Hydrated copper oxalate, moolooite, in lichens

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Abstract

Vivid blue inclusions in white whewellite or weddellite, occurring within the medulla of four lichen species growing on copper-bearing rocks, have been identified as the hydrated copper oxalate, moolooite, $CuC_2O_4.nH_2O$ ($n \sim 0.4$–0.7), by infrared spectroscopy and X-ray powder diffraction. The mineral is believed to have been formed by reaction between oxalic acid secreted by the lichen and ground or surface water containing copper.

KEYWORDS: moolooite, lichens, copper oxalate, whewellite, weddellite.

Introduction

THE hydrated copper oxalate, moolooite, has been identified in lichen species growing in areas of copper mineralisation. The examples in the present paper are believed to have been the first reported occurrences of a copper oxalate in lichens and were originally described by Purvis (1984, 1985) from a lichenological standpoint. Other oxalates have been described in lichens and at rock–lichen interfaces. The calcium oxalates whewellite and weddellite are most common in lichens (e.g. Ascaso *et al.*, 1982; Jones *et al.*, 1980; Wadsten and Moberg, 1985) but magnesium oxalate dihydrate, glushinskite, manganese oxalate dihydrate and anhydrous ferric oxalate have also been found (Wilson *et al.*, 1980; Wilson and Jones, 1983, 1984; Ascasco *et al.*, 1982).

The natural occurrence of the hydrated copper oxalate, moolooite ($CuC_2O_4.0.44H_2O$) has recently been reported for the first time by Clarke and Williams (1986). The mineral was found on a sulphide-bearing quartz outcrop 12 km east of Mooloo Downs station homestead, Western Australia. The most likely source of oxalate for its formation was thought to be bird guano although none was found on the specimens collected. Alternative sources of oxalate such as lichens were considered unlikely because of the association of phosphates and oxalates on the surface of the quartz. Other examples of phosphates derived from bird guano are known in the same region of Western Australia.

Naturally occurring copper oxalate has also been briefly described by Bari (1982). It occurs as a blue to blue-green veinlet in baryte, some metres from a collapsed adit containing tree roots, in the lower Chrétien mine, Sainte Marie aux Mines (Haut-Rhin). Copper oxalate was also encountered during studies on the resistance of certain wood-destroying fungi to timber preservatives containing Cu, Cr and As (Antonovsky, 1983).

Material studied

Copper oxalate hydrate was found during a study of copper-tolerant lichens from two localities in Scandinavia (Purvis, 1984, 1985). At the first of these, near an abandoned mine at Gjersvik (Gj), Nord Trøndelag, Norway (13° 25′ E, 64° 53′ N), chalcopyrite and pyrite mineralisation occurs disseminated and in stratiform concentrations in basaltic lavas and metamorphosed volcanic rocks (greenschist facies) of more siliceous composition. In the second similar lichen habitat at Ramundberget (R), Härjedalen, Sweden (12° 25′ E, 62° 42′ N), chalcopyrite occurs in a mixed sequence of volcanic rocks, metamorphosed in upper greenschist to amphibolite facies.

The copper oxalate hydrate was found in four lichen specimens: *Acaraspora rugulosa* from both Gjersvik and Ramundberget, *Lecidea lactea* from Gjersvik and *Lecidea inops* from Ramundberget, and in a specimen of *Lecidea inops* from the Coniston copper mines, Lake District, England; *L. inops* is remarkable because, in spite of its wide geographical distribution, it is found only on copper-rich substrates (Purvis and James, 1985).

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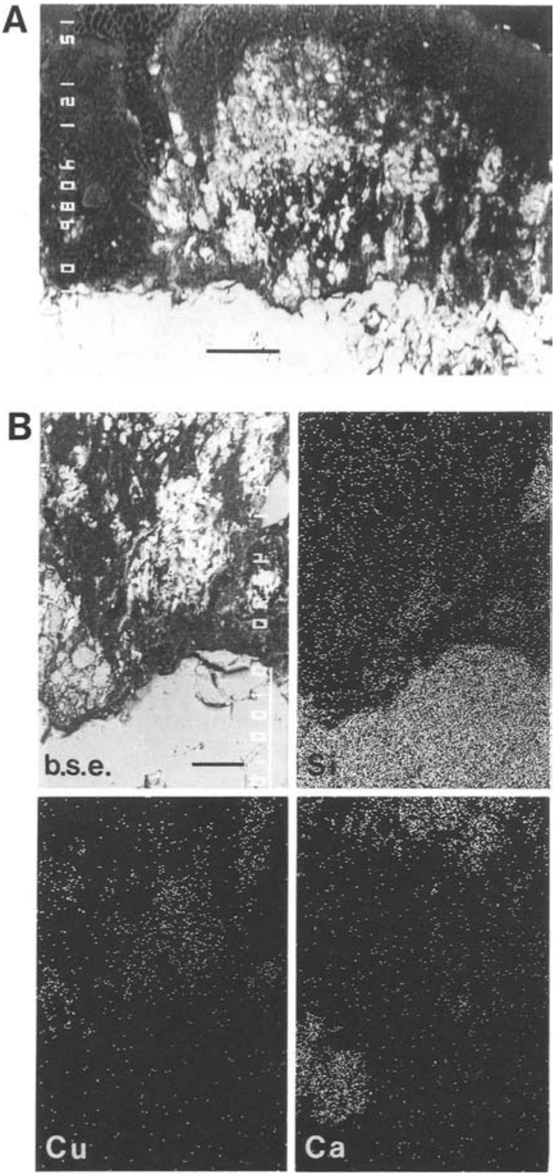

