

SHORT COMMUNICATIONS

MINERALOGICAL MAGAZINE, SEPTEMBER 1989, VOL. 53, PP. 505-7

A naturally occurring alpha magnesium oxalate dihydrate from the northern Jordan Valley (Israel)

GLUSHINSKITE, $\text{Mg}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$, was initially and inadequately described by Zhemchuzhnikov and Ginzberg (1960) who found it as colourless platy aggregates in some Cretaceous coals in Arctic Russia. Since that time this mineral has been found in the lichen *Lecanora atra* (Huds.) Ach growing in northeast Scotland near Inch (Wilson *et al.*, 1980, 1981). It is formed by the secretion of oxalic acid on the serpentine substrate upon which *L. atra* grows. More recently, glushinskite has been described from the Island of Rhum in the Inner Hebrides of Scotland where it was formed by lichen activity on magnesium-rich rocks (Wilson and Bayliss, 1987). Glushinskite is the beta form of $\text{Mg}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ and is now considered a valid species by the CNMMN (Wilson and Bayliss, 1987). The present study reports the occurrence of the alpha form in a number of plants growing in the Lake Huleh Preserve in the northern Jordan Valley of Israel. Only X-ray diffraction data are presented. The only other occurrence of the alpha form is in the renal appendages of the mollusc *Nautilus pompilius* Linne 1758 (Crick *et al.*, 1985).

Materials and Methods. The Lake Huleh basin occupies a section of the Jordan Rift Valley lying between Pleistocene basalts on the east and Cretaceous limestones of the Naphtali Mountains on the west (Picard, 1963). The basin is dammed by the Yarda basalt. At the south end of the basin, wells drilled near Aiyelet Hashahar show intercalations of basalt and gravel layers (Picard, 1963).

Lake Huleh, the first lake that the Jordan River used to form, was drained between 1951 and 1958. A small area of this lake was retained as a nature preserve. Twenty-nine plant families are represented here by 57 genera containing 71 species. Plants were gathered from the nature preserve and from contiguous areas that extended no more than 800 m from its supposed boundaries. Identifi-

cation of all plants was confirmed by comparing the Huleh Collection with plants deposited in the Herbarium of the Hebrew University and herbaria of both Yale and Harvard Universities.

In arid regions such as the Huleh Valley, the preponderance of contaminated materials adhering to plant surfaces are aeolian in origin. Thus all plant samples were cleaned with a high-speed vacuum cleaner (cf. Cowgill and Prance, 1982). This method removes about 99% of the contaminating material. Adhering particles of colloidal size cannot be removed by this procedure. However, past experience has indicated that contamination of this type in plant specimens is minimal and usually consists of phases containing Al, Si, and Ca, these elements being always abundantly concentrated in plants.

The X-ray diffraction study was carried out using an XRD-6 General Electric X-ray diffractometer. Tracings were made with Ni-filtered Cu radiation at 50 kV and 32 mA. Greater detail of instrument specifications may be found elsewhere (Cowgill, 1975). All peaks were scanned using the goniometer manually and counting three times employing the ten-second count and then, once the peak was located, counting again using an average of three 100-second counts. Background positions were estimated from diffractograms and verified by hand counts. No attempt was made to estimate percentage of minerals since matrix effects were too complicated to achieve actual concentrations with any kind of confidence.

For purposes of mineral identification the preferred orientation method was employed. Sixty milligrams of oven-dried plant material (60°C, 72 hours) ground to 200 mesh were weighted into a 50 ml beaker to which 3 ml of dimethyl sulphoxide had been added. Since states of hydration become variable when exposed to laboratory atmosphere it was found that the use of dimethyl sulphoxide as a liquid in which to disperse powdered plant

material was vastly superior to water. The mixture was magnetically stirred for one hour. The resulting suspension was evenly distributed on a glass slide that was placed on a levelled sheet of plate glass. These slides were allowed to dry at laboratory atmosphere (21°C, 50% relative humidity). All plant samples were examined by X-ray diffraction using this air-dried glass slide preparation.

