinc oxalate dihydrate formed during growth on zinc phosphate (e) lead oxalate formed after growth of *B. caledonica* on lead tetraoxide (f) cadmium oxalate formed after growth of *B. caledonica* on cadmium phosphate. Bar markers = (a, f) 500 μm (b, c, d) 10 μm (e) 100 μm. Adapted from Fomina *et al.* (2005, 2010) and unpublished.**

$$(COOH)_2 \rightarrow CO_2 + HCOOH$$
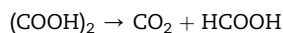
The formate may be broken down by formate dehydrogenase also yielding CO_2 and NADH (Watanabe *et al.*, 2005, 2008). Oxalate decarboxylase expression may be induced by the presence of oxalate, low pH, and other environmental factors (see Dutton and Evans, 1996; Gadd, 1999; Tang *et al.*, 2013).

Another oxalate degrading enzyme is oxalate oxidase (OXO) which cleaves oxalic acid into CO_2 and hydrogen peroxide:

$$(COOH)_2 + O_2 \rightarrow 2CO_2 + H_2O_2$$
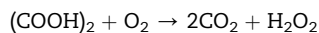
This is not as widespread as ODC but is found in some white-rots (Aguilar *et al.*, 1999; Graz *et al.*, 2009; Moussatche *et al.*, 2011).

It has been found that *Saccharomyces cerevisiae* expresses a novel oxalyl-CoA synthetase capable of catalyzing the conversion of oxalate to oxalyl-CoA. The enzyme appears to catalyze the first step in a novel pathway of oxalate degradation that offers protection from the inhibitory effects of endogenous or exogenous oxalate. A similar enzyme was shown to catalyze the first step in an oxalate catabolic pathway discovered in plants (Foster *et al.*, 2012; Foster and Nakata, 2014).

Degradation of oxalic acid by the mycoparasite *Coniothyrium minitans* may improve mycoparasitism on *Sclerotinia sclerotiorum* by stimulating production and/or activity of β-1,3-glucanase by *C. minitans* and might also be a mechanism by which it can protect plants from infection by *S. sclerotiorum* (Ren *et al.*, 2007).

5. Oxalate in geomycology

(1) Oxalate in bioweathering

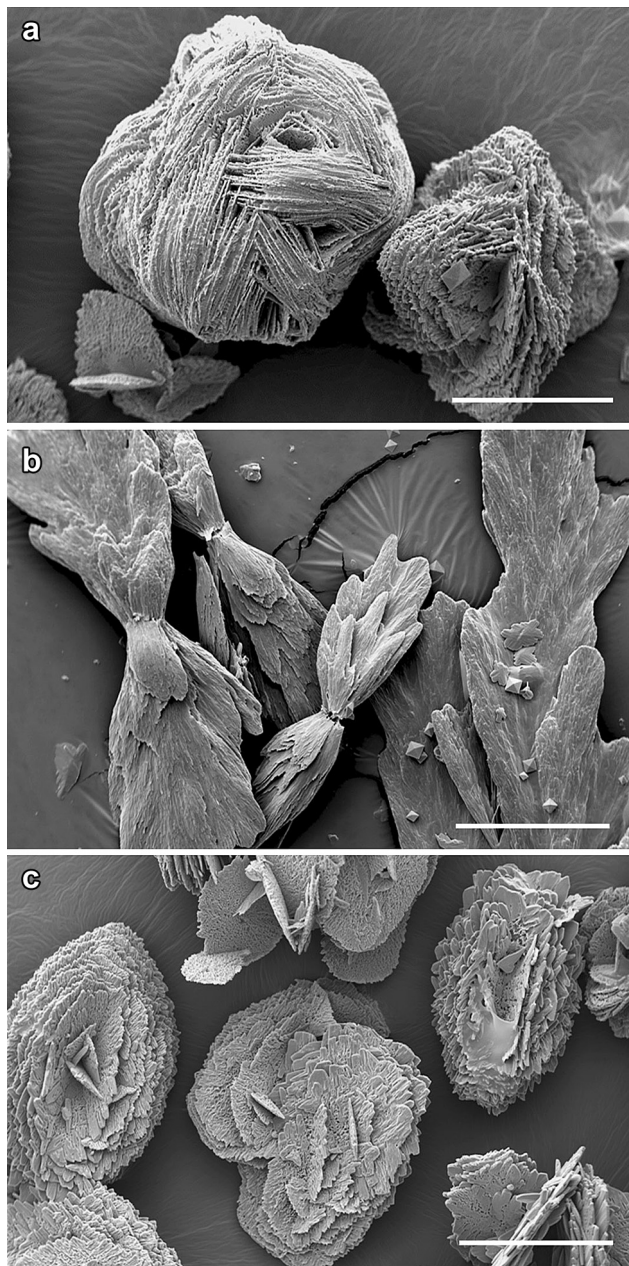Bioweathering is the erosion, decay and decomposition of rocks and minerals mediated by living organisms, and takes

Fig. 3 − **Manganese oxalates produced after fungal growth in the presence of 0.5 % (w/v) birnessite. (a) Manganese oxalate produced by *Aspergillus niger* after growth for 15 d at 25 °C in the dark (b) manganese oxalate trihydrate produced after growth of *Serpula himantioides* for 5 d at 25 °C in the dark. The small diamond-shaped crystals are calcium oxalate. (c) Manganese oxalate dihydrate produced after growth of *S. himantioides* for 23 d at 25 °C in the dark. Bar markers = (a, c) 200 μm (b) 500 μm. Adapted from Wei *et al.* (2012).**

place through physical and chemical mechanisms (Gadd, 2007). Microbial organic acids are important bioweathering agents of stone, minerals and related structural materials including such cultural heritage as monuments, statues, rock paintings, friezes and frescoes (Gadd, 1999; Warscheid

and Braams, 2000; Lisci *et al.*, 2003; Adeyemi and Gadd, 2005; Sverdrup, 2009; Rosling *et al.*, 2009; Bonneville *et al.*, 2009, 2011; Cutler and Viles, 2010; Wei *et al.*, 2011; Smits *et al.*, 2012). Oxalate can have a significant role in bioweathering, whether produced by free-living or symbiotic fungi, coupled with biophysical effects caused by hyphal penetration of the substrate (Lisci *et al.*, 2003; Lian *et al.*, 2008a,b). This arises through the metal complexing and dissolution effects on minerals mentioned previously (Gadd, 1999) as well as physical damage caused by expansive formation of the secondary oxalate biominerals (Chen *et al.*, 2000; Fomina *et al.*, 2007b) (Figs 7, 9 and 10).

The origin of fungal tunnels within weatherable soil minerals has been explained as a result of dissolution and "burrowing" within the mineral matrix—the "rock-eating fungi" hypothesis (Jongmans *et al.*, 1997; Smits, 2006). An additional hypothesis for tunnel formation may depend on biomineralization by "rock-building fungi" which highlights fungal involvement in mineral formation (Fomina *et al.*, 2010). In natural limestone microcosms, calcium oxalate monohydrate (whewellite) and dihydrate (weddellite) formed as a result of oxalic acid excretion by *Penicillium corylophilum*, and this formed a substantial biomineralized crust of secondary precipitates and hyphal coating. *Beauveria caledonica* also formed crusts and precipitated a mixture of whewellite and weddellite and copper oxalate (moolooite) when grown on media containing calcium carbonate and copper phosphate, respectively. Cryo-preservation and cryo-fracturing of these mycogenic crusts revealed an intimate relationship between the fungal hyphae and the secondary mycogenic minerals. Tunnel formation was observed within the mineral matrix which resulted from extensive precipitation of secondary mineral on living hyphae followed by hyphal death resulting in a tunnel in the mineral of similar diameter and shape as the fungal hyphae (Fomina *et al.*, 2010) (Fig. 2).

