

Moolooite, a naturally occurring hydrated copper oxalate from Western Australia

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ABSTRACT. Moolooite, a naturally occurring hydrated copper oxalate has been identified in a sulphide-bearing quartz outcrop 12 km east of Mooloo Downs station homestead (25° 01' 30" S., 116° 06' 30" E.), Western Australia. It has apparently formed by the interaction of solutions derived from bird guano and weathering copper sulphides. Partial microchemical analysis indicates a composition corresponding to $\text{CuC}_2\text{O}_4 \cdot 0.44\text{H}_2\text{O}$. The infra-red spectrum is similar to that of the artificial compound with diagnostic absorption bands at 3490, 2975, 2935, 1980, 1940, 1660, 1365, 1320, 830, 510, 390, and 315 cm^{-1} . Powder X-ray diffraction patterns indicate a disordered structure with orthorhombic symmetry; a 5.35, b 5.63, c 2.56 Å, $Z = 1$. The strongest lines of the powder pattern are [d Å, l , hkl]: 3.88, 100, (110); 2.50, 30, (120); 2.33, 18, (011); 2.31, 25, (101); 2.14, 20, (111); 1.938, 18, (220); 1.787, 25, (121); 1.753, 30, (211); 1.216, 15, (112). Unindexed very weak diffuse lines on some patterns can be indexed assuming a supercell with $a' = a$, $b' = 2b$, $c' = 2c$ indicating the presence of ordered crystallites.

Moolooite occurs as micro-concretionary crusts and powder in cracks and solution cavities resulting from sulphide oxidation. It is found associated with opaline silica, gypsum, brochantite, antlerite, atacamite, whewellite, sampleite, and libethenite. It is turquoise-green in colour with similar streak, lustre dull to waxy, calculated density 3.43 g/cm^3 . Moolooite is composed of aggregates of generally sub-micrometre sized equidimensional crystallites with $\alpha \sim 1.57$ and $\gamma \sim 1.95$.

By analogy with artificial copper oxalate, moolooite is constructed from infinite ribbon-like elementary structural units consisting of alternating Cu^{2+} and $(\text{C}_2\text{O}_4)^{2-}$ ions. These units are arranged *en echelon* in layers which are stacked with displacements so that octahedral coordination of copper ions is completed by oxygen atoms in adjacent layers. The minimal role played by water in the structure and composition of moolooite distinguish it from other oxalate minerals. Because of the zeolitic character of the water a general formula $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ ($0 \leq n \leq 1$) appears to be appropriate.

KEYWORDS: moolooite, new mineral, oxalates, Western Australia.

MOOLOOITE was discovered in May 1977 during regional geological mapping by one of the authors (I.R.W.) on the Glenburgh 1:250 000 sheet, reference SG/50-6 of the International Series. It was found 12 km east of the homestead on Mooloo Downs pastoral station in the Precambrian Gascoyne Province of Western Australia, approximately 1 km north of Bunbury Well, latitude 25° 01' 30" S., longitude 116° 06' 30" E. The specimens were obtained from a surface exposure of white glassy quartz cropping out of a quartz-strewn colluvial surface. The outcrop was about 1 m to 1.5 m high, with several smaller boulders along strike, probably a quartz vein in direction 070. The vein carries scattered grains of chalcopyrite, digenite, and covellite and the oxidation of these has produced a variety of secondary minerals including brochantite, antlerite, atacamite, gypsum, baryte, and jarosite. In the outer few centimetres of the quartz, solution cavities and cracks are lined with moolooite associated intimately with sampleite and libethenite and an as yet unidentified mineral believed to be an oxalate. The association of phosphates and oxalates near the surface of the quartz is most readily explained by reaction between solutions derived from bird excreta and the soluble secondary copper minerals. No excreta was found on the specimens collected although one had a crust of whewellite. The prominent quartz boulders located on flat ground near Mooloo Creek would have provided an ideal roosting spot for passerine birds in recent geological time. Several examples of avian-guano-derived phosphates have previously been recognized on hilltops in the inland Gascoyne region of Western Australia. Other sources of oxalate such as lichen are considered less likely because of the phosphate association.

Moolooite is the first reported natural occurrence of hydrated copper oxalate. A second occurrence has been reported to the authors from the Sainte-Marie-aux-Mines silver mining district of the Vosges mountains (H. Bari, pers. comm.). The mineral is named for the locality. Both mineral and name were approved by the IMA Commission on New Minerals and Mineral Names. Type material is preserved at Perth, Western Australia, in the mineral collection of the Government Chemical Laboratories.

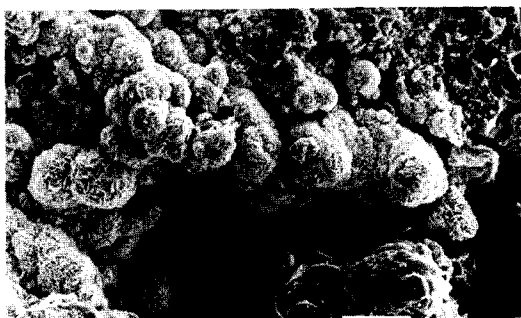


FIG. 1. Scanning electron microscope photograph of moolooite micro-concretions. Scale bar = 100 μm .

