

## Glushinskite, a naturally occurring magnesium oxalate

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**SUMMARY.** Glushinskite, a dihydrate of magnesium oxalate, occurs at the lichen/rock interface on serpentinite colonized by *Lecanora atra* at Mill of Johnston, near Inch in north-east Scotland. It is found in a creamy white layer intermingled with the hyphae of the lichen fungus. It consists of crystals mainly 2 to 5  $\mu\text{m}$  in size showing a distorted pyramidal form, often with curved and striated faces. X-ray, infrared, and chemical data are given.

SEVERAL oxalates occur as minerals, the most common being whewellite ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ), weddellite ( $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ), and humboldtine ( $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ). The occurrence of magnesium oxalate as a mineral appears to have been reported only once, as colourless, platy aggregates in some Cretaceous coals in Arctic Russia (E. I. Nefedov in Zhemchuzhnikov and Ginzburg, 1960). Nefedov called the mineral glushinskite, and recorded the following data: hardness, 2; sp. gr. 1.85;  $\alpha$  1.365,  $\beta$  1.530,  $\gamma$  1.595; biaxial negative. Hey (1963) lists the mineral as a doubtful species, presumably because of the lack of X-ray diffraction and other data. The present study reports an occurrence of glushinskite together with X-ray diffraction, infrared, and electron-probe microanalysis data, all of which indicate glushinskite to be a definite mineral species.

**Materials and methods.** The mineral occurs in a creamy white, fine-grained layer at the rock/lichen interface (fig. 1) of a serpentinite outcrop (NJ 572247) directly opposite Mill of Johnston on the Clatt road approximately 6 km WSW of Inch. The outcrop is sparsely covered with various lichens, the mineral being found only at rock surfaces associated with *Lecanora atra* (Huds.) Ach; it is not found either with a foliose species, *Xanthoria parietina*, or with *Ochrolechia posella* (L.) Massal (identified by D. L. Hawksworth). The upper part of the lichen thallus was removed in the laboratory with a scalpel and the white material adhering to the rock surface scraped off and collected. A small quantity ( $\approx 1$  mg) of other material was also hand-picked from the under-surface of the lichen thallus, care being taken to

avoid contaminating rock-mineral particles. For X-ray diffraction a Philips powder camera of 114.83 mm diameter was used with Fe-filtered  $\text{Co-K}\alpha$  radiation. For infrared spectroscopy samples were incorporated in a 13 mm diameter KBr pressed disk and spectra recorded in a Perkin Elmer 577 instrument over the range 4000 to 200  $\text{cm}^{-1}$ . Small fragments of material showing the rock/lichen interface were freeze-dried, coated with gold, and studied with a Cambridge S-4 scanning electron microscope equipped with an energy dispersive X-ray analyser.

**X-ray diffraction.** The white material scraped from the rock/lichen interface yielded a powder pattern showing it to be predominantly magnesium oxalate dihydrate with subordinate whewellite and trace amounts of serpentine and quartz. The pattern remaining after subtraction of the lines attributable to these impurities is shown in Table I and is in good agreement with the pattern for the dihydrate of magnesium oxalate given by Walter-Lévy *et al.* (1971). The crystallography of the dihydrated oxalates of the magnesium series (Mg, Mn, Fe, Co, Ni, and Zn) has been extensively discussed by Lagier *et al.* (1969) and Dubernat and Pézérat (1974) who showed that there is a three-dimensionally well-ordered phase isostructural with humboldtine and a disordered phase with stacking faults parallel to the (001) planes. These forms were termed the  $\alpha$  and  $\beta$  forms, respectively, and they can be distinguished on the basis of their powder patterns. The naturally occurring form described here is closest to the  $\beta$  form although not all the weak reflections were observed.