Mycorrhizal fungi can exhibit considerable mineral bioweathering properties with effects on metal mobility (Landeweert *et al.*, 2001; Martino *et al.*, 2003a,b; Hoffland *et al.*, 2004; Bonneville *et al.*, 2009, 2011; Smits *et al.*, 2012; McMaster, 2012). For many tested ericoid mycorrhizal and ectomycorrhizal fungi grown with ammonium as nitrogen source, the main mechanism of dissolution of toxic metal phosphates was acidolysis (Fomina *et al.*, 2004, 2005b). However, if the fungus was capable of excreting large amounts of oxalate, the mechanism switched to ligand-promoted dissolution and became much more efficient than acidolysis, especially evident for pyromorphite ($Pb_5(PO_4)_3Cl$) (Fomina *et al.*, 2004, 2005a,b). It has been shown that the main compounds originating from extramatrical mycelium of *Hebeloma crustuliniforme* (in association with *Pinus sylvestris*) were oxalate and ferricrocin. The exudation rate for oxalate was 19 ± 3 fmol per hyphal tip h^{-1} or 488 ± 95 fmol hyphae $mm^{-2}\ h^{-1}$. These results clearly indicate that oxalate excretion can alter the chemical conditions of soil microsites and affect mineral dissolution (van Hees *et al.*, 2006). In six different ectomycorrhizal fungi (*Hebeloma velutipes*, *Piloderma byssinum*, *Paxillus involutus*, *Rhizopogon roseolus*, *Suillus bovinus* and *Suillus variegatus*) and two saprotrophic fungi (*Hypholoma fasciculare* and *Hypholoma capnoides*) exposed to Pb, Cd and As stress, it was found that oxalate exudation increased
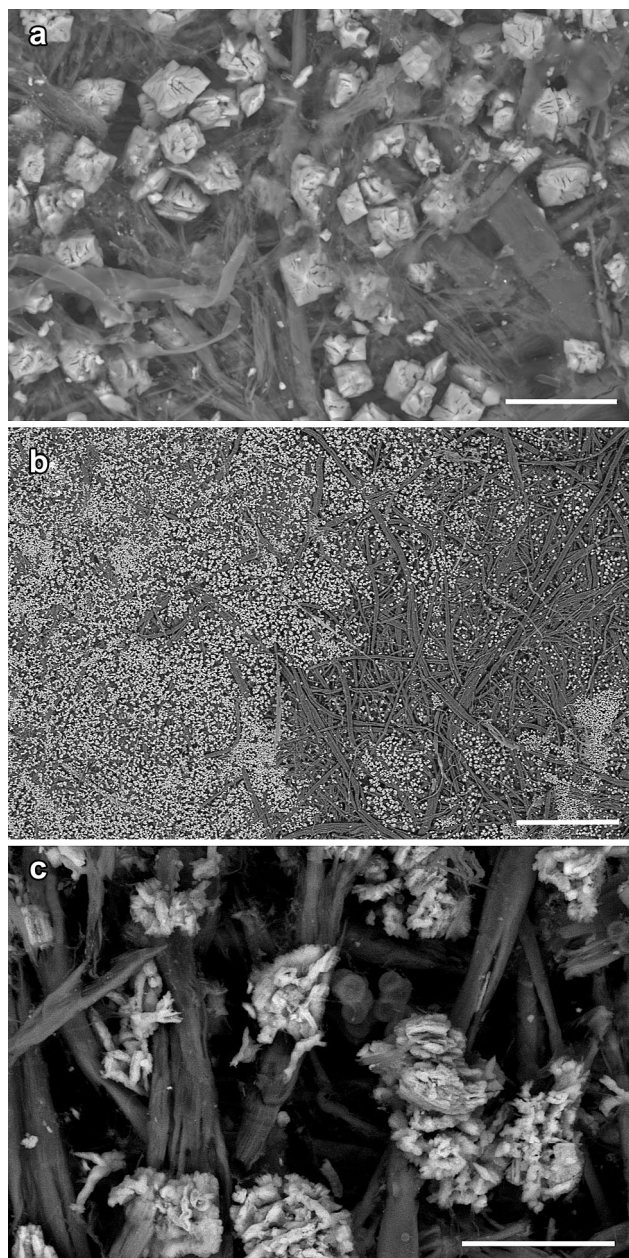
Fig. 4 — Calcium oxalate formation during fungal biodeterioration of paper. (a,b) High and low magnification images of calcium oxalate crystals produced by *Aspergillus terreus* (ATCC 10690) after growth at 27 °C for 7 d on paper containing calcium carbonate as sizing material (c) calcium oxalate aggregates in naturally-attacked paper from modern archival material that had been subject to waterlogging in 1970. Bar markers = (a, c) 40 μm (b) 400 μm. Images produced with kind permission of Flavia Pinzeri; see Pinzari et al. (2010) for further details.

significantly in response to both low and high Pb and Cd concentrations (Johansson et al., 2008). Oxalate was the dominant low molecular weight organic acid (LMWOA) produced (>90 % of total LMWOAs) and generally, the ectomycorrhizal (ECM)

species produced more oxalate than the saprotrophic fungi studied (Johansson et al., 2008).

Lichens are significant bioweathering agents (Jones et al., 1980; Wilson et al., 1980; Purvis, 1984; Chisholm et al., 1987; Wilson and Jones, 1983, 1984; Jones and Wilson, 1985; Wilson, 1995; Viles, 1995; Banfield et al., 1999; Adamo and Violante, 2000; Stretch and Viles, 2002; Purvis et al., 2008) and can penetrate rock substrates to over 1 cm depths (Lisci et al., 2003). The ubiquity of oxalate production in lichens, as well as other metal-complexing or solubilizing/precipitating metabolites, including H^+ and respiratory CO_2, has long been appreciated (Edwards et al., 1997; Chen et al., 2000; Purvis and Pawlik-Skowronska, 2008). A series of different oxalate minerals may be formed depending on the substrate, calcium oxalate being the most common, and these may form at the rock—thallus interface, within the thallus or be deposited on thallus surfaces (Ascaso et al., 1990; Bjelland et al., 2002; Giordani et al., 2003) (Fig. 5). Calcium oxalate may precipitate at concentrations <0.1 mM (Eick et al., 1996) and may form even in low Ca environments (Chen et al., 2000). Metal oxalates are the most frequently occurring bioweathering products of lichens and all divalent metal oxalates may be found (Na, K, Al, and Fe oxalates are soluble) (Chen et al., 2000). It has been suggested that oxalate patinas on ancient monuments may have arisen from prior lichen activities (Del Monte and Sabbioni, 1987; Pinna, 1993; Caneva, 1993), and these may have a protective effect because of their insolubility (Lisci et al., 2003). Oxalates have been implicated in Fe, Si, Mg, Ca, K and Al mobilization, as well as other elements, from e.g. sandstone, basalt, granite, calcareous rocks and silicates, leading to alterations in the substrate and other secondary mineral formations (Johnston and Vestal, 1993; Chen et al., 2000; Wei et al., 2012). Other secondary oxalates that have been associated with lichen growth are glushinskite (magnesium oxalate dihydrate), manganese oxalate dihydrate (lindbergite), copper oxalate (moolooite), and ferrous oxalate (humboldtine), the formation of which is dependent on the metal composition of the rock substrate (Wilson et al., 1980; Purvis, 1984; Wilson and Jones, 1983, 1984; Jones and Wilson, 1985; Chisholm et al., 1987; Wilson, 1995; Purvis and Halls, 1996; Frost, 2004; Purvis and Pawlik-Skowronska, 2008; Purvis et al., 2008) (Figs 3, 5 and 6). In some cases, lichen bioweathering may occur by biophysical means and/or from effects of other metabolites in the absence of oxalate (Scarciglia et al., 2012).