Results. Alpha magnesium oxalate [$\text{Mg}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$] was detected in the following plants: *Nuphar lutea* (L.) Sm. in Sibith et Sm. (Nymphaeaceae); *Atriplex rosea* L., *Chenopodium album* L., *C. opulifolium* Schrad. ex. Koch et Ziz., *C. murale* L. (Chenopodiaceae); *Amaranthus gracilis* Desf., *A. albus* L., *A. graecizans* L. (Amaranthaceae) and *Polygonum salicifolium* Brouss. ex. Willd. (Polygonaceae). Whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) was detected in all the plants listed above except *N. lutea* while weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) was absent from *N. lutea* and *A. albus*. Calcite was found only in *N. lutea*, *A. roseas* and *Am. gracilis*. Sylvite was encountered only in the flowers of *C. opulifolium*. The low cristobalite form of opal and that of tridymite was present in all specimens studied. Each one of these minerals had at least one reflection that enhanced the intensity of some lines of the naturally occurring alpha magnesium oxalate dihydrate. Table 1 presents the X-ray powder diffraction data for the magnesium oxalate dihydrate found in the Huleh plant samples and, for comparative purposes, the original data of Walter-Levy *et al.* (1971) for the synthetic magnesium oxalate dihydrate alpha form are included. The naturally occurring mineral encountered in the Huleh plants is closest to the alpha form of Walter-Levy *et al.* (1971), although many weaker reflections are absent, in particular those below 1.682 Å. Despite these absent reflections, agreement between the two patterns is quite good. In Table 1, in cases where a given mineral is not present in all plants, two intensities are presented, one where the mineral is present and the second where it is absent.

Table 1 shows the d spacings typical of the plants in which the alpha magnesium oxalate dihydrate was formed. The 202 and 402 reflections varied the most and the d spacings for these variations found among the plants studied are so noted. Major reflections of other minerals found in the plants that have d spacings greater than those for magnesium oxalate dihydrate, alpha form (e.g. whewellite, 5.9 Å, and weddellite, 6.1 Å) or those that have reflections not shared by the alpha form (e.g. calcite, 3.03 Å are not noted).

Discussion. Alpha magnesium oxalate dihydrate has a number of major reflections (d spacings

Table 1. X-ray powder diffraction data for alpha magnesium oxalate dihydrate found in nine plants. Variations were noted for the 202 and 402 reflections, the ranges of which are noted.

1		2		h	k	l
d	I	d	I			
4.91-4.94 Å	100	4.89 Å	100	2	0	2
4.72	5	4.72	5	1	1	0
3.86 ^o	30, 40 ^f	3.853	10	0	0	2
3.61	50	3.570	40	1	1	2
3.30	60	3.252	60	3	1	2
3.17-3.19	90, 100 ^e	3.171	80	4	0	2
2.79 ^d	50	2.793	5	3	1	3
2.62	60	2.617	60	1	1	3
2.55	60	2.546	40	0	2	1
2.49 ^{abc}	40	2.482	5	2	2	1
2.45	5	2.447	5	4	0	4
2.40	50	2.378	60	2	0	4
2.095 ^f	5, 10 ^f	2.096	5	5	1	4
2.085	40	2.085	40	2	2	3
2.040	80	2.040	80	6	0	4
2.015	50	2.012	40	1	1	4
1.926	5, 10 ^f	1.925	5	0	0	4
1.863	60	1.859	60	0	2	3
1.842	5	1.841	5	5	1	5
1.770	10	1.768	10	1	3	1
--		1.682	5	1	3	2
--		1.663	5	6	2	3
--		1.646	5	3	3	2
--		1.630	5	7	1	5
1.620	5	1.617	5	1	1	5
1.600	5	1.604	10	4	2	5
1.589	5	1.587	10	8	0	4
1.528	50	1.528	40	6	2	5

1. Magnesium oxalate dihydrate, alpha form, from the nine plants of the Huleh basin. a) partly low tridymite opal; b) partly low cristobalite opal; c) partly whewellite; d) partly weddellite; e) partly sylvite; f) partly calcite.

2. Synthetic magnesium oxalate dihydrate, alpha form (Walter-Levy *et al.*, 1971). This form is monoclinic, space group $C2/c$ with $a_0 = 12.689$ Å; $b = 5.391$ Å; $c = 9.977$ Å; $\beta = 129.82^\circ$. The naturally occurring alpha form must have similar cell parameters.

Å, intensity; 3.570-40, 3.252-60, 2.617-60, 2.085-40, 2.012-40) and minor reflections (4.72-5, 2.793-5, 1.925-5, 1.841-5, 1.768-10, 1.682-5, 1.630-5, 1.617-5) that are not shared by beta mag-

nesium oxalate dihydrate (Walter-Levy *et al.*, 1971). In addition, the latter has a broad band at 3.322 Å with an intensity of 30 that is not noted in the alpha form (Walter-Levy *et al.*, 1971).

