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Review

Discoveries and identification methods of metal oxalates in lichens and their mineral associations: A review of past studies and analytical options for lichenologists



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ARTICLE INFO

Article history:

Received 15 February 2022

Received in revised form

21 July 2022

Accepted 23 September 2022

Keywords:

Metal oxalate

Lichen

Analytical method

Metal oxalate-associated minerals

ABSTRACT

Lichens are generally acknowledged as the main agents of the initial bioweathering of rock substrates. The most direct evidence of a chemical interaction between lichens and their mineral substrata is the production of oxalic acid, of which interaction with ions present in a close lichen environment occasionally results in the precipitation of metal oxalates. In the past, only a few studies revealed the presence of metal oxalates in lichens, and currently, almost no new discoveries are arriving. Therefore, the main goal of this review is to bring the focus back to this phenomenon. To date, only Mg oxalate dihydrate, Mn oxalate dihydrate, Cu oxalate hemihydrate, Zn oxalate dihydrate, and anhydrous Pb oxalate have been detected in lichens. The most reliable diagnostic methods of metal oxalates in lichens are powder X-ray diffraction (pXRD), infrared spectroscopy (IR), extended X-ray absorption fine structure (EXAFS) spectroscopy, and Raman spectroscopy. Prospective lichen specimens for investigations may be found in anthropogenically-polluted environment or naturally metal-rich rock substrata. This review acts as an initial guide that provides analytical options for field lichenologists, offers a few suggestions for further research on this matter, and encourages to new biomineral discoveries in the scope of mineralogy. Survival in the metal-toxic environment, ability to produce oxygen, and extremophile nature, are the reasons why lichens are good subjects for research within the context of currently expanding astrobiochemistry sciences, as well.

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1. Introduction

Oxalic acid (ethanedioic acid) is a common product of biochemical processes in organisms. This acid acts like a reducing agent, and its conjugate base, known as oxalate, is

a chelating agent for cations. Precipitation of oxalate salts is known in humans (in the form of kidney stones) (Narula et al., 2016; Langdon and Grohe, 2016; Daudon et al., 2016), as well as in animals (Khan, 2013), insects (Moscona, 1950; Farkaš et al., 2016), plants (Brown et al., 2013), algae

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<https://doi.org/10.1016/j.fbr.2022.09.003>

(Friedmann et al., 1972; Pueschel, 1995), fungi (e.g. Tuason and Arocena, 2009; Gadd et al., 2014), or bacteria (Rusakov et al., 2016; Sazanova et al., 2020). Oxalates also occur in the context of decaying organic matter (Holakooei and Karimy, 2015; Elliott, 2019). Oxalate crystals are often referred to as “organic minerals” or “biominerals”, and have been described from lichens on several occasions.

Lichens, or lichenized fungi, are symbiotic organisms consisting of photobionts (algae and/or cyanobacteria) and mycobionts (fungi). In lichens, oxalic acid is secreted mostly as a fungal by-product. Oxalic acid excretion in lichens results in the precipitation of crystalline oxalic salts, which are deposited (1) inside the lichen thallus, prevalingly attached directly to fungal hyphae (Jones et al., 1980, 1981; Purvis, 1984; Chisholm et al., 1987; Purvis et al., 1987; Frank-Kamenetskaya et al., 2019, 2021); (2) on the surface of lichen thallus, in cortex encrustation also known as “pruina” (Smith, 1921; Wadsten and Moberg, 1985; Gehrman et al., 1988; Edwards and Seaward, 1993; Giordani et al., 2003); and (3) at the contact zone of the lichen and its substrate (Wilson et al., 1980; Ascaso et al., 1982, 1990; Favero-Longo et al., 2005b).

The most common oxalate salt in lichens is calcium oxalate. Both whewellite (calcium oxalate monohydrate $[\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}]$) and weddellite (calcium oxalate dihydrate $[\text{CaC}_2\text{O}_4 \cdot (2.5-x)\text{H}_2\text{O}]$) were reported in lichens in numerous cases (Syers et al., 1967; Wadsten and Moberg, 1985; Del Monte et al., 1987; Gehrman and Krumbein, 1994; Adamo et al., 2002; Giordani et al., 2003; and Frank-Kamenetskaya et al., 2019). One single study evidenced the presence of a trihydrate form of calcium oxalate known as mineral caoxite $[\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}]$ in lichens as well (Gehrman and Krumbein, 1994). The process of oxalate precipitation in lichens is considered biomineralization, since this process appears to be either induced (McIlroy de la Rosa et al., 2013) or at least partially biologically controlled (Giordani et al., 2003).

In the natural environment, the existence of various metal oxalates is acknowledged (Echigo and Kimata, 2010; Baran, 2014, 2016). This review article provides a list of all metal oxalates identified in lichens to date, excluding, however, calcium oxalates. Previously published reviews, which generally cover the presence of metal oxalates in lichens, include: Easton (1997); Chen et al. (2000); Adamo and Violante (2000); Adamo et al. (2002); Baran and Monje, 2008; and Purvis (2014). This review article provides a complex list (Table 1) of metal oxalate discoveries in lichens from 1937 to 2021, with emphasis on analytical methods used for the identification of oxalates, as well as the mineral composition of lichen substrates (Table 2). This review maps analytical options, lichen species suitable for investigations, and provides a list of studies in which metal oxalate investigations in lichens have failed to bring new discoveries (Table 3).