(2) Oxalate in metal and mineral transformations

Fungal oxalates have significant effects on minerals, both in mineral dissolution and in mineral formation, and this can have important consequences for component metal mobility (Gadd, 1999; Gadd and Fomina, 2011) (Fig. 7). Biomineralization refers to the processes by which living organisms form minerals, and biomineral production by fungi is an example of biologically-induced mineralization (BIM) where the organism modifies the local microenvironment creating conditions that favour extracellular precipitation of mineral phases (Gadd, 2010; Gadd et al., 2012). Mycogenic oxalates are one important example of fungal biomineral formation
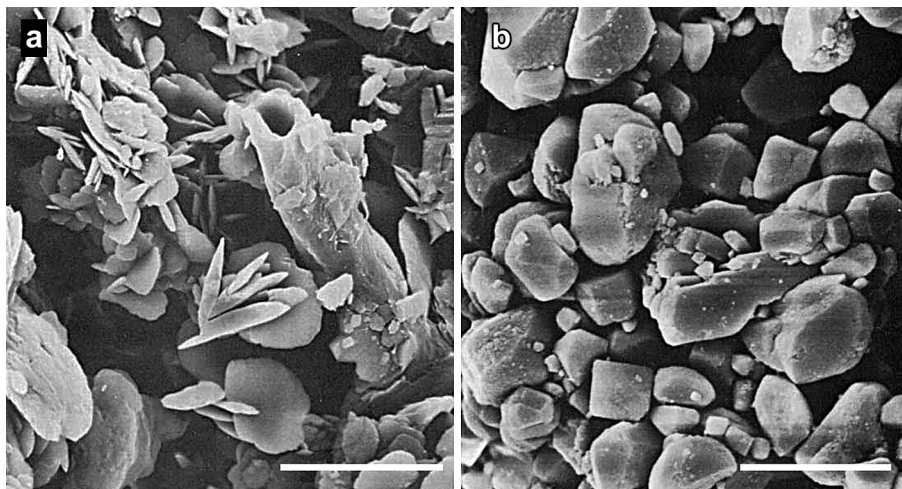
Fig. 5 − **Crystalline inclusions of (a) moolooite (copper oxalate hydrate) and (b) whewellite (calcium oxalate monohydrate) within the medulla of the lichen *Acarospora rugulosa* (R). Bar markers = 3.8 μm. Images adapted from Purvis (1984) and Chisholm et al. (1987), with permission.**

(see Burford *et al.*, 2003a,b; Gadd, 2007, 2010; Gadd and Fomina, 2011; Gadd *et al.*, 2012 for other mycominerals). Calcium oxalate precipitation has an important influence on biogeochemical processes in soils, acting as a calcium reservoir, and also influencing phosphate availability where Ca is removed from P-containing minerals (Graustein *et al.*, 1977; Cromack *et al.*, 1979) (Fig. 8). Gypsum ($CaSO_4 \cdot 2H_2O$) was effectively solubilized by both *A. niger* and *Serpula himantioides* resulting in calcium oxalate formation (Gharieb *et al.*, 1998; Gharieb and Gadd, 1999). Various ectomycorrhizal (EcM) fungi form dense aggregations of hyphae known as mats which may cover as much as 25−40 % of the forest floor in Douglas-fir forest ecosystems (Cromack *et al.*, 1979; Kluber *et al.*, 2010). These mats are of lower pH than the surrounding soil and have high levels of oxalate: a mean calcium oxalate content of 82 g m^{-2} has been recorded (Cromack *et al.*, 1979). Many EcM can excrete oxalate (Lapeyrie *et al.*, 1987; Landeweert *et al.*, 2001; Arvieu *et al.*, 2003; Tuason and Arocena, 2009; Courty *et al.*, 2010) and it is suggested that oxalate aids the acquisition of P by the fungus and plant through bioweathering (Kluber *et al.*, 2010). Weathering of clay minerals is more pronounced in these mats, resulting from Fe and Al solubilization (Cromack *et al.*, 1979). P may be directly released from oxide surfaces, and from Fe and Ca phosphates, e.g. apatite:

$$Ca_5(PO_4)_3OH + 5H_2C_2O_4 \rightarrow 5CaC_2O_4 + 3H_2PO_4 + H_2O$$
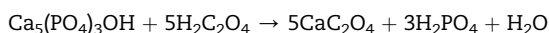
Oxalate is common in many soils and may range from 25 to 1000 μM (Fox and Comerford, 1990, 1992). Average organic acid concentrations in soils are generally <1 mM, but high concentrations may occur in local microenvironments (Cromack *et al.*, 1979; Banfield *et al.*, 1999; McMaster, 2012).

Fungi produce other metal oxalates besides calcium on interacting with a variety of different metals and metal-bearing minerals, including those of Ca, Cd, Co, Cu, Mg, Mn, Sr, Zn, Ni and Pb (Sayer and Gadd, 1997; Gadd, 1999, 2007; Sayer *et al.*, 1999; Adeyemi and Gadd, 2005; Fomina *et al.*, 2007a; Wei *et al.*, 2013) (Fig. 7). The formation of toxic metal oxalates may contribute to fungal metal tolerance (Gadd, 1993; Clausen *et al.*, 2000; Jarosz-Wilkolazka and Gadd, 2003; Green and Clausen, 2003). Mycogenic oxalate minerals produced by free-living fungi include glushinskite ($MgC_2O_4 \cdot 2H_2O$) (Burford *et al.*, 2003a,b; Kolo and Claeys, 2005, Gadd, 2007), moolooite ($Cu(C_2O_4) \cdot 0.4H_2O$) (Fomina *et al.*, 2005a, 2007a), and lindbergite ($MnC_2O_4 \cdot 2H_2O$) (Wei *et al.*, 2012) (Figs 2, 3, 5 and 6).