Physical and optical properties. The colour of moolooite varies from blue to green but most typically is Turquoise Green 41 d (Ridgway, 1912) with a dull to waxy lustre. Hardness and density could not be measured due to paucity of pure mineral. The micro-concretionary form of the mineral is shown in the scanning electron micrograph (fig. 1). The foil-like elements making up the concretions are themselves aggregates of much smaller crystallites generally less than 1 μm in size. These appear as highly birefringent platelets exhibiting Brownian motion in transmitted light but are too small for precise optical characterization. The largest crystallite observed (approximately 4 $\mu\text{m} \times 1 \mu\text{m}$) was lath-like or prismatic with maximum and minimum refractive indices of 1.95 and 1.57, perpendicular to, and parallel to the axis of elongation. A Gladstone-Dale calculation using the data of Mandarino (1976), the empirical chemical composition and calculated density of 3.43 g/cm^3 gives a mean refractive index $\bar{n} = 3\sqrt{\alpha\beta\gamma} = 1.77$.

Chemical composition. Partial microchemical analysis of a 1.8 mg hand-picked sample, performed by R. MacDonald, Division of Applied Organic Chemistry, CSIRO, gave C 14.10, H 0.52% corresponding to C_2O_3 42.3, H_2O 4.65%. The analysis

was carried out simultaneously on a CHN analyser. The mineral decomposes rapidly under the electron beam and therefore quantitative determination of Cu by microprobe analysis was not possible. However no elements with an atomic number of 11 or greater other than Cu and Si were detected consistently. The Si is variable and attributed to intergrown opaline silica, since no extraneous X-ray diffraction lines of quartz or silicates were detected. A microchemical spot test for oxalate radicle gave a positive result. Moolooite dissolves in warm dilute hydrochloric acid without effervescence. Allowing sufficient Cu^{2+} for oxalate stoichiometry gives CuO 46.7, C_2O_3 42.3, H_2O 4.65, total 93.6%. Assuming the shortfall from 100% to be due to silica impurity, an empirical formula of $\text{CuC}_2\text{O}_4 \cdot 0.44 \text{H}_2\text{O}$ is derived after recalculation. Extensive studies of the analogous artificial compound (Schmittler, 1968) indicate that the water is of 'zeolitic' character, i.e. not essential to maintain structural integrity. A general formula for the mineral of $\text{CuC}_2\text{O}_4 \cdot n \text{H}_2\text{O}$ is therefore appropriate. Schmittler has defined the limits of n as $0 \leq n \leq 1$; however, the largest water content of copper oxalate determined experimentally and reported in the literature is 0.5 H_2O (Dollimore *et al.*, 1963).

Infra-red spectroscopy. Samples for infra-red spectroscopy were incorporated into KBr pressed discs, and spectra recorded on an internally calibrated Mattson Fourier-transform instrument over the range 4000 to 500 cm^{-1} , and on a Perkin Elmer 680 dispersive instrument to extend the range to 200 cm^{-1} . The spectra for moolooite and artificial copper oxalate prepared by precipitation from solutions of copper acetate and oxalic acid are shown in fig. 2. Both are characterized by very broad absorption bands corresponding to the H_2O and carbonyl stretching frequencies at approximately 3500 and 1650 cm^{-1} . It is evident that there is considerably less water in the synthesized compound. Otherwise the only significant difference between the spectra occurs in the region between 900 and 1100 cm^{-1} , where there are additional absorption bands on the moolooite spectrum. These are probably due to silica and possibly phosphate impurity.

X-ray diffraction. Debye-Scherrer X-ray powder diffraction patterns were obtained using a Philips 114.83 mm diameter camera and Fe-filtered $\text{Co-K}\alpha$ radiation. Internal calibration was obtained from lines due to quartz impurity. The pattern can be indexed satisfactorily using an orthorhombic cell with refined parameters a 5.35, b 5.63, c 2.56 \AA , $Z = 1$ as shown in Table I. The data are similar to that given for the artificial compound $\text{CuC}_2\text{O}_4 \cdot 0.1 \text{H}_2\text{O}$, on pattern 21-297 from the JCPDS