2. The first discoveries of metal oxalates in lichens

Perhaps the first thought regarding the existence of metal oxalate depositions in lichens arose from the work of Sambo (1937). In this work, the presence of magnesium and oxalic acid in the lichen thallus was determined. However, the

presence of magnesium oxalate as a mineral phase itself was not identified, even though the existence of such a phase had been suggested. The first analytically, well-founded discovery of a metal oxalate in lichens dates back to Wilson et al. (1980, 1981). In their research, magnesium oxalate dihydrate (mineral glushinskite $[\text{Mg}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}]$) was detected at the lichen-rock interface of lichen *Tephromela atra* var. *atra* on serpentinite by powder X-ray diffraction (pXRD). The pXRD pattern was “in good agreement” with the reference magnesium oxalate dihydrate provided by Walter-Levy et al. (1971). At the same time, the obtained infrared (IR) spectrum from the lichen interface material was “virtually identical” to the synthesized reference material of magnesium oxalate dihydrate (Wilson et al., 1980). It was also found that in glushinskite, Mg(II) can be substituted by small amounts of Fe(II), Mn(II) and Ni(II) (Wilson et al., 1980). Taking into account that $\text{Mg}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ and the dihydrated metal complexes of the first row transition metals are isostructural it is relatively easy to explain the incorporation of these three cations, and eventually also Co(II) and Zn(II), in the glushinskite lattice (Baran and Monje, 2008; Baran, 2014).

The first discovery of copper oxalate in lichens was introduced by Purvis (1984). He identified the copper(II) oxalate in *Lecidea inops*, *Lecidea lapicida*, as well as in two specimens of *Acarospora rugulosa* by pXRD and IR (Purvis, 1984; Chisholm et al., 1987). The copper oxalate depositions were later acknowledged as the mineral moolooite $[\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}; n = 0.4-0.7]$ (Chisholm et al., 1987).

The first manganese oxalate deposition in lichen was discovered by SEM-EDX and pXRD in the thallus of *Pertusaria corallina* growing on manganese ore. The crystals were identified as manganese oxalate $[\text{MnC}_2\text{O}_4]$ (Jones et al., 1981), or more specifically, manganese oxalate dihydrate $[\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$ (Wilson and Jones, 1984). When pXRD data of synthetic manganese oxalate dihydrate and the unknown crystals in the lichen thallus were compared, a very close agreement between the two materials was “obvious”; similar results were obtained by IR spectroscopy as well (Wilson and Jones, 1984). Manganese oxalate dihydrate is known as the mineral lindbergite.

Saret et al. (1998) detected zinc oxalate dihydrate, mineral katsarosite $[\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$ and lead oxalate $[\text{PbC}_2\text{O}_4]$ (or a compound very close to the anhydrous lead oxalate) in *Diploschistes muscorum* from a polluted soil. Identification of Zn-oxalate dihydrate was done by pXRD. Speciation of zinc and lead in the lichen was investigated by the extended X-ray absorption fine structure (EXAFS) spectroscopy. The spectra revealed the presence of anhydrous Pb-oxalate and confirmed the pXRD detection of zinc oxalate dihydrate.

3. Discussion

3.1. Sample preparation method

Exploring metal oxalates in lichens is a difficult task, starting with a non-existent uniform sample preparation method. Oxalate crystals in lichens are rarely larger than a few microns. Oxalates usually form thin surface coatings or precipitate as individual crystals attached to mycobiont hyphae in the

Table 1 – List of metal oxalate discoveries in lichens and identification methods.

Year	Authors	Metal Oxalate	Associated Calcium Oxalate	Species (as stated by authors)	Species (according to GBIF.org)	Identification Method
1980	Wilson et al.	Mg	COM	<i>Lecanora atra</i> (Huds.) Ach.	<i>Tephromela atra</i> var. <i>atra</i> (Huds.) Hafellner ex Kalb	pXRD, IR, SEM-EDX
1981	Wilson et al.	Mg	COM, COD	<i>Lecanora atra</i> (Huds.) Ach.	<i>Tephromela atra</i> var. <i>atra</i> (Huds.) Hafellner ex Kalb	pXRD, SEM-EDX
1981	Jones et al.	Mg	Ca-Ox	not stated, crustose lichen	–	pXRD, SEM-EDX
1981	Jones et al.	Mn	–	<i>Pertusaria corallina</i>	<i>Lepra corallina</i> (L.) Hafellner	pXRD, SEM-EDX
1984	Wilson & Jones	Mn	–	<i>Pertusaria corallina</i> (L.) Arnold	<i>Lepra corallina</i> (L.) Hafellner	pXRD, IR, SEM-EDX
1984	Purvis	Cu	COD	<i>Lecidea inops</i> Th.Fr.	<i>Lecidea inops</i> Th.Fr.	pXRD
1984	Purvis	Cu	COM	<i>Lecidea lactea</i> Flörke ex Schaerer (or <i>Lecidea theiodes</i> Sommerf.)	<i>Lecidea lapicida</i> (Ach.) Ach (corrected by Purvis et al., 2011)	pXRD, IR
1984	Purvis	Cu	COD	<i>Acarospora rugulosa</i> Körber	<i>Polysporinopsis rugulosa</i> (Körb.) Vězda	pXRD
1984	Purvis	Cu	COM	<i>Acarospora rugulosa</i> Körber	<i>Polysporinopsis rugulosa</i> (Körb.) Vězda	pXRD, IR, SEM
1985	Purvis & James	Cu	–	<i>Lecidea inops</i> Th.Fr.	<i>Lecidea inops</i> Th.Fr.	XRD?
1994	Gehrmann & Krumbein	Mg	COD	<i>Protoblastenia incrustans</i>	<i>Protoblastenia incrustans</i> (DC.) J.Steiner	pXRD
1994	Gehrmann & Krumbein	Mg	COM, COD, COT	<i>Bagliettoa parmigerella</i>	<i>Bagliettoa parmigerella</i> (Zahlbr.) Vězda & Poelt	XRD
1996	Purvis & Halls	Cu	–	<i>Acarospora rugulosa</i> Körber	<i>Polysporinopsis rugulosa</i> (Körb.) Vězda	–
1996	Purvis & Halls	Cu	–	<i>Acarospora rugulosa</i> Körber	<i>Polysporinopsis rugulosa</i> (Körb.) Vězda	–
1996	Purvis & Halls	Cu	–	<i>Lecanora ludwigii</i> Ach.	<i>Lecanora frustulosa</i> (Dicks.) Ach.	–
1996	Purvis & Halls	Cu	–	<i>Lecidea inops</i> Th.Fr.	<i>Lecidea inops</i> Th.Fr.	–
1998	Sarret et al.	Pb, Zn	COM, COD	<i>Diploschistes muscorum</i>	<i>Diploschistes muscorum</i> (Scop.) R.Sant.	pXRD (Zn-oxalate only), EXAFS
2008	Purvis et al.	Cu	–	<i>Lecanora polytropa</i>	<i>Lecanora polytropa</i> (Ehrh.) Rabenh.	XRD-PDS
2021	Frank-Kamenetskaya	Cu	–	<i>Lecidea inops</i> Th.Fr.	<i>Lecidea inops</i> Th.Fr.	pXRD, Raman spectroscopy