The significance of low molecular weight organic acids in mineral dissolution and bioweathering is increasingly appreciated, as discussed earlier, and oxalic acid can mediate acidolysis (arising from H$^+$), ligand-promoted dissolution (arising from metal complexation by oxalate) and reductive mobilization of metals from minerals (Gadd *et al.*, 2012; Wei *et al.*, 2012). For montmorillonite, oxalate did not catalyze the dissolution reaction between pH 2 and 4 and dissolution took place through protonolysis. However, oxalate markedly enhanced montmorillonite dissolution at pH 4−8, with dissolution taking place through a ligand-promoted mechanism (Ramos *et al.*, 2014). Oxalate production by *A. niger* and *S. himantioides* has been shown to induce the dissolution and conversion of both rhodochrosite and Mn oxides to Mn oxalate minerals (Sayer *et al.*, 1997; Wei *et al.*, 2012) (Fig. 3). Oxalate can act as a reductant of Mn(IV) oxides, and this can result in mobilization of Mn(II), which can then precipitate. Both *A. niger* and *S. himantioides* were capable of solubilizing the insoluble manganese oxides MnO_2 and Mn_2O_3, mycogenic manganese oxide (MnO_x) and birnessite [$(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4 \cdot 1.5H_2O$]. Precipitation of insoluble manganese oxalate occurred and manganese oxalate trihydrate was detected after growth of *S. himantioides* with birnessite which subsequently was transformed to manganese oxalate dihydrate (Wei *et al.*, 2012) (Fig. 3). Ligand-promoted dissolution of uranium oxides was much more significant than proton-promoted acidification. Uranium oxide solubilization

and accumulation of mobilized uranium from uranium oxides and depleted uranium correlated with the amount of excreted oxalate (Fomina et al., 2007c). Accumulated uranium was biomineralized as uranyl phosphate minerals of the meta-
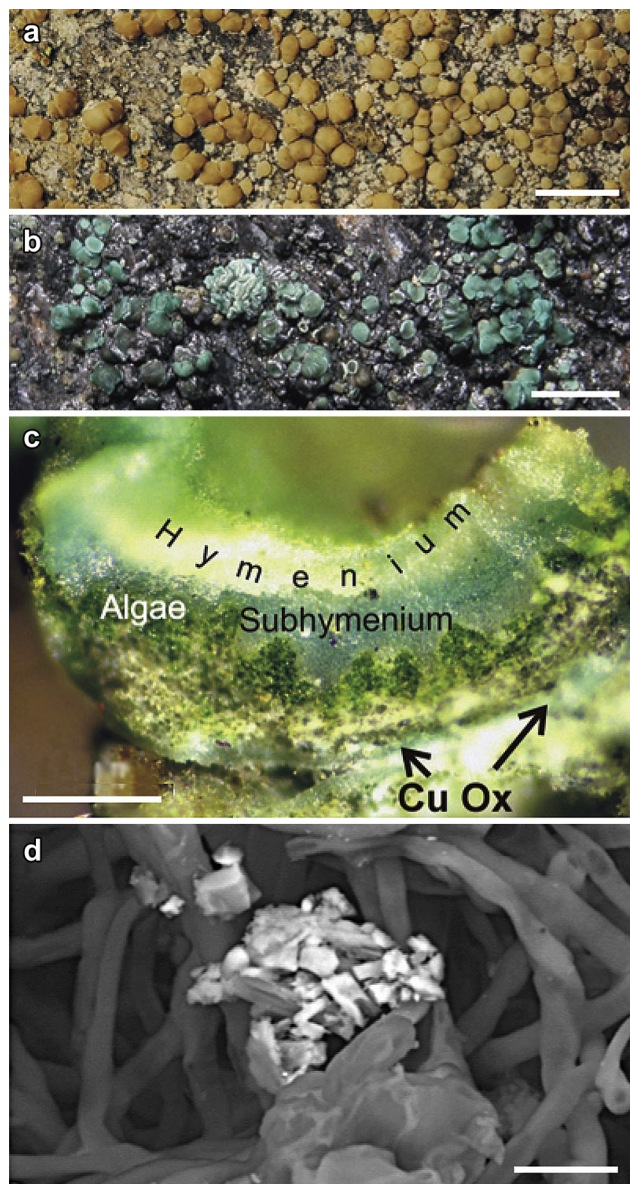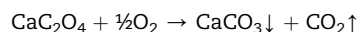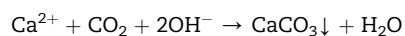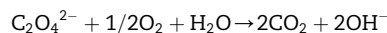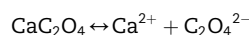
Fig. 6 — Moolooite (copper oxalate hydrate) formation within the lichen *Lecanora polytropa*. (a) *L. polytropa* sampled from schistose rocks Folgefonn Peninsula, Norway (b) Turquoise-coloured *L. polytropa* sampled from a psammite boulder of a retaining wall supporting mine spoil at Ridarhyttan Kopparverket, Bergslagen District, Sweden (c) Section through *L. polytropa* fruit showing the internal turquoise region (subhymenium) above the irregular algal layer. Vivid blue inclusions (copper oxalate) are present in the medulla below. (d) Back-scattered electron image of crystalline aggregate of copper oxalate in association with fungal hyphae within the lichen medulla. Bar markers = (a, b) 2 mm; (c) 200 μm (d) 6 μm. Adapted from Purvis et al. (2008) with kind permission of the author and the Mineralogical Society of Great Britain and Ireland.

autunite group with abundant uranium precipitates encrusting the hyphae (Fomina et al., 2007c, 2008; Gadd and Fomina, 2011). New biominerals resulted from fungal interactions with zinc silicate and zinc sulfide ores. Zinc oxalate dihydrate was formed through oxalate excretion by the test fungi and the mineral surfaces showed varying patterns of bioweathering and biomineral formation. In addition, calcium oxalate was formed from the calcium present in the mineral ore fractions, as well as calcite (Wei et al., 2013) (Fig. 7).

Mineral dissolution may result in release of toxic (Sayer et al., 1999) or essential metals like K (Lian et al., 2008a,b) as well as nutrients like P or S (Gharieb et al., 1998; Gharieb and Gadd, 1999; Smits et al., 2012). Oxalic acid can leach those metals that form soluble oxalate complexes, including K, Al and Fe (Strasser et al., 1994; Lian et al., 2008a,b) as well as toxic metals. The latter may biomineralize as oxalates or other secondary minerals, including phosphates, depending on the local microenvironment (Gadd, 2010, 2011). Novel mycogenic phosphates resulted on fungal transformations of uranium oxides, depleted uranium (Fomina et al., 2007a,c, 2008) and metallic lead (Rhee et al., 2012, 2014). Fungal dissolution of pyromorphite ($Pb_5(PO_4)_3Cl$) resulted in lead oxalate formation (Sayer et al., 1999). Organic acid excretion may be inter- and intra-specific, and can be strongly influenced by pH, nutrition, and the toxic metals and minerals present (Sayer et al., 1995; Rosling et al., 2004a,b; Fomina et al., 2004, 2005b; Sayer and Gadd, 2001; Arvieu et al., 2003; Jarosz-Wiłkołazka and Grąz, 2006; Johansson et al., 2008; Li et al., 2011).