FIG. 1. A. Back-scattered electron image showing the presence of high atomic number elements (bright) among the organic material (darker) of the lichen, *L. lactea*, from Gjersvik. (Scale bar: 125 μm). B. Close up back-scattered electron image (b.s.e.) of the rock–lichen interface and the corresponding X-ray element distribution maps for Cu, Ca and Si ($K\alpha$ radiation in each case). Cu-rich and Ca-rich regions within the lichen can be recognised and are believed to correspond to moolooite and whewellite. The distribution map shows that the substrate is highly siliceous, most probably quartz, and that some Si-rich particles are present in the lichen. (Scale bar: 50 μm.)

Occurrence and characterisation of oxalates in the lichens

The copper oxalate hydrate occurs as vivid blue inclusions, up to 0.5 mm in size, in white crystalline material within the lichen medulla at the rock–lichen interface. The abundance of blue material is variable as is the intensity of the blue colour. In extreme cases, almost two-thirds of the cross-section of the lichen thallus consists of the blue material, as in *A. rugulosa* growing on secondary atacamite and gypsum at Gjersvik and the same species growing on brochantite at Ramundberget. Specimens of *L. lactea* (Gj) have been found with blue inclusions amounting to one-third of the cross-sectional area of the thallus, even when no copper minerals are visible in the rock in direct contact with the lichen.

Analysis in a JEOL 733 scanning electron microscope fitted with a Link Systems energy-dispersive X-ray spectrometer demonstrated the presence of Cu in the blue inclusions and Ca in the white crystalline material. Cu-rich and Ca-rich areas within the lichen thallus are revealed in the X-ray element distribution maps (Fig. 1); in the example shown the lichen is growing on a highly siliceous substrate low in Cu and Ca, but still contains moolooite and whewellite. Quantitative analysis was not practicable because of electron beam damage and volatilisation of the adjacent organic material.

Material from *A. rugulosa* (R) and *L. inops* (R) was examined in the scanning electron microscope to see whether any changes in the biological structure of the lichen had occurred as a result of their high Cu content. The blue areas, subsequently identified as hydrated copper oxalate, were found to consist of aggregates of platy crystals 1–3 μm in diameter encrusting medullary hyphae (Fig. 2A); in some instances, the crystals are so numerous that it is difficult to see the hyphae. The moolooite crystals described by Clarke and Williams (1986) are also platelets, though sometimes lath-like or prismatic. They were generally less than 1 μm in size, although the largest was 4 μm × 1 μm. The copper oxalate crystals illustrated by Antonovsky (1983) are also platy.

The white crystalline material from *A. rugulosa*, identified as whewellite (see below), consisted of stubby prisms 1–4 μm long (Fig. 2B). The appearance of these white crystals differs from the platy habit of whewellites described in other lichens (Jones *et al.*, 1981; Ascaso *et al.*, 1982; Wadsten and Moberg, 1985) and is more like the equant or short prismatic [001] habit described for whewellite in Palache *et al.*, 1951.