COM = calcium oxalate monohydrate, COD = calcium oxalate dihydrate, COT = calcium oxalate trihydrate, Ca-Ox = not specified calcium oxalate, ? = suggests uncertainty.

lichen thallus. This makes it almost impossible to gain a pure pinch of crystals by hand without accompanying organic matter or mineral fragments, especially in the case of crustose saxicolous lichens. However, nowadays there is a technology capable of microgripping and micromanipulation with micron-scaled materials (Lyu and Xu, 2021).

In cases of successful identification of metal oxalates, lichens were scraped off from the substrate. The lichen-mineral mixture or the underlying material were powdered (e.g., Wilson et al., 1981; Sarret et al., 1998) or the material of interest was hand-picked from the lichen under a microscope (Purvis, 1984). Ascaso et al. (1982) attempted to remove the organic matter from the lichen-mineral mixture by boiling samples in 80% hydrogen peroxide solution; however, this approach was not considered appropriate (Adamo and Violante, 2000) since H₂O₂ may induce the precipitation of metal oxalates (Farmer and Mitchell, 1963). On the other hand, Dormaar (1968) used hydrogen peroxide during the lichen sample preparation process and no metal oxalates were discovered in their investigation. They admitted, though, that stimulation of oxalate neoprecipitation by peroxidation is

possible. To remove organic matter, Gehrmann and Krumbein (1994) tried Eau de Javelle (bleach, consisting of sodium hypochlorite or potassium hypochlorite) instead. This sample preparation process received no critique in the meantime.

Sample preparation is an important matter, as it was demonstrated in 1982 by Ascaso et al. (1982), who detected anhydrous iron(III) oxalate [Fe₂(C₂O₄)₃] at the interfaces of two lichens (*Variospora aurantia* and *Xalocoa ocellata*). This discovery was repeatedly discussed and considered rather dubious, due to solubility of iron(III) oxalate complexes (Chen et al., 2000; Baran and Monje, 2008; Baran, 2016) and H₂O₂ usage (Adamo and Violante, 2000).

3.2. Imaging methods

Initial investigations of metal oxalates can be provided by scanning electron microscopy (SEM) imaging (Wilson et al., 1981; Jones et al., 1981; Wilson and Jones, 1984; Purvis, 1984). The well-distinguishable bipyramidal crystal habitus of weddellite (Wadsten and Moberg, 1985) makes SEM imaging a very useful tool, since the crystals with such appearance

Table 2 – Metal oxalate discoveries in lichens with substrate mineral associations.