**Infrared spectroscopy.** The infrared spectrum of the hand-picked white material from the rock/lichen interface (fig. 2a) is virtually identical with that of a sample of magnesium oxalate dihydrate (fig. 2b), synthesized by digesting magnesium hydroxide in an excess of oxalic acid in dilute aqueous suspension for 24 hours at 20°C. In the spectrum of the natural material an additional weak, sharp band at 780  $\text{cm}^{-1}$  is consistent with the presence of about 5% whewellite and a weak,

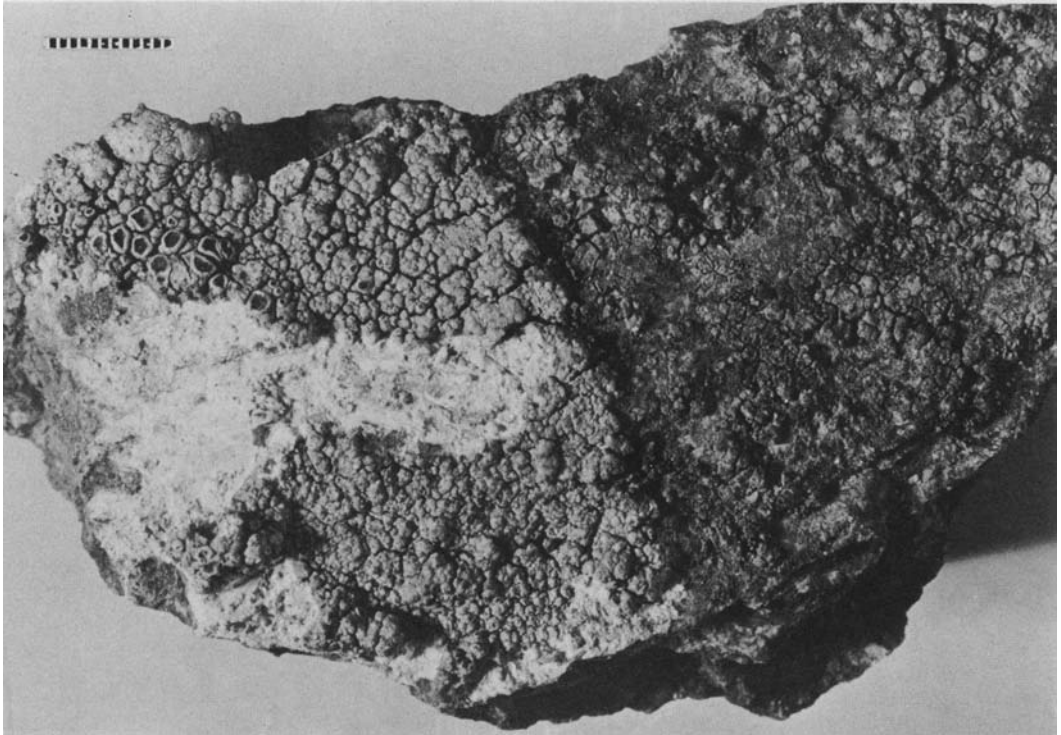


FIG. 1. Serpentinite encrusted with *Lecanora atra*, part of which has been scraped away to reveal white material, which contains glushinskite. Bar equals 5 mm.