(3) Oxalate—carbonate cycle

Degradation of calcium oxalate by oxalotrophic bacteria resulting in $CaCO_3$ formation is part of the oxalate—carbonate cycle (Verrecchia et al., 2006; Martin et al., 2012). In semi-arid environments, this process may act to cement pre-existing limestones by filling pores with recrystallized calcite (Verrecchia, 1990; Verrecchia et al., 1990, 1993). Oxalate oxidation by oxalotrophic bacteria increases alkalinity and media can reach >pH 9, enabling calcite precipitation (Braissant et al., 2002, 2004). Salient steps in the oxalate—carbonate cycle are degradation of oxalate-containing plant biomass and biodegradation of the oxalate, followed by precipitation of calcite above pH 8.5 accompanied by release of 1 mol CO_2 for each mol oxalate oxidized (Aragno and Verrecchia, 2012). Overall equations are as follows:

$$CaC_2O_4 \leftrightarrow Ca^{2+} + C_2O_4{}^{2-}$$

$$C_2O_4{}^{2-} + 1/2 O_2 + H_2O \rightarrow 2CO_2 + 2OH^-$$

$$Ca^{2+} + CO_2 + 2OH^- \rightarrow CaCO_3\downarrow + H_2O$$

$$CaC_2O_4 + \tfrac{1}{2}O_2 \rightarrow CaCO_3\downarrow + CO_2\uparrow$$

Fungi may participate in the oxalate—carbonate cycle by oxalate synthesis and formation of calcium oxalate, but also by plant biomass and oxalate degradation (Verrecchia et al., 1993; Guggiari et al., 2011; Martin et al., 2012). It has been concluded that interactions between bacteria and fungi are essential to drive the oxalate—carbonate cycle in soil (Martin et al., 2012). The formation of oxalate and carbonate has
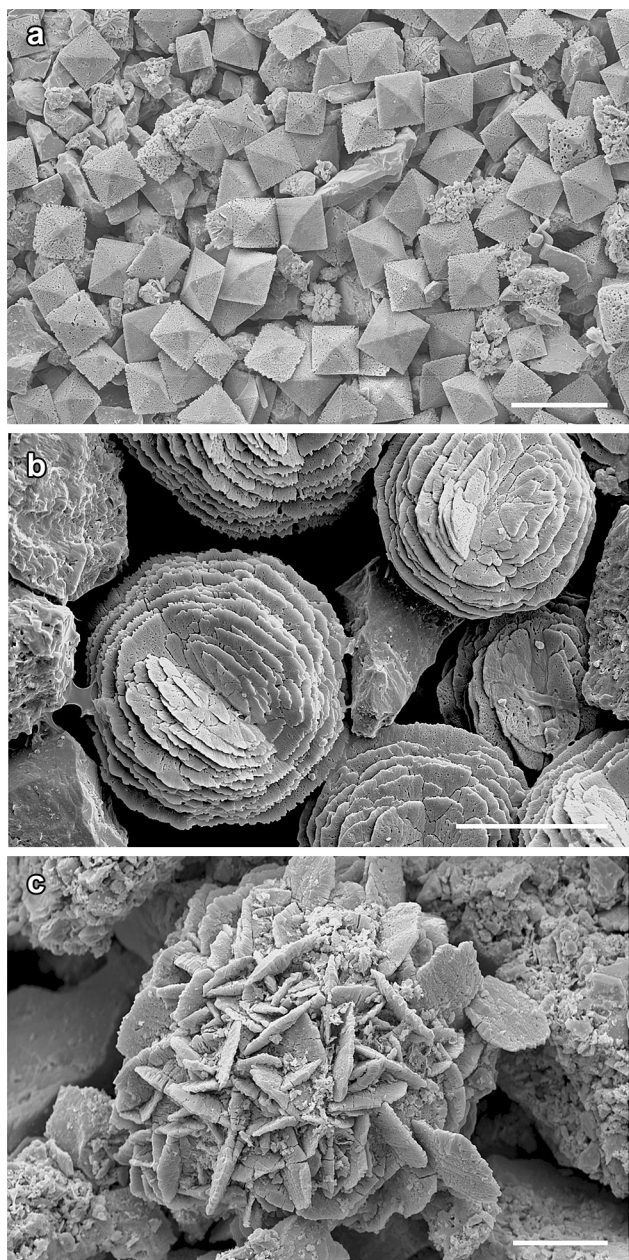
Fig. 7 — Secondary mycogenic oxalates produced after fungal transformation of zinc silicate and zinc sulfide mineral ores (a) calcium oxalate produced by *Beauveria caledonica* after growth on zinc sulfide-amended medium for 60 d, bar marker = 50 μm (b) zinc oxalate produced by *Aspergillus niger* after growth on zinc silicate-amended medium for 20 d, bar marker = 50 μm (c) zinc oxalate produced by *Serpula himantioides* after growth on zinc sulfide-amended medium for 20 d, bar marker = 20 μm. All incubations were carried out at 25 °C in the dark. Images adapted from Wei *et al.*, 2013.

been regarded as representing a long term C sink and mechanism for CO_2 storage, and this has been demonstrated for the Iroko and other tree systems where extensive carbonate biomineralization occurs due to complex interactions between plants, fungi and bacteria (Cailleau *et al.*, 2011, 2014).

6. Oxalate in biodeterioration

Fungi are important biodeterioration agents of natural and synthetic substances and oxalate commonly features in the decay and spoilage of rock and mineral based structures and building components, including cultural heritage, concrete, cement and mortars, metals, and lignocellulosic materials, such as wood and paper (de la Torre *et al.*, 1991, 1993; Gadd, 1999; Gadd *et al.*, 2005; Schilling and Jellison, 2007; Lian *et al.*, 2008a,b; Sterflinger, 2000, 2010; Cutler and Viles, 2010; McMaster, 2012; Sterflinger and Pinzari, 2012) (Figs 4, 9 and 10).

(1) Cultural heritage

Calcium oxalates (whewellite and weddellite) occur widely in patinas on the surfaces of marble and limestone buildings and monuments, as well as on sandstone, granite, plasters, cave and wall paintings and sculptures (Del Monte and Sabbioni, 1986; Garcia-Valles *et al.*, 1997; Sterflinger *et al.*, 1999; Sterflinger, 2000; Monte, 2003). It has been stated that this kind of attack is the most important weathering process affecting historic monuments (Del Monte *et al.*, 1987). The oxalate patina represents a record of such alteration, and this subsequently results in protecting the underlying marble and limestone (Del Monte *et al.*, 1987). Because of their widespread occurrence in such cultural heritage, and in natural rock outcrops, weddellite and whewellite must therefore not be considered rare minerals, as asserted in the mineralogical literature, but as widely distributed in nature (Del Monte *et al.*, 1987). Black crusts are often found on stone and mortar surfaces exposed to atmospheric deposition and reflect transformations of materials in the substrate: oxalate seems nearly always to be present (Sabbioni *et al.*, 1998, 2003).

For marble or limestone artefacts, the surface calcium oxalate patinas can form a relatively uniform thickness of around 80—150 μm (Doherty *et al.*, 2007). These calcium oxalate films are very stable, and both whewellite ($CaC_2O_4 \cdot H_2O$) and weddellite ($CaC_2O_4 \cdot 2H_2O$) may be present (Monte, 2003; Perez-Rodriguez *et al.*, 2011). Copper(II) oxalate [$Cu(C_2O_4) \cdot xH_2O$] has been found in patinas on copper metal (de la Fuente *et al.*, 2008).

Some have suggested that the oxalate films originate from degradation of past surface treatments (Rampazzi *et al.*, 2004; Perez-Rodriguez *et al.*, 2011) although this must be mediated by microbes and, as described earlier, oxalate may be produced from organic degradation. However, this hypothesis is considered unlikely by others especially in view of patina occurrence on untreated surfaces (Del Monte *et al.*, 1987). Both standpoints may be reconciled by the need for an organic substrate for oxalate biosynthesis however, and all rock surfaces receive organic deposition in rainwater, animal wastes, etc. as well as from microbial biofilm exudation and decay (Burford *et al.*, 2003b). It should be noted that another oxalate source may be atmospheric deposition, although oxalate has been detected in locations regardless of local climate, and generally concluded to be of biogenic origin (Sabbioni *et al.*, 2003).