Year	Authors	Metal Oxalate	Species (as stated by authors)	Substrate	Country
1980	Wilson et al.	Magnesium oxalate dihydrate (glushinskite)	<i>Lecanora atra</i> (Huds.) Ach.	serpentinite (chrysotile $[\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4]$, antigorite $[(\text{Mg},\text{Fe})_3(\text{Si}_2\text{O}_5)(\text{OH})_4]$)	Mill of Johnston, near Inch, Scotland, United Kingdom
1981	Wilson et al.	Magnesium oxalate dihydrate (glushinskite)	<i>Lecanora atra</i> (Huds.) Ach.	serpentinite (chrysotile, antigorite)	Mill of Johnston, near Inch, Scotland, United Kingdom
1981	Jones et al.	Magnesium oxalate	not stated, crustose lichen	allivalite (olivine $[(\text{Mg},\text{Fe})_2\text{SiO}_4]$, anorthitic plagioclase feldspar $[\text{CaAl}_2\text{Si}_2\text{O}_8]$)	Isle of Rhum, Scotland, United Kingdom
1981	Jones et al.	Manganese oxalate	<i>Pertusaria corallina</i>	manganese ore	Lecht mines, Tomintoul, Scotland, United Kingdom
1984	Wilson & Jones	Manganese oxalate dihydrate	<i>Pertusaria corallina</i> (L.) Arnold	manganese ore (cryptomelane $[\text{KMn}_8\text{O}_{16}]$, hollandite $[\text{Ba}(\text{Mn}_8)\text{O}_{16}]$)	Lecht mines, Tomintoul, Scotland, United Kingdom
1984	Purvis	Copper(II) oxalate	<i>Lecidea inops</i> Th.Fr.	chalcocopyrite $[\text{CuFeS}_2]$ mineralization with brochantite $[\text{Cu}_4(\text{SO}_4)(\text{OH})_6]$	Ramundberget, Sweden
1984	Purvis	Copper(II) oxalate	<i>Lecidea lactea</i> Flörke ex Schaerer (or <i>Lecidea theiodes</i> Sommerf.)	chalcocopyrite and pyrite $[\text{FeS}_2]$ mineralization with atacamite $[\text{Cu}_2(\text{OH})_3\text{Cl}]$ and gypsum $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$	Gjersvik, Norway
1984	Purvis	Copper(II) oxalate	<i>Acarospora rugulosa</i> Körber	chalcocopyrite and pyrite mineralization with atacamite and gypsum	Gjersvik, Norway
1984	Purvis	Copper(II) oxalate	<i>Acarospora rugulosa</i> Körber	chalcocopyrite mineralization with brochantite	Ramundberget, Sweden
1985	Purvis & James	Copper oxalate	<i>Lecidea inops</i> Th.Fr.	quartz $[\text{SiO}_2]$, malachite $[\text{Cu}_2(\text{CO}_3)(\text{OH})_2]$, azurite $[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]$, chrysocolla $[\text{Cu}_2(\text{H}_2\text{Si}_2\text{O}_5)(\text{OH})_4]$, covellite $[\text{CuS}]$, bornite $[\text{Cu}_5\text{FeS}_4]$	Coniston copper mines, Lake District, United Kingdom
1994	Gehrmann & Krumbein	Glushinskite	<i>Protoblastenia incrustans</i>	limestone/marble	–
1994	Gehrmann & Krumbein	Glushinskite	<i>Bagliettoa parmigerella</i>	limestone/marble, nesquehonite $[\text{MgCO}_3 \cdot 3\text{H}_2\text{O}]$, goethite $[\text{FeO}(\text{OH})]$	–
1996	Purvis & Halls	Copper oxalate	<i>Acarospora rugulosa</i> Körber	calcite $[\text{CaCO}_3]$, epidote $[\text{Ca}_2(\text{Al}_2,\text{Fe})(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})]$, magnetite $[\text{Fe}_3\text{O}_4]$, chalcocopyrite, brochantite	Glimsjön Lake, Ramundberget, Sweden
1996	Purvis & Halls	Copper oxalate	<i>Acarospora rugulosa</i> Körber	epidosite (epidote, actinolite $[\text{Ca}_2(\text{Mg},\text{Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2]$, quartz)	Glimsjön Lake, Ramundberget, Sweden
1996	Purvis & Halls	Copper oxalate	<i>Lecanora ludwigii</i> Ach.	epidosite (epidote, actinolite, quartz)	Glimsjön Lake, Ramundberget, Sweden
1996	Purvis & Halls	Copper oxalate	<i>Lecidea inops</i> Th.Fr.	epidosite (epidote, actinolite, quartz)	Glimsjön Lake, Ramundberget, Sweden
1998	Sarret et al.	Lead oxalate anhydrous, zinc oxalate dihydrate	<i>Diploschistes muscorum</i>	soil in vicinity of (Zn, Pb)S smelter (personal communication, G. Sarret, 2022)	Auby, France
2008	Purvis et al.	Copper oxalate hydrate (moolooite)	<i>Lecanora polytropia</i>	psammite (quartz)	Riddarhyttan, Sweden
2021	Frank-Kamenetskaya et al.	Copper oxalate hydrate (moolooite)	<i>Lecidea inops</i> Th.Fr.	chalcocopyrite ore (malachite, azurite, goethite)	Voronov Bor deposit, Central Karelia, Russia

Table 3 – Unsuccessful prospections of metal oxalates in lichens; with associated mineral substrate and identification method.

Year	Authors	Metal Oxalate	Associated Calcium Oxalate	Species (as stated by authors)	Substrate	Identification Method
1966	Mitchell et al.	No Mg-ox	COM	<i>Aspicelia/Aspicilia calcaria</i>	limestone	DTA, IR
		No Mg-ox	COM	<i>Physcia adscendens</i>	limestone	DTA, IR
		No Mg-ox	COM	<i>Verrucaria nigrescens</i>	limestone	DTA, IR
		No Mg-ox	COM	<i>Rhizocarpon calcareum</i>	limestone	DTA, IR
		No Mg-ox	COM	<i>Caloplaca heppiana</i>	limestone	DTA, IR
		No Mg-ox	COM	<i>Physcia caesia</i>	limestone	DTA, IR
		No Mg-ox	COM	<i>Xanthoria parietina</i>	limestone	DTA, IR
1980	Wilson et al.	No Mg-ox	–	<i>Xanthoria parietina</i>	serpentinite (chrysotile, antigorite)	pXRD, IR?
		No Mg-ox	–	<i>Ochrolechia posella</i> (L.) Massal. (typing error for “parella”, personal communication with D. L. Hawksworth, 2021))	serpentinite (chrysotile, antigorite)	pXRD, IR?
		No Mg or Fe-ox	COM	<i>Pertusaria corallina</i> (L.) Arnold	basalt (labradorite [(Ca, Na)(Al, Si) ₄ O ₈], clinopyroxene, olivine, magnetite)	pXRD, SEM-EDX
1982	Ascaso et al.	No Mg or Fe-ox	COM	<i>Squamarina oleosa</i> (Zahlbr. et Poelt.)	Fe-rich dolomite (calcite, dolomite [CaMg(CO ₃) ₂])	pXRD
		No Mg or Fe-ox	COM	<i>Protoblastemia testacea</i> (Hoffm.) Clauz. et Rond.	Fe-rich dolomite (calcite, dolomite)	pXRD
		No Mg or Fe-ox	COM	<i>Squamarina oleosa</i> (Zahlbr. et Poelt.)	limestone (calcite, dolomite)	pXRD
		No Mg or Fe-ox	COM	<i>Protoblastemia testacea</i> (Hoffm.) Clauz. et Rond.	limestone (calcite, dolomite)	pXRD
		No Mg or Fe-ox	COM	<i>Diploschistes ocellatus</i> (Will.) Norm.	limestone (calcite, dolomite)	pXRD
1990	Ascaso et al.	No Mg or Fe-ox	COM	<i>Caloplaca callospisma</i> (Ach.) Th. Fr.	limestone (calcite, dolomite)	pXRD
		No Mg or Fe-ox	–	<i>Xanthoria elegans</i> (Link) Th Fr.	andesite (plagioclase, clinopyroxene, orthopyroxene)	pXRD, IR, TEM
		No Mg or Fe-ox	COM	<i>Lecidea lapicida</i> (Ach.)	andesite (plagioclase, clinopyroxene, orthopyroxene)	pXRD, TEM
		No Mg or Fe-ox	–	<i>Rhizocarpon geographicum</i> (L.) DC	volcanigenic sediment (plagioclase, olivine, amphibole, pyroxene)	pXRD, IR, TEM
1990	Ascaso et al.	No Mg or Fe-ox	COD	<i>Bacidia stipata</i> Lamb	volcanigenic sediment (plagioclase, olivine, amphibole, pyroxene)	pXRD, IR, TEM
		No Mg or K-ox	COM	<i>Dirina massiliensis</i> Durieu & Mont. forma <i>sorediata</i> (Mull. Arg.) Tehler	Zuccari frescoes (lead, mercury, and manganese compounds)	Raman microspectroscopy