Both the alpha and beta forms are monoclinic, having the same space group (*C2/c*) and similar cell constants ($a = 12.689, 12.675$; $b = 5.391, 5.406$; $c = 9.977, 9.984$ Å and $\beta 129.82^\circ, 129.45^\circ$ for the alpha and beta forms respectively (Walter-Levy *et al.*, 1971).

Lagier *et al.* (1969) and Dubernat and Pezerat (1974) have described the crystallography of the dihydrated oxalates of the magnesium series (Mg, Mn, Fe, Co, Ni and Zn). They showed that there is a three-dimensional well-ordered phase that may be isomorphous with humboldtine. They called this phase the alpha form. Multivariate analyses of the Huleh plant samples suggest that a number of trace elements may be involved as the magnesium oxalate dihydrate is formed. Details of this aspect of the study will be published elsewhere but it suffices to state that of the 46 elements detected, only Na, K, Rb, Sn, Bi, Mo, F, Cl and Br appear to be concerned. The major line (reflection 202) of the magnesium oxalate dihydrate varied from 4.918–4.939 Å (cf. Table 1). Whether these elements are incorporated into the mineral's structure or merely precipitated at the same time or, as has been noted elsewhere (Cowgill, 1975), are possibly involved with the two water molecules, remains to be discovered. Unfortunately, the available samples were too small to pursue this line of investigation any further. However, the variation around the 4.89 Å line and 3.171 Å line would suggest that some element or elements have been incorporated in the structure during the formation of the mineral.

Humboldtine, ferrous oxalate dihydrate, would not be expected to be present in the above-ground portions of green plants. A variety of statistical procedures failed to show any statistically significant relationship between Fe content, d spacing or net peak intensity. It may, therefore, be concluded that humboldtine was below the limits of detection possible with the instruments used in this study. Crick *et al.* (1985) in their study of *Nautilus pompilius* failed to encounter any significant quantity of Fe in their analyses of the mollusc's renal appendages.

Acknowledgements. The field work was carried out during the time the author was a member of the Biology Department of Yale University. The laboratory work was completed during a tenure in the Department of Biological Sciences of the University of Pittsburgh. This work was supported by a series of grants from the National Science Foundation awarded to Professor G. E. Hutchinson of Yale University and/or Professor U. M. Cowgill. I am grateful to all the people acknowledged in previous papers relating to the Huleh project. Sincere appreciation is owed to Rafi Roth, the naturalist at the Lake Huleh Preserve, who assisted this study in many ways and to Professor John Reeder, Curator of the Yale University Herbarium, for his help in confirming the identity of the Huleh plants and ascertaining their most recent Linnean names.

References

- Cowgill, U. M. (1975) *Verh. Internat. Verein. Limnol.* **19**, 2749–57.
 —and Prance, G. T. (1982) *Int. Revue ges. Hydrobiol.* **67**, 235–44.
 Crick, R. D., Burkart, B., Chamberlain, J. A., Jr. and Mann, K. O. (1985) *J. Mar. Biol. Ass. U.K.* **65**, 425–20.
 Lagier, J.-P., Pezerat, H. and Dubernat, J. (1969) *Rev. Chim. Mineral.* **6**, 1081–93.
 Picard, L. (1963) *Proc. Israel Acad. Sci. 7 Humanities* **1**, 1–34.
 Walter-Levy, L., Perrotey, J. and Visser, J. W. (1971) *Bull. Soc. Chim.* 757–61.
 Wilson, M. J. and Bayliss, P. (1987) *Mineral. Mag.* **51**, 327–8.
 —Jones, D. and Russell, J. D. (1980) *Ibid.* **43**, 837–50.
 ———and McHardy, W. J. (1981) *Lichenologist* **13**, 167–76.
 Zhemchuzhnikov, Yu. A. and Ginzberg, A. I. (1960) *Abstr. Am. Mineral.* **47**, 1482 (2962); (M.A. 16–555).

[Manuscript received 19 September 1988:
 revised 6 December 1988]

© Copyright the Mineralogical Society

KEYWORDS: glushkinskite, alpha magnesium oxalate dihydrate, plants, Lake Huleh Preserve, Israel.

PO Box 2047, Midland, MI 48641, USA

U. M. COWGILL