Infrared spectroscopy. The infrared spectra of

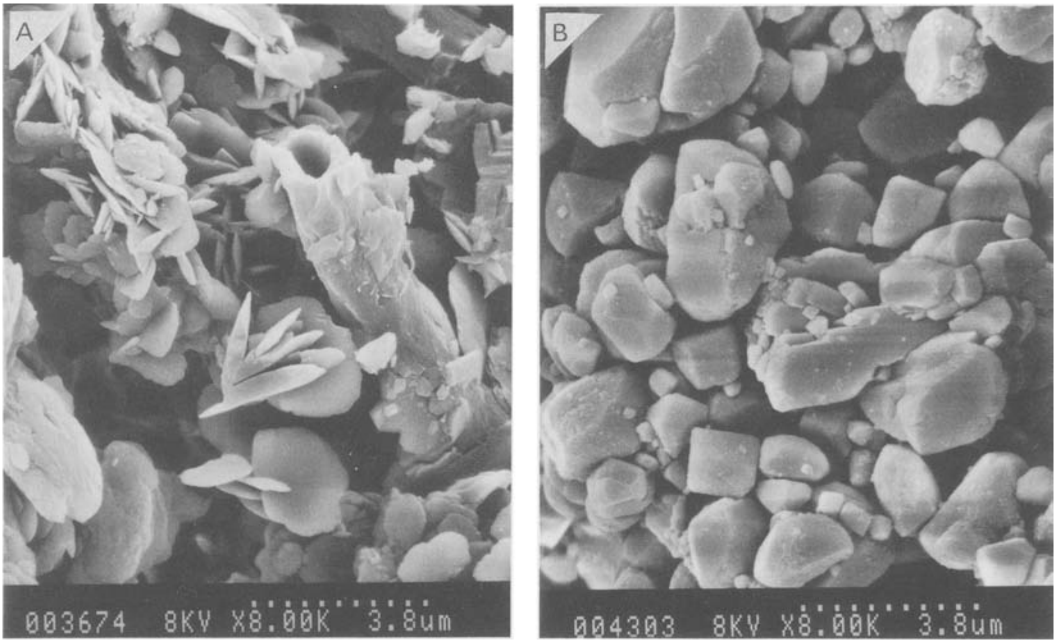

FIG. 2. Scanning electron micrographs of crystalline inclusions within the medulla of *Acarospora rugulosa* (R): A. Platy crystals of copper oxalate hydrate from the blue inclusions. B. Short prismatic crystals of whewellite from the white included material.

hand-picked white and blue material from *A. rugulosa* (R) and *L. lactea* (Gj) were recorded over the range 4000–200 cm^{-1} using the KBr disc method. The spectrum of copper oxalate prepared by precipitation from solutions of $CuCl_2$ and oxalic acid was also recorded. Our infrared spectra (Fig. 3 of Purvis, 1984) of both natural and synthetic materials are almost identical to those of Clarke and Williams (1986) even down to the lower water content of the synthetic moolooite shown by its weaker absorption at 3500 cm^{-1}. Our natural material lacks the strong absorption in the 900–1100 cm^{-1} region found by Clarke and Williams in their natural moolooite and supports their assignment of that absorption to silica and possibly phosphate impurity. A weak absorption in this region does however occur in the spectra of both our lichen copper oxalate hydrate and Clarke and Williams' synthetic material.

The white crystalline material from *A. rugulosa* (R) and *L. lactea* (Gj) gave an infrared spectrum identical to that of whewellite, $CaC_2O_4 . H_2O$. But white material from the other two lichens, *A. rugulosa* (Gj) and *L. inops* (R), was identified as weddellite, $CaC_2O_4 . (2+x)H_2O$ with $x < 0.5$.

X-ray powder diffraction. Blue and white crystalline material was extracted from the lichen specimens for X-ray powder photography using a Philips 11.46 cm diameter camera and Cu-$K\alpha$ radiation. The powder patterns of the blue material matched the reference pattern for copper oxalate hydrate (JCDPS, PDF card 21-297) and the similar pattern of moolooite (Table I of Clarke and Williams, 1986) with only very slight differences in lattice spacings. Least-squares refinement of the unit cell dimensions was carried out for the prominent orthorhombic sub-cell with space group *Pnnm* (see Schmittler, 1968). The cell dimensions of the lichen material lie in the ranges *a* 5.381–5.348, *b* 5.625–5.639, *c* 2.548–2.559 Å. A rough estimate of the water content *n* in the formula $CuC_2O_4 . nH_2O$ (within ± 0.1) can be obtained from the *a* and *b* dimensions using Schmittler's (1968) extrapolated determinative curves, though these are based on only a limited number of data points. Water contents corresponding to *n* 0.4–0.7 in the formula are indicated for the copper oxalate hydrates from the lichens as compared with *n* 0.44 determined by microchemical analysis of type moolooite (Clarke and Williams, 1986) and $n \sim 0.6$ from the cell dimensions (R. M. Clarke, pers. comm.).