Lichens are also significant biodeteriorative agents of stone monuments, buildings, cements and mortars and oxalate is again often implicated in the process (Seaward *et al.*, 1989; Viles, 1995; Seaward, 1997; Arino *et al.*, 1997; Edwards *et al.*,
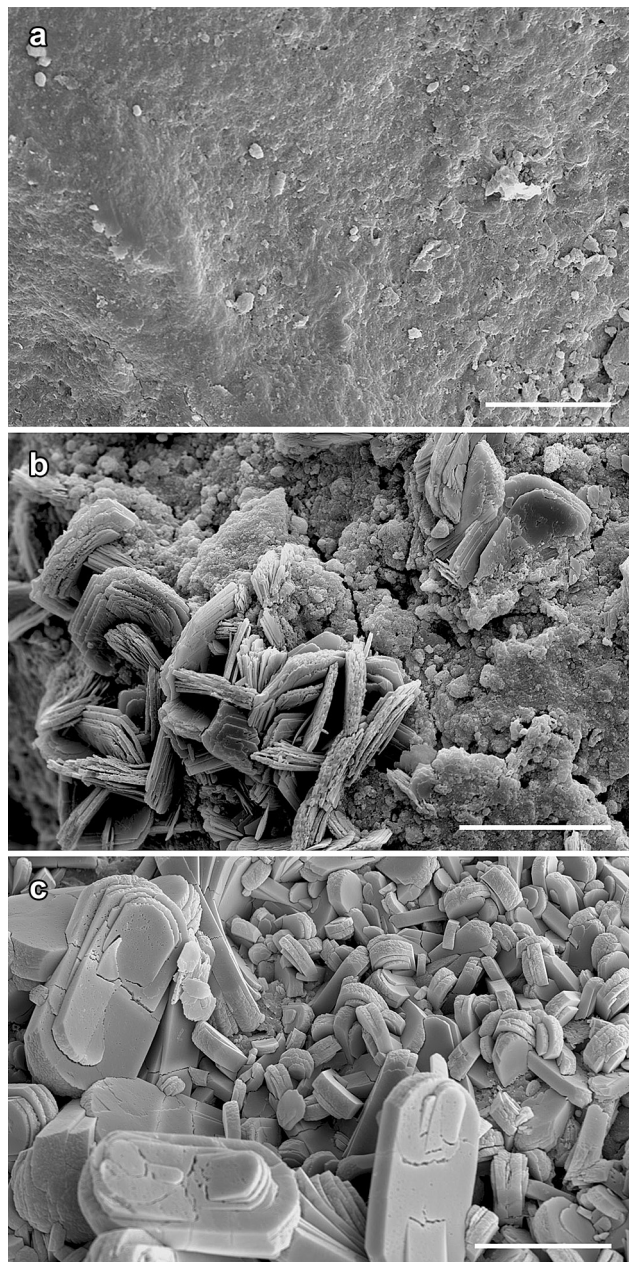
Fig. 8 – Alteration of the surface of rock phosphate (RP) by fungal activity and production of whewellite (calcium oxalate monohydrate). (a) Control RP surface (b) RP after incubation with *Trametes versicolor* for 6 d (c) RP after incubation with *Serpula himantioides* for 7 d. Bar markers = 20 μm. The crystalline formations in (b) and (c) were identified as whewellite. RP was incorporated into malt extract agar to 0.3 % (w/v) and all incubations were at 25 °C in the dark (Bahri-Esfahani J, George TS, Gadd GM, unpublished data).

1991, 1997) (Fig. 10). Conversely, in some instances physico-chemical weathering may be a more significant process than bioweathering, and in more labile rock substrates such as limestone, lichens may act in bioprotection through an "umbrella effect" by reducing contact of the stone with water (Carter and Viles, 2003, 2005; Concha-Lozano et al., 2012).

Fungal growth in wall murals and frescoes can cause structural damage, and calcium and other oxalates may be produced from the calcite or metal-containing pigments (which may be mineral-based) in the paint used. This can cause efflorescence, expansion cracking, peeling and spalling of outer layers, as well as colour changes and stains in the paintings (Krumbein et al., 1989; Nevin et al., 2008; Rosado et al., 2013). Interestingly, radiocarbon dating of calcium oxalate coatings of rock paintings can provide a method for testing chronological models, and define, with acceptable accuracy, the time period during which pictographs were produced (Ruiz et al., 2006; Rowe, 2009). As long as the stratigraphic relationship between oxalate crusts and a painting event can be established, minimum and maximum ages for pictographs can be obtained (Ruiz et al., 2012).

Medieval stained glass often shows corrosion, patina development, and mineral crust growth, which has caused serious damage to many Central European stained glass windows (Pinar et al., 2013). Such glass biodeterioration arises from complex microbial communities, including bacteria, fungi and lichens, with oxalate again being commonly found (Pinar et al., 2013).

Fungal biodeterioration of ivory was investigated regarding the possible origins of the surface damage observed on early medieval sculptures made largely from walrus tusks, 'the Lewis hoard of gaming pieces'. Colonization of ivory and/or exposure to fungal activity lead to extensive secondary biomineral formation, mainly as calcium oxalate monohydrate (whewellite) concomitant with leaching of apatite from the ivory (Pinzari et al., 2013) (Fig. 9).

(2) Paper

Modern and ancient paper can contain large amounts of calcium carbonate. This originates from ground natural calcium carbonates, such as limestone, dolomite, marble, chalk and seashells, and chemically precipitated calcium carbonates (Pinzari et al., 2010). Other metals can arise from impurities, while Cu and Fe are found in inks (Sterflinger and Pinzari, 2012). Fungal interaction with the carbonate substrates in paper results in replacement of the original minerals with calcium oxalate with both the fungal hyphae and cellulose fibrils providing preferential sites for precipitation of calcium oxalate dihydrate and monohydrate (Pinzari et al., 2010) (Fig. 4).

Paper machine water circuits have pH, temperature and nutrients favourable for microbial growth which can cause biodeterioration and biocorrosion problems. It was found that large amounts of thiosulfate, sulfite and oxalate were generated from sulphate and sheets of chemical pulp in a splash area simulator fed with artificial paper machine white water. Stainless steel coupons placed in the simulator developed significant corrosion pits within 4 weeks, and this was most extensive proximal to patches where large amounts of thiosulfate and oxalate (the latter presumably of fungal origin) accumulated in the pulp sheet (Uutela et al., 2003).