(continued on next page)

Table 3 (continued)						
Year	Authors	Metal Oxalate	Associated Calcium Oxalate	Species (as stated by authors)	Substrate	Identification Method
1993	Adamo et al.	No Mg-ox	COM, COD	<i>Ochrolechia parella</i>	serpentinite (pyroxene, olivine, chrysotile, antigorite, carbonates)	pXRD, SEM-EDX
		No Mg-ox	COM	<i>Caloplaca</i> sp.	serpentinite (pyroxene, olivine, chrysotile, antigorite, carbonates)	pXRD, SEM-EDX
		No Mg-ox	COM	<i>Parmelia conspersa</i>	gabbro (plagioclase, orthopyroxene, amphiboles)	pXRD, SEM-EDX
		No Mg-ox	COM	<i>Aspicilia radiosa</i>	gabbro (plagioclase, orthopyroxene, amphiboles)	pXRD, IR, SEM-EDX
		No Mg-ox	–	<i>Xanthoria ectaneoides</i>	dolerite (plagioclase, pyroxene, olivine, calcite)	pXRD, SEM-EDX
		No Mg-ox	COM	<i>Parmelia subrudecta</i>	dolerite (plagioclase, pyroxene, olivine, calcite)	pXRD, SEM-EDX
1998	Sarret et al.	No Pb- and Zn-ox	COM	<i>Xanthoria parietina</i>	bark/cement poles near a lead factory	pXRD, EXAFS
2002	de Oliveira et al.	No Mg-ox	COM	<i>Calenia triseptata</i> Zahlbr.	leaves (rainforest trees)	FT-Raman microspectroscopy
		No Mg-ox	COM	<i>Echinoplaca strigulacea</i> (Müll. Arg.) R.Sant.	leaves (rainforest trees)	FT-Raman microspectroscopy
2003	Edwards et al.	No Mg-ox	COM	<i>Tricharia carnea</i> (Müll. Arg.) R.Sant	leaves (rainforest trees)	FT-Raman microspectroscopy
		No Mg-ox	COM	<i>Aspicilia calcarea</i> (L.) Mudd	dolomite	FT-Raman microspectroscopy
		No Mg-ox	COM, COD	<i>Tephromela atra</i> (Huds.) Hafellner & Kalb	dolomite	FT-Raman microspectroscopy
		No Mg-ox	COM, COD	<i>Dirina massiliensis</i> f. <i>massiliensis</i> Durieu & Mont.	dolomite	FT-Raman microspectroscopy
		No Mg-ox	COM, COD	<i>Dirina massiliensis</i> f. <i>sorediata</i> (Müll.Arg.) Tehler	Mg-rich carbonate (calcite, dolomite)	FT-Raman microspectroscopy
		No Mg-ox	COM	<i>Lecanora sulfurea</i> (Hoffm.) Ach.	Mg-rich carbonate (calcite, dolomite)	FT-Raman microspectroscopy
2005a	Favero-Longo et al.	No Mg-ox	COM, COD	<i>Sporastatia testudinea</i> (Ach.) A. Massal.	serpentinite (antigorite, magnetite, diopside [CaMgSi ₂ O ₆], chlorites, Ti-clinohumite [(Mg, Ti) ₉ [(SiO ₄) ₄ (OH, F) ₂]], pentlandite [(FeNi) ₉ S ₈], olivine, pyroxenes, Cr-spinel)	pXRD
		No Mg-ox	COM, COD	<i>Lecidea atrobrunnea</i> (Lam and DC.) Schaer.	antigorite serpentinite (antigorite, magnetite, diopside, chlorites, Ti-clinohumite, pentlandite, olivine, pyroxenes, Cr-spinel)	pXRD
		No Mg-ox	–	<i>Rhizocarpon geographicum</i> gr.	antigorite serpentinite (antigorite, magnetite, diopside, chlorites, Ti-clinohumite, pentlandite, olivine, pyroxenes, Cr-spinel)	pXRD
2013	Purvis et al.	No Fe-ox	–	<i>Acarospora</i> cf. <i>badiofusca</i> (Nyl.) Th. Fr.	Fe-stained quartz mica schists	XRD-PSD