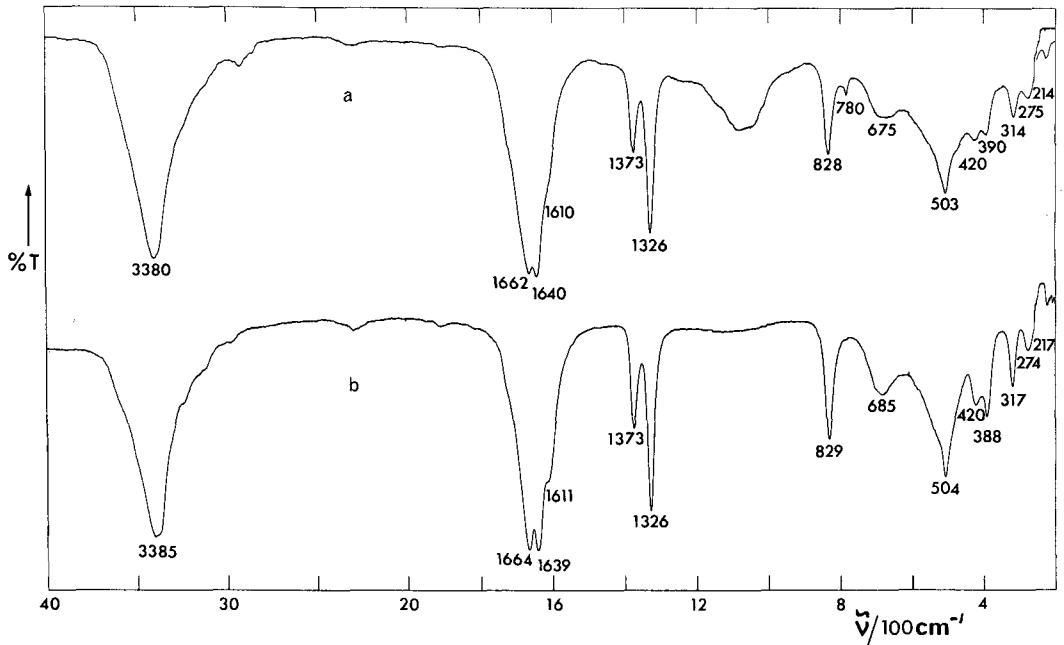


FIG. 2. Infrared spectra of (a) hand-picked material from the under-side of the lichen thallus and (b) magnesium oxalate dihydrate ( $\beta$  form synthesized by digesting magnesium hydroxide in an excess of oxalic acid in dilute aqueous suspension for 24 h)  $\bar{\nu}$  is wavenumber,  $T$  is transmission.

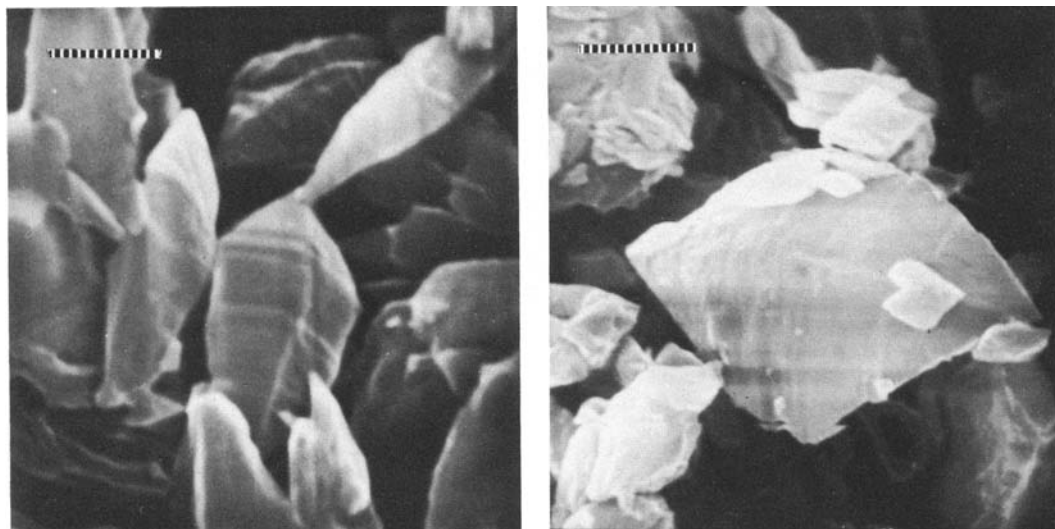


FIG. 3. Scanning electron micrographs of glushinskite crystals showing: *a*, left, distorted pyramidal form and *b*, right, curved and striated faces. Bar equals 1.25  $\mu\text{m}$  and 2.5  $\mu\text{m}$  respectively.

TABLE I. X-ray powder diffraction data

1		2		<i>hkl</i>
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	
4.89 Å	100	4.89 Å	100	200
3.849	10	3.853	20	002
*3.340	50	3.322	40 br	
3.179	70	3.168	80	40 $\bar{2}$
2.541	40	2.551	40	021
2.492	10	2.487	10	22 $\bar{1}$
—	—	2.447	10	40 $\bar{4}$
—	—	—	—	400
2.379	50	2.379	60	202
2.086	40	2.090	40	22 $\bar{3}$
—	—	—	—	221
2.039	60	2.036	60	60 $\bar{2}$
1.861	50	1.863	40	023
—	—	1.782	5 br	—
—	—	1.663	5	62 $\bar{3}$
—	—	1.647	5	40 $\bar{6}$
—	—	—	—	402
—	—	1.606	20	42 $\bar{5}$
—	—	—	—	421
—	—	1.585	10	80 $\bar{4}$
1.526	30	1.529	40	62 $\bar{5}$