(3) Concrete and nuclear decommissioning

Cement and concrete are used as barriers in all kinds of nuclear waste repositories. Despite the service life of concrete supposedly reaching up to 1 M years, biodeterioration and
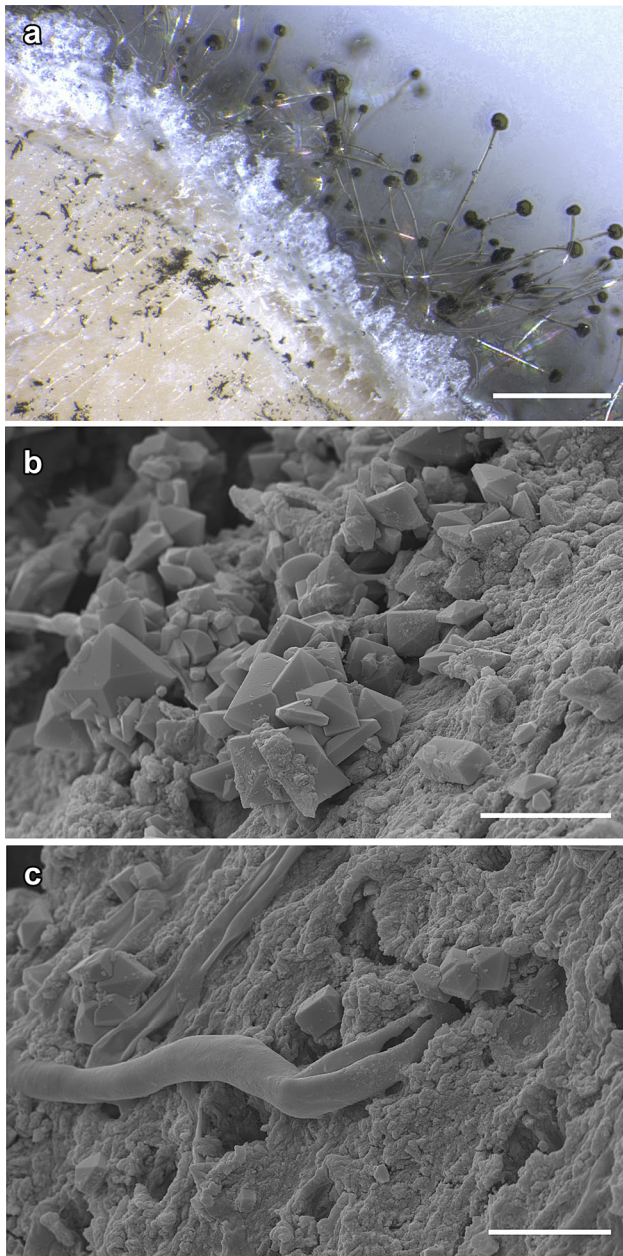
Fig. 9 – Calcium oxalate formation during fungal attack of ancient ivory. (a) *Aspergillus niger* **colonizing the surface of a boar tusk fragment and development of a biomineralized surface crust of calcium oxalate monohydrate (whewellite) below the mycelial mat (b) calcium oxalate crystals and (c) oxalate deposition and tunnelling on the surface of walrus tusk after incubation with** *Serpula himantioides* **for 14 d at 25 °C. Bar markers = (a) 500 μm (b, c) 10 μm. Image (a) adapted from Pinzari** *et al.* **(2013), and unpublished.**

biocorrosion are important factors to take into account yet this, as well as bacterial processes, are almost completely ignored by the nuclear industry. Many studies have shown that fungi can play an important role in biodeterioration of concrete (Perfettini *et al.*, 1991; Gu *et al.*, 1998; Nica *et al.*, 2000; Fomina *et al.*, 2007b; George *et al.*, 2013). Complexolysis

appears to be the main mechanism of calcium mobilization (Gu *et al.*, 1998) and this can be followed by calcium oxalate precipitation (and secondary calcite) (Fomina *et al.*, 2007b; George *et al.*, 2013). Several fungi exhibit radiation-resistance and can colonize concrete barriers even under severe radioactive contamination such as that which occurred after the Chernobyl accident in 1986 (Zhdanova *et al.*, 2000). Fungi from the genera *Aspergillus*, *Alternaria* and *Cladosporium* were able to colonize concrete used as the radioactive waste barrier and leached iron, aluminium, silicon and calcium, reprecipitating calcium oxalate in their microenvironment (Olishevskaya *et al.*, 2004; Fomina *et al.*, 2007b). Fungi are, of course, also important members of microbial communities (including lichens) that colonize and deteriorate 'normal' concrete and cement used in buildings and other structures (Perfettini *et al.*, 1991; George *et al.*, 2013).

(4) Other building materials

Biodeterioration of ceramic roof tiles by lichens has been identified as being caused by oxalic acid excretion, causing ceramic matrix deterioration (Radeka *et al.*, 2007). Incorporation of a Cu-slag (10 %wt) into model tiles caused retardation of biodeterioration presumably because of Cu toxicity (Radeka *et al.*, 2007).

Oxalic acid is implicated in lichen biodeterioration of asbestos roofing material, which attacks the cement matrix over time (Favero-Longo *et al.*, 2009). Lichens have been shown to colonize and weather chrysotile asbestos-bearing rocks (Favero-Longo *et al.*, 2005) with their metabolites modifying the surface activity of the fibres (Martino *et al.*, 2003a,b, 2004) Calcium oxalate monohydrate was detected at the lichen-asbestos interface and it has been suggested that oxalate is the agent responsible for depletion of MgO from chrysotile and that of Na_2O and FeO_{tot} from crocidolite (Favero-Longo *et al.*, 2005, 2009). Lichen cover on asbestos may therefore have some positive benefits in stabilizing the surface and preventing asbestos detachment and dispersal, as well as chemically modifying the asbestos, particularly decreasing Fenton activity, an important factor related to asbestos toxicity (Daghino *et al.*, 2005; Favero-Longo *et al.*, 2005, 2009).

7.   Oxalate in environmental technology

(1) Bioprotection

Precipitation of calcium oxalate monohydrate (COM) within the pore spaces of concrete has been investigated as a waterproofing material to enhance hydraulic properties as well as minimize water leakage (Arveniti *et al.*, 2010).

Biomineralization phenomena also provide a biotechnology applicable to the conservation or protection of stone surfaces in heritage structures (Cezar, 1998; Webster and May, 2006). Artificial calcium oxalate treatment to protect marble sculptures and a mural facade has been reported (Doherty *et al.*, 2007). This artificially-produced calcium oxalate layer is based on transformation of surficial calcium carbonate by application of an ammonium oxalate poultice (Cezar, 1998; Doherty *et al.*, 2007). *Beauveria* spp. have been

Fig. 10 — Lichens are important geochemical agents and oxalate is produced by many species, contributing to physical and chemical biodeterioration of the substrate. This can lead to profound changes that are especially evident in cultural heritage. The figure shows successive images of a gravestone taken over an approximate seven-year period, showing phases of lichen colonization and also areas of detachment of biomass with resulting loss of underlying substrate. Images recorded (a) 07.07.2007 (b) 23.01.2010 (c) 04.05.2014.

well described in their ability to overproduce oxalate, especially in the presence of toxic metals such as Cu (Fomina et al., 2005a). In a biotechnological attempt to produce protective oxalate films, oxalate patinas were investigated for various metals incubated with *Beauveria bassiana*, with the best results obtained for ancient and modern copper metal (Joseph et al., 2012).