COM = calcium oxalate monohydrate, COD = calcium oxalate dihydrate, ox = oxalate, DTA = differential thermal analysis, FT = Fourier transform, ? = suggests uncertainty.

may be automatically excluded from further analyses when investigations are focused on locating metal oxalates with metals other than Ca. Crystal habitus of some metal oxalates precipitated by fungi is documented well in a review by Gadd et al. (2014), although the morphology can be influenced by a variety of factors (Kuz'mina et al., 2019; Frank-Kamenetskaya et al., 2021). SEM itself cannot be considered a diagnostic method that can enable the definitive identification of the studied minerals; however, SEM equipped with energy-dispersive X-ray spectroscopy (EDS/EDX) can offer valuable additional information about the element content and metal ratio in oxalate crystal.

In some studies, researchers have used back-scattered electron imaging (BSE) (Chisholm et al., 1987; Williamson et al., 1998; Purvis et al., 2008) or electron probe microanalysis (EPMA) (Williamson et al., 1998; Purvis et al., 2008) to map the interfaces of lichens with rock substrates and observe the distribution of metals. These techniques can also be employed in the search for metal oxalates.

3.3. Analytical identification methods

The most successful identification method of metal oxalates in lichens seems to be the pXRD (Table 1). Samples subjected to pXRD analysis must be powdered, and the minimum amount of material is required (at least ca 1 mg). This is a complication, since some lichen species inhabiting metal-rich environments are usually rather scarce. The greatest disadvantage of pXRD is that minerals present in a powder mixture, especially in small quantities, can remain hidden by signals of minerals present in larger quantities. Also, some minor minerals may also go undetected due to the detection limit of the instrument. In the future, this problem may be addressed by single-crystal XRD (SC-XRD).

Infrared spectroscopy proves to be of similar value for oxalate identification as pXRD (Table 1), even though it is not a rule, as witnessed by Purvis et al. (2008): "Only a very poor spectrum [Fourier transform IR spectroscopy] was obtained, which was consequently not of diagnostic use."

Successful detection of lead oxalate provided by EXAFS (Sarret et al., 1998) is the only one of its kind. The findings of this study indicate that many metal oxalates unreported from lichens before may be discovered in the future by this analytical method. Typically, to prepare samples for EXAFS, whole lichen specimens need to be powdered and pelleted.

Out of all the identification methods used in the investigations in past years, Raman spectroscopy revealed the presence of metal oxalate in lichens only in one case (Frank-Kamenetskaya et al., 2021), even though there had been several previous attempts (Table 3). For instance, Edwards et al. (1991) investigated *Dirina massiliensis* forma *sorediata* growing on metal-rich frescoes (lead, mercury, and manganese compounds). Although 0.4% of magnesium was calculated to be present as a component of magnesium oxalate, its presence was not confirmed by Raman spectroscopy. In other cases (De Oliveira et al., 2002; Edwards et al., 2003), one must admit that Raman spectroscopy was perhaps unsuccessful simply due to the absence of metal oxalates and not due to inability of the Raman spectroscopy to detect them. Several successful metal oxalates discoveries were provided

by Raman spectroscopy of pigments and historical artifacts (Castro et al., 2008; Holakooei and Karimy, 2015). The downsides of Raman spectroscopy are the emission of strong fluorescent background or thermal degradation due to laser light absorption. Oxalates in lichens are also present in mixtures with other organic and inorganic compounds, resulting possibly in overlaps of the detected Raman signals. The most significant advantage of this method lies in simple sample preparation process. Lichens can be analyzed directly after drying and crystals of interest can be diagnosed on a microscopic scale. It must be remembered that fluorescence can be widely avoided using the 1064 nm radiation of the solid state Nd:YAG laser as the excitation source for Raman measurements. This laser is particularly useful for the investigation of biological samples, including plant material (Schrader, 1996, 1997; Schrader et al., 1999).

3.4. Metal oxalates – where and how to find it

Following all successful metal oxalate discoveries in lichens, it can be summarized that there are three typical environments in which the precipitation of metal oxalates occurs: (a) Anthropogenically polluted areas, especially due to mining and the presence of smelters (Jones et al., 1981; Wilson and Jones, 1984; Purvis, 1984; Purvis and James, 1985; Purvis and Halls, 1996; Sarret et al., 1998; Purvis et al., 2008); (b) microenvironment in ultrabasic rocks and serpentinites (Wilson et al., 1980, 1981; Jones et al., 1981); and, if taken into consideration, (c) iron-rich dolomites (Ascaso et al., 1982). The occurrence of metal oxalates can be expected more in metal-hyperaccumulator species rather than in pollution-tolerant species (Sarret et al., 1998). However, the term hyperaccumulator is best avoided in the case of lichens when the fixation of metals is extracellular (Purvis, 2014).

Metallophyte lichen floras occur in cooler, more mountainous areas, due to faster weathering and a more rapid release of ions when compared to temperate regions (Purvis and Halls, 1996). Connecting this information with the results of Favero-Longo et al. (2018), who observed that pruinosity is a common feature of higher-altitude living lichens, one may assume that in the future, interesting metal oxalate discoveries can be offered by former mining areas, especially those in higher altitudes. Production of oxalic acid and oxalates in lichens seems to be amplified by exposure to a polluted environment (Sarret et al., 1998; Mossmann Koch et al., 2019). Consonantly, most of the authors agree that the significance behind the precipitation of metal oxalates by lichens lies in the tolerance mechanism of metal toxicity (Sambo, 1937; Wilson et al., 1980, 1981; Purvis, 1984; Wilson and Jones, 1984; Chisholm et al., 1987; Sarret et al., 1998; Pawlik-Skowrońska et al., 2006).