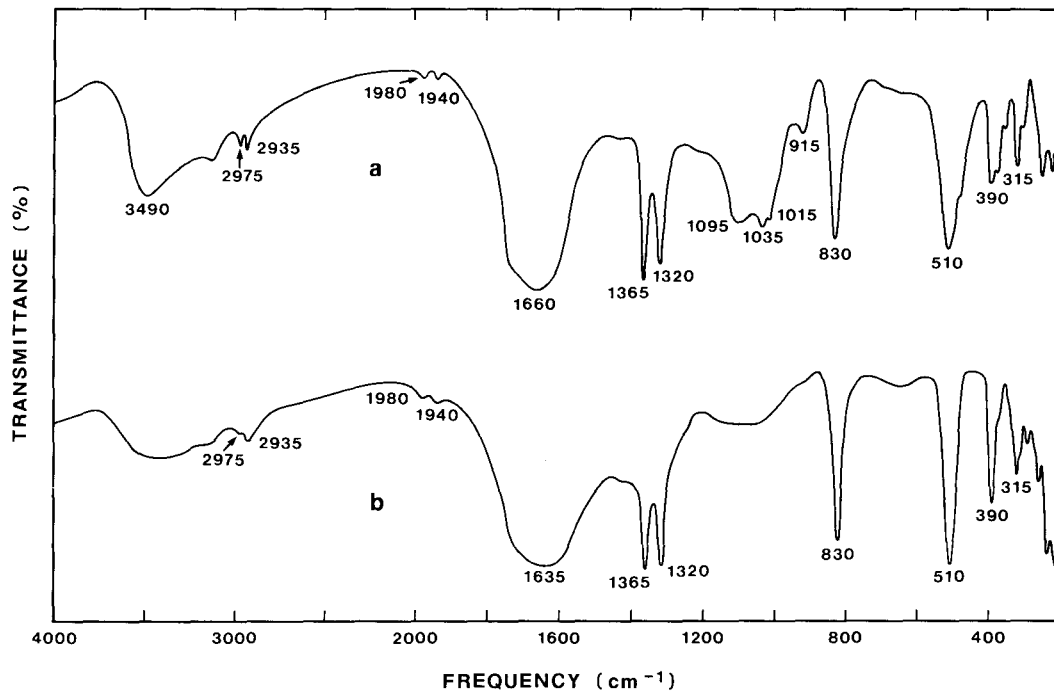


FIG. 2. Infra-red absorption spectra of (a) moolooite and (b) copper oxalate hydrate synthesized from solutions of copper acetate and oxalic acid.

Table I. X-ray powder data for moolooite; Philips 114.83 mm diameter camera, CO-K α , I visual

hkl	d_{calc}	d_{obs}	I	hkl	d_{calc}	d_{obs}	I
n.i.	-	4.61 _d	<5	321	1.299	1.293 _b	10
110	3.881	3.88	100	330	1.294		
n.i.	-	3.54 _d	<5	002	1.280	1.279	12
020	2.817	2.83	12	012	1.248	1.247 _b	<5
120	2.493	2.50	30	240	1.246		
210	2.418	2.41 _b	10	102	1.245		
011	2.331	2.33	18	112	1.216	1.216	15
101	2.309	2.31	25	022	1.165	1.163	<5
111	2.137	2.14	20	411	1.161		
220	1.940	1.938	18	202	1.155	1.154	<5
121	1.786	1.787	25	331	1.155		
300	1.784			122	1.139	1.138	<5
211	1.758	1.753	30	222	1.068	1.069	10
310	1.701	1.689	<5	302	1.040	1.038	<5
031	1.514	1.518 _b	15	250	1.038		
301	1.464	1.459 _b	10	132	1.038		
131	1.457			412	0.913	0.910	5

b = broad reflection; d = diffuse reflection; n.i. = not indexed (see text)

compilation. Two very weak and diffuse low-angle lines on some patterns can be indexed assuming a supercell with $a' = a$, $b' = 2b$, $c' = 2c$. This phenomenon appears to be related to the presence of more ordered crystallites. Line broadening due to the combined effects of small crystallite size, line overlap and disorder is general, but the effect is greater in some samples than in others.

Order-disorder phenomena in artificial copper oxalate have been described in Schmittler (1968). Due to inability to grow suitable crystals, no single crystal X-ray structure analysis has yet been reported. Nevertheless, Schmittler's early X-ray powder diffraction study and a more recent study of inter-atomic distances by extended X-ray absorption fine structure spectroscopy—EXAFS—(Michalowicz *et al.*, 1979) has revealed considerable structural detail. These studies show that the basic structural unit is an infinite linear ribbon-like chain consisting of alternating Cu^{2+} and $(\text{C}_2\text{O}_4)^{2-}$ ions. The repeat distance along the chain is equal to $2c$. The chains are arranged in parallel orientation (*en echelon*) in layers which are stacked to complete the three-dimensional structure. Ribbons in adjacent layers are approximately mutually perpendicular. Displacements of the layers allows the copper ions to complete octahedral co-ordination by forming two Cu—O bonds with oxygen atoms belonging to ribbons in adjacent layers. In this respect copper oxalate differs from oxalates of other divalent metals (e.g. $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ —humboldt-

tine) which utilize oxygens from interlayer water molecules to complete co-ordination (see Lagier *et al.*, 1969; Dubernat and Pezerat, 1974). Thus water plays a negligible role in the structure and composition of copper oxalate.

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