Our synthetic copper oxalate gives broader powder lines and is not so well crystalline as the material from the lichens. Its cell dimensions are accordingly less precise: *a* 5.42 (1), *b* 5.58 (1), *c* 2.557 (2) Å; they nevertheless indicate a lower water content ($n \sim 0.1$) than in the natural copper oxalate hydrates. The poorer crystallinity or disorder may be related to rapid growth, as the line broadening almost certainly is, or to some other factor in the growth conditions. The more intense O-H stretching absorption at ~ 3500 cm^{-1} in the infrared spectra of the natural copper oxalate crystals has already been noted.

X-ray powder diffraction confirms the identification of the white crystalline material as whewellite in *A. rugulosa* (R) and *L. lactea* (Gj), and weddellite in *L. inops* (R) and *A. rugulosa* (Gj).

Discussion

The copper oxalate hydrate occurs within the lichen thallus, encrusting the fungal hyphae which secrete oxalic acid. The oxalate required for the formation of moolooite clearly comes from that source within the lichen. In the type occurrence, moolooite was associated with phosphates and the source of oxalate there was thought to be bird guano. None of the secondary minerals identified in association with the lichen occurrences of moolooite was a phosphate.

Botanically, the lichens studied are remarkable in their ability to grow in environments where the concentration of Cu would be toxic to most plants. The deposition of insoluble copper oxalate hydrate outside the fungal hyphae should help prevent the copper concentration in the cells reaching toxic levels and is one possible explanation for the tolerance of these lichens to copper. A similar explanation was given by Antonovsky (1983) for the ability of some wood-destroying fungi to tolerate high Cu concentrations.

The lichens studied also have remarkably high Cu contents, over 5% Cu dry weight (Purvis, 1984, 1985) as compared with 2 wt. % and 0.5 wt. % Cu in other copper-containing lichens (Czehura, 1977; Poelt and Huneck, 1968). The lichens appear to be able to concentrate Cu from their environment. It is known that lichens can play a part in weathering and soil formation. Oxalic acid, and perhaps phenolic acids, produced by the lichen have been shown to etch the underlying mineral surface and leach out cations such as Al and Fe, leaving as residues amorphous silicate and poorly crystallised hydrated oxides (Jones *et al.*, 1980, 1981; Wilson and Jones, 1983). Oxalate minerals may occur at the rock-lichen interface as secondary weathering products. The lichens studied do not always grow in direct contact with Cu minerals and this seems to rule out direct leaching of Cu by these lichens except possibly in the examples of *Acaraspora rugulosa* growing on atacamite and brochantite mentioned earlier. It seems most probable that reaction of ground or surface water containing Cu with the oxalic acid excreted by the lichen lead to the precipitation of copper oxalate hydrate.

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References

Antonovsky, A. (1983) *CSIRO Division of Chemical and Wood Technology Research Review* 1983.

Ascaso, C., Galvan, J., and Rodriguez-Pascual, C. (1982) *Pedobiologia* **24**, 219–29.

Bari, H. (1982) *Minéralogie des Filons du Neuenberg a Sainte Marie-aux-Mines (Haut-Rhin)*, Thesis, Universite Louis Pasteur, Strasbourg.

Clarke, R. M., and Williams, I. R. (1986) *Mineral. Mag.* **50**, 295–8.

Czehura, S. J. (1977) *Econ. Geol.* **72**, 796–803.

Jones, D., Wilson, M. J., and Tait, J. M. (1980) *Lichenologist* **12**, 277–89.

——— and McHardy, W. J. (1981) *J. Microscopy* **124**, 95–104.

Palache, C., Berman, H., and Frondel, C. (1951) *System of Mineralogy*, 7th ed., Vol. 2. John Wiley and Sons Inc., New York, p. 1100.

Poelt, J., and Huneck, S. (1968) *Öst. Bot. Zeitschr.* **115**, 411–22.

Purvis, O. W. (1984) *Lichenologist* **16**, 197–204.

——(1985) *The Effect of Mineralization on Lichen Communities with Special Reference to Cupriferous Substrata*, Ph.D. thesis, Imperial College, London and British Museum (Natural History), London.

—— and James, P. W. (1985) *Lichenologist* **17**, 221–37.

Schmittler, H. (1968) *Mber. Dt. Akad. Wiss. Berlin* **10**, 581–604.

Wadsten, T., and Moberg, R. (1985) *Lichenologist* **17**, 239–45.

Wilson, M. J., and Jones, D. (1983) In *Residual Deposits: Surface Related Weathering Processes and Materials* (Wilson, R. C. L., ed.), *Geol. Soc. Spec. Pub.* **11**, 5–12.

———(1984) *Pedobiologia* **26**, 373–9.

——— and Russell, J. D. (1980) *Mineral. Mag.* **43**, 837–40.

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