The color of metal oxalates is both an advantageous and disadvantageous attribute. The majority of metal oxalates are white (e.g., magnesium oxalate, manganese oxalate, lead oxalate, etc.), and therefore, distinguishing them from calcium oxalates (also white) simply by the naked-eye or microscopic observation of lichen specimens is not possible. However, there are some exceptions; some metal oxalates have a specific color (e.g., turquoise-green or blue to green copper oxalate, yellow ferric and ferrous oxalates, pink cobalt

oxalate, green nickel oxalate, etc.). A variation in the color of crystals attached to lichen thalluses in any way may be an indication of presence metal oxalates. In nature, there are several metal oxalates (containing more than one metal ion) that also have a specific color, for example, bright blue wheatleyite $[\text{Na}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2(\text{H}_2\text{O})]$, green or yellow-green minguzzite $[\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}]$, or light green stepanovite $[\text{NaMg}(\text{Fe}(\text{C}_2\text{O}_4)_3) \cdot 9\text{H}_2\text{O}]$. Experimentally, it is suggested that all the cations except Si^{4+} could exist in the form of an oxalate (Chen et al., 2000), yet some oxalates are unlikely to be discovered in lichens in nature, for instance Al^{3+} and Fe^{3+} oxalates, due to their solubility (Varadachari et al., 1994; Chen et al., 2000).

Wilson et al. (1980, 1981) suggested the potential existence of nickel, cobalt, iron, zinc, and manganese oxalates in lichens. Manganese and zinc oxalate were, in fact, discovered a little later (Jones et al., 1981; Wilson and Jones, 1984; Sarret et al., 1998). Purvis (1984) forecasted the existence of barium, lead, and silver oxalate in lichens, out of which the lead oxalate was later discovered (Sarret et al., 1998).

3.5. Current status

One may suspect that discoveries of metal oxalates in lichens would be on the rise in numbers with the improvement of analytical instrumentation. However, the opposite is true, and no new discoveries of metal oxalates in lichens have been published since 2008, with the exception of the very recent work of Frank-Kamenetskaya et al. (2021). Unsuccessful explorations of metal oxalates in lichens (Table 3) suggest that identification methods were either insufficient, or the metal oxalate depositions in lichens are a very rare, almost species-specific phenomenon, and therefore, a good choice of lichen specimens for investigations is imperative. Baran (2016) proposed that another reason may be the formation of whewellite itself; its precipitation lowers the dissolved oxalate level to a point where other oxalates cannot form. Therefore, a low level of dissolved calcium is needed for the formation of other, more soluble oxalates, and so calcium-rich rocks are considered to be an unfavorable environment for the generation of oxalates, other than those of calcium. This conclusion contradicts the discovery by Ascaso et al. (1982) who described Fe(III) oxalate in a calcium-rich environment. On the other hand, it could explain the absence of metal oxalates in other studies. For instance, no Raman bands of metal oxalates are present in lichen spectra from polluted environments on sandstones and limestones (Ibarrondo et al., 2017), or in lichen spectra from dolomites and Mg-rich carbonates (Edwards et al., 2003). There are cases when metal oxalates were discovered in co-presence with calcium oxalates (Table 1), but never in a calcareous environment (Table 2). There is one case of magnesium oxalate discovery in calcareous environment (Gehrmann and Krumbein, 1994), but this discovery is very rarely cited.

Iron(II) oxalate dihydrate, the mineral humboldtine $[\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}]$, was never found in lichens (Baran and Monje, 2008; D'Antonio et al., 2009), even though the opposite is claimed in some reviews (e.g. Del Monte et al., 1996 in Piervittori et al., 1998; Burford et al., 2003; Gadd et al.,

2014), the reason most likely lies in that Easton (1997) cited Purvis et al. (1987) improperly. No humboldtine was ever identified in *Myriospora smaragdula* (Wahlenb.) Nägeli ex Uloth (= *Acarospora smaragdula* (Wahlenb.) Massal), *Bellemeria alpina* (Sommerf.) Clauzade & Cl. Roux (= *Aspicilia alpina* (Sommerf.) Arnold), nor *Lecidea lapicida* (Ach.) Ach (= *Lecidea lactea* (Flörke ex Schaerer)). Although it is common that some iron-bearing rocks tend to support lichen species that have rust-like coloration, no research supports the notion that iron oxalate is the reason for this visual phenomenon. So far, these rusty minerals on and near lichens have been mostly identified as various iron oxides, hydroxides, and oxyhydroxides (e.g., Weber, 1962; Jackson and Keller, 1970; Jones et al., 1980, 1981; Adamo et al., 1997; Purvis et al., 2013). Along the same lines, Purvis et al. (2013) investigated lichen *Acarospora* cf. *badiofusca*, that colonizes iron-stained quartz mica schists. No iron oxalates were revealed by position-sensitive-detector XRD (XRD-PSD), despite iron being present in the outer rust-colored part of the cortex of the studied lichen, as it was verified by X-ray element mapping. Oxalate crystals were either too small for XRD-PSD detection (Purvis et al., 2013) or simply not present. It is also possible to speculate that if Fe(II) is incorporated by a lichen, it may suffer a rapid microbial oxidation to Fe(III), followed by hydrolysis and precipitation of iron(III) oxides or oxo-hydroxides or can be, eventually, stabilized in the form of the highly stable and soluble Fe(III)-oxalato complex. The same stabilization possibly occurs in the case of Al(III) (Baran and Monje, 2008; Baran, 2014).