(2) Bioleaching and bioremediation of metals

Chemoorganotrophic bioleaching of metals by fungi from industrial wastes and by-products, low grade ores and metal-bearing minerals is relevant to recycling and biorecovery of valuable metals, and bioremediation of contaminated solid wastes (Burgstaller and Schinner, 1993; Strasser et al., 1994; Gadd, 1999, 2001, 2007, 2010; Brandl, 2001; Brandl et al., 2001; Mulligan and Galvez-Cloutier, 2003; Fomina et al., 2005b; Asghari et al., 2013). It may also be relevant to release of, e.g. phosphate from mineral sources such as rock phosphate (Fig. 8). Fungi such as *Aspergillus* and *Penicillium* spp., have been used to leach metals such as zinc, copper, nickel and cobalt from a variety of solid materials, including low-grade mineral ores, spent refinery catalysts, fly ash and electronic waste (e-waste) (Burgstaller and Schinner, 1993; Brandl, 2001; Brandl et al., 2001; Mulligan and Galvez-Cloutier, 2003; Wu and Ting, 2006; Cui and Zhang, 2008; Xu and Ting, 2009; Asghari et al., 2013). While citric acid is commonly implicated in fungal bioleaching because of its ability to form many soluble metal complexes, oxalate has some relevance for those metals forming soluble oxalate complexes. Oxalic acid production by fungi can be manipulated to over 400 mM for solubilization of Al or Fe that form soluble oxalate complexes (Strasser et al., 1994). A spent refinery processing catalyst was physically and chemically characterized and subjected to a one-step and two-step bioleaching process using a high-yield oxalic acid producing strain of *A. niger* (Santhiya and Ting, 2005). Metals may be recovered from leachates by a variety of processes including cementation, solvent extraction, activated carbon, and ion exchange (Cui and Zhang, 2008) with biotechnological processes, including biomineralization, being potential options (Gadd, 2007, 2010; Gadd et al., 2012).

Soil washing is one of the few permanent treatment alternatives to remove metal contaminants from soils (Dermont et al., 2008). Oxalate has had limited attention in this technology for obvious reasons, though was more effective than EDTA to remove metals associated with soil Fe−Mn oxides due to attack on the oxides (Elliot and Shastri, 1999).

Chemical and hydrometallurgical processes based on vacuum pyrolysis, oxalate leaching and precipitation have been applied to recover cobalt and lithium from spent lithium-ion batteries and zinc plant residue (Wang and Zhou, 2002; Chen et al., 2011; Sun and Qiu, 2012). Oxalate acts as a leaching and precipitation reagent, precipitating cobalt from $LiCoO_2$ and CoO as $CoC_2O_4 \cdot 2H_2O$ with 1.0 M oxalate solution at 80 °C, and separating Co and Li (Sun and Qiu, 2012). Selective oxalate precipitation was used to separate Ca and Mg oxalates from mixed-metal brine. K and Li could be removed by washing, and a high purity magnesium oxalate

(MgC$_2$O$_4$·2H$_2$O) obtained which is an important precursor for MgO production by roasting (Tran *et al.*, 2013).

The precipitation of actinide (III) and actinide (IV) oxalates is widely used as a method for the precipitation and recovery of actinides in the reprocessing of spent nuclear fuel (Abraham *et al.*, 2014). Crystalline lead oxalate and aqueous lead complexes may be important in nuclear waste isolation, as oxalate is present in waste streams and metallic lead is present as radiation shielding. Crystalline lead oxalate could be a potentially important solubility-limiting phase for lead, or oxalate, or both. Further, aqueous lead oxalate complexes are strong and soluble Pb can therefore compete with actinides for dissolved oxalate, lowering the total soluble fraction of actinides such as Am and Np (Xiong *et al.*, 2013).

8. Oxalate in nanotechnology

Oxalates are extremely important industrial substances, because of their chemical properties outlined previously, and are used in, e.g. nuclear reprocessing, nanotechnology, catalysis, superconductor and laser technology, as precursors for other industrially-important substances and in the development of hybrid-chemical structures (Aimable *et al.*, 2011; Behnoudnia and Dehghani, 2013; Abraham *et al.*, 2014; Vimal *et al.*, 2014). The precipitation of various oxalates is also often used to make precursors of high-quality ceramic materials (Bhargarva *et al.*, 1995; Van Herle *et al.*, 1997).

Cobalt oxalate synthesis is an important component in cobalt hydrometallurgy (Zhang *et al.*, 2012). Copper oxalate has unusual antiferromagnetic properties and is also a precursor material for the production of CuO and Cu nanoparticles (Zhang *et al.*, 2008; ul Haq and Haider, 2009). CuO has potential applications in various fields, such as gas sensors, solar energy and catalysis (Aimable *et al.*, 2011). High surface area CuO has been produced most successfully *via* the decomposition of nanostructured copper oxalate precipitates (Soare *et al.*, 2006; Aimable *et al.*, 2011). Copper oxalate has also been used to produce Cu(OH)$_2$ and Cu$_2$O nanostructures (Behnoudnia and Dehghani, 2013). Chemical research seeks to find better ways of producing nanosized particles of copper oxalate by precipitation under different conditions (ul Haq and Haider, 2009; Singh *et al.*, 2012). Zinc oxalate is frequently used in organic synthesis reaction as a catalyst, and is also a precursor for the preparation of zinc oxide particles (Kim and Kim, 2010; Shamsipur *et al.*, 2013). Zinc oxalate nanoparticles can be produced by an electrochemical process (Shamsipur *et al.*, 2013). Other nanoscale oxalates to receive attention include MgC$_2$O$_4$·2H$_2$O and some rare earth elements (Reddy *et al.*, 2014), Rare earth oxalates are of particular importance because of their applications in the fields of molecular based magnetic materials, luminescent materials, as a precursor for superconducting oxides, and solid state lasers (Vimal *et al.*, 2014). Nanostructured samarium oxalate crystals have been synthesized (Vimal *et al.*, 2014). Some rare earth oxalates have been found in natural environmental locations (Rouse *et al.*, 2001).

It is interesting to speculate whether any future biotechnology based on fungal systems could be developed to contribute to the physical and chemical technologies outlined above. Biomineral technology and production of new biomaterials is a growing field although microbes are often given scant attention in this regard, most attention being given to more advanced biologically-controlled biomineralization processes (Chen *et al.*, 2012). It is clear that novel metal oxalate formation may be mediated by fungal systems, but whether particle size and properties can be adequately controlled for nanoscience applications is a matter for conjecture at present.

9. Conclusions

Oxalate is a key fungal metabolite although it is clear there are still gaps in knowledge regarding biosynthesis and biodegradation, particularly in organisms not considered to be traditional fungal model systems. Oxalate production is a widely distributed property in free-living and symbiotic fungi (mycorrhizas, lichens) with a multiplicity of biotic and abiotic factors affecting production. Central to the effects of oxalate is the ability of the oxalate anion to complex and/or precipitate metals as secondary biominerals which can result in mineral dissolution (bioweathering) or metal immobilization, as well as the ability to act as a metal reductant, e.g. Mn(IV) to Mn(II), all of which influence metal speciation and mobility. Metal solubilization and immobilization mechanisms are relevant to biorecovery, bioleaching, and bioremediation approaches for metal-rich liquid and solid matrices. Oxalate is frequently associated with fungal-mediated rock and mineral transformations and seems ubiquitous in the context of biodeterioration of rock and mineral-based structural materials and cultural heritage. Oxalate is widely-found in wood-rotting fungi and has other important roles in lignocellulose degradation and plant pathogenesis. Oxalate production by mycorrhizal fungi can affect essential and toxic metal bioavailability as well as phosphate, thus influencing plant productivity. Metal oxalates have important chemical properties and are of industrial importance in a variety of processes: novel mycogenic oxalates may have potential applications in biomineral technology. Oxalate may therefore be concluded to be one of the most important fungal metabolites in terms of geomycology and of considerable economic significance in view of its roles in biodeterioration, biocorrosion, bioweathering, plant pathogenesis and productivity, and with potential applications in biomineral technology, such as bioprotection, synthesis of novel biomaterials, metal bioleaching and biorecovery.

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