1. Glushinskite from rock/lichen interface, Mill of Johnston, near Inch. \* Partly quartz.

2. Synthetic magnesium oxalate dihydrate  $\beta$  form (Walter Levy *et al.* 1971). This form is monoclinic, space group *C2/c* with  $a = 12.675$  Å,  $b = 5.406$  Å,  $c = 9.984$  Å,  $\beta = 129.45$ . The unit cell parameters of glushinskite must be similar.

broad feature between 950 and 1200  $\text{cm}^{-1}$  indicates a small amount of cellular polysaccharide from fungal hyphae and a trace of silicate. The spectrum of the sample characterized by X-ray diffraction was predominantly magnesium oxalate but contained about 10% of the total oxalate as whewellite, as well as some chrysotile and some material similar to silica gel.

*Electron-probe microanalysis.* Scanning electron microscope observations of the rock/lichen interface revealed an abundance of crystalline material ranging from about 2 to 5  $\mu\text{m}$  in size. The majority of the crystals show a distorted pyramidal form (fig. 3a), often with curved and striated faces (fig. 3b). Lagier *et al.* (1969) have previously observed surface striations on synthetic magnesium oxalate crystals during transformation from the  $\beta$  to the  $\alpha$  form. The X-ray spectrum obtained from these pyramidal crystals is dominated by magnesium but there is also appreciable iron and traces of nickel and manganese (fig. 4). The Mg:Fe ratio is approximately 20:1. Other crystals were observed to have a tabular or a well-developed tetragonal pyramidal form. These yielded a spectrum completely dominated by calcium—with no magnesium, iron, nickel, or manganese—and are, presumably, whewellite.

*Discussion.* The above observations show the occurrence of magnesium oxalate dihydrate—termed glushinskite by Nefedov (Zhemchuzhnikov and Ginzburg, 1960)—on the weathered surface of a lichen-encrusted serpentinite. Evidently, the mineral originates following reaction between the

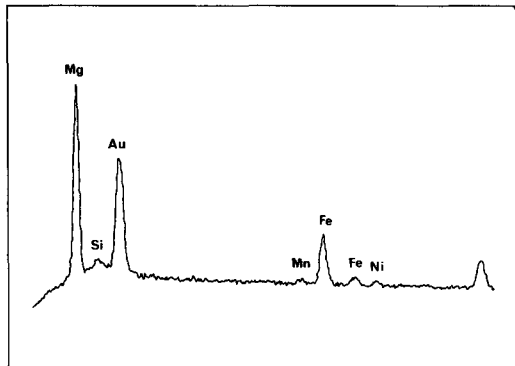


FIG. 4. X-ray spectrum from glushinskite crystals.

oxalic acid excreted by the mycobiont of *L. atra* and the magnesium-rich serpentine minerals in the substrate rock. In the same way, Jones *et al.* (1980) have recently shown that in lichen-covered basalt the decomposition of labradorite by the oxalic-acid producing mycobiont of *Pertusaria corallina* leads to the formation of crystalline calcium oxalate. It seems that glushinskite is likely to be a common weathering product where oxalic acid-producing lichens colonize magnesium-rich rocks; indeed, in the present instance the mineral was deliberately sought before it was known that it had been previously reported. The fact that the mineral

contains significant quantities of ferrous iron and minor amounts of nickel and manganese is readily understandable since Lagier *et al.* (1969) have shown that the oxalates of these metals form a series with the magnesium form. Indeed, the small shifts in frequency shown by some of the absorption bands in the spectra in fig. 2, particularly those near  $315$  and  $215\text{ cm}^{-1}$ , may reflect the isomorphous substitution of Mg by  $\text{Fe}^{2+}$ . All the evidence now available, therefore, indicates that glushinskite is indeed a valid mineral species.

Specimens will be donated to the Royal Scottish Museum and the British Museum (Natural History).

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[Manuscript received 14 January 1980]