3.6. Future visions and suggestions for research

In the recent decades, the most sought after oxalate species appeared to be the magnesium oxalate, glushinskite (Table 3). It is interesting that after its initial discovery in 1980, it was discovered only two more times (Jones et al., 1981; Gehrmann and Krumbein, 1994). Apart from the previously studied lichen species, which could also bear some re-investigations with novel equipment, as was demonstrated by Frank-Kamenetskaya et al. (2021), a few other lichen species could spark academic interest. For instance, "copper salts" depositions in lichen *Lecanora galactiniza* Nyl. (Wild, 1968), which grew on ferruginous gossan with malachite $[\text{Cu}_2\text{CO}_3(\text{OH})_2]$, have never been analytically determined. Similarly, the presence of magnesium oxalate discovered in lichen on serpentinite by Sambo (1937) was only assumed upon numerous subsequent chemical reactions. Potential copper oxalate deposition was observed in *Parmelia subrudecta* (= *Punctelia subrudecta* (Nyl.) Krog) but could not be identified by pXRD (Adamo et al., 1993). Rola et al. (2016) observed remarkable bioaccumulation factor (BAF) values of zinc, lead, cadmium, and nickel in lichens growing on post-smelting wastes. One of the studied species, *Lecidea fuscoatra* (L.) Ach., is an oxalate-producing species and it could contain oxalates of these metals.

There is a review of lichens reported as rust-stained, stained green, or with blue-green inclusions (Purvis and Halls, 1996). Similarly, Easton (1997) listed lichens enriched in various substrate-related elements. Listed species may be a subject for metal oxalate investigation.

3.7. Concluding remarks

Formerly, the interface, the contact zone of the lichens with the mineral substrata, appeared to be the most promising place for investigations, since the presence of metal oxalates was the most expected in spot of direct contact of mycobiont hyphae with metal-rich mineral grains. The majority of successful metal oxalate discoveries came from saxicolous lichen species, apart from *D. muscorum*, which can be considered terricolous. Embracing this simple observation, one may assume that metal oxalate precipitation is a feature of lichens living closest to mineral environments, since no metal oxalate has yet been described from epiphytic species (Table 1).

The origin of metals in the oxalates has still not been resolved. The sources of metals may be divided into four groups: (a) primary rock-forming minerals (Wilson and Jones, 1984); (b) secondary minerals (Wilson et al., 1980, 1981); (c) Metal-enriched water “run-off” from secondary minerals (Czehura, 1977; Purvis, 1984, 2014; Chisholm et al., 1987); and (d) polluted wet and dry atmospheric deposition (Sarret et al., 1998). The existent literature upon organic acid-mineral interaction is sparse (Barman et al., 1992; Varadachari et al., 1994; Drever and Stillings, 1997) and this gap in knowledge offers the space for another review.

Lichens are not only symbiotic organisms, but also micro-environments for other organisms, such as bacteria, fungi, lichenicolous fungi, and algae. All of these organisms secrete various acids, and their influence on the neoformation of oxalates deposited on lichens cannot be excluded.

It is important to continue investigations of metal oxalates in lichens, since these biominerals are so far the only prospective evidence of chemical interaction between the lichens and their substrata; a process that is generally acknowledged, but scarcely documented. Some discoveries of metal oxalates may possibly have gone unnoticed simply due to the absence of reference data of metal oxalates in libraries of analytical instruments. In previous works, reference materials of presumably present oxalates were often synthesized (Wilson et al., 1980; Purvis, 1984; De Oliveira et al., 2002), or purchased (Edwards et al., 2003) in advance. (See also Piro and Baran, 2018). It is proposed that oxalates may be used as a marker for the pre-existence of life, since after the death of lichens, oxalates tend to remain stable on the rock surface for many years (Russ et al., 1996). Nevertheless, the very extremophile nature of lichens, especially those of saxicolous or terricolous environment, including their ability to photosynthesise, further emphasize the need for their investigation and future application in extra-terrestrial life research.

4. Conclusion

The main message of this review is to bring the focus back to the biomineralization activity of lichens, as this process is the only link to the unexplored bioweathering action of these organisms. Despite the fact that fungi are well-investigated in this area, very few new discoveries of metal oxalates are being made in the field of lichenology. Many discoveries of metal oxalate depositions in lichens may have gone unnoticed due to their white coloration, small size, and instrument detection

limits. Existing research deserves new re-evaluation with novel analytical methods. To date, only magnesium oxalate dihydrate, manganese oxalate dihydrate, copper oxalate hemihydrate, zinc oxalate dihydrate, and lead oxalate anhydrous have been detected in lichens. The most used and reliable diagnostic methods of metal oxalates in lichens were pXRD, IR, EXAFS, and Raman spectroscopy. Prospective lichen specimens for investigations may arise from the anthropogenically-polluted environment or naturally metal-rich rock substrata. The significance of analytical investigations of metal oxalates lies in new biomineral discoveries in the field of mineralogy. In conclusion, this review acts as an initial guide that provides analytical options for field lichenologists, brings attention to forgotten articles that had been avoided in many recent reviews, corrects citation and other errors, and offers a few suggestions for further research in this field. Survival in the metal-toxic environment, ability to produce oxygen and extremophile nature, are the reasons why lichens are good subjects for research within the context of currently expanding astrobiology sciences.

Declaration of competing interest

The author declares that no competing interests exist.

Acknowledgments

This work was supported by the Slovak Research and Development Agency under contract No. APVV-17-0317 and by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic, VEGA (1/0467/20), and by the Grants of Comenius University (UK/167/2021) and (UK/153/2022).

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