Kleemanite, a new zinc aluminium phosphate

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SUMMARY. A new hydrated zinc aluminium phosphate mineral has the composition $ZnAl_2(PO_4)_2(OH)_2 . 3H_2O$. It has been named kleemanite. It occurred rarely both as veinlets 1–2 mm thick, and as thin layers on surfaces of cracks and small cavities in one section of the iron ore deposit at Iron Knob, South Australia. Chemical, X-ray, thermal analysis, and optical data are given.

AN unusual occurrence of phosphate minerals has recently been found in isolated cracks and fissures in the Precambrian iron ore deposits at Iron Knob, South Australia. Amongst a group of specimens from this locality was a mineral with the superficial appearance of yellow ochre, but which on close inspection proved to be composed of fine hair-like crystals forming a felted mass. The X-ray diffraction pattern could not be matched with any recorded mineral, and the chemical composition confirmed a distinct new species.

The new mineral has been named for Dr Alfred William Kleeman, formerly Reader in the Department of Geology, The University of Adelaide, and the mentor of a generation and more of students of mineralogy and petrology in that department. The name and data have been approved prior to publication by the Commission on New Minerals and Mineral Names, IMA. A type specimen has been lodged with the National Museum of Victoria.

Occurrence. Operations at the Iron Knob and Iron Monarch iron ore quarries are gradually removing the tops of hills that originally stood between 100 and 200 m above the surrounding plains. The secondary minerals, which include wardite, cyrilovite, strengite, variscite, kidwellite, crandallite, gorceixite, wavellite, apatite, millisite, montgomeryite, turquoise, baryte, alunite, malachite, calcite, and dolomite occur randomly and very sparsely. The new mineral, which occurred as an ochre-like coating and thin veins 1–2 mm thick on manganiferous iron ore, occurred on the RL187 level some 100 m below the original top of the hill.

This particular area was somewhat unusual in the orebody in that it was enriched in manganese, phosphorus, and zinc. A fault zone recorded from this level had been partly filled with manganese oxides, and variscite occurred in cavities near the walls of the ore. The ore on both sides of the fault was enriched in manganese and zinc, with the east side containing small, zinc-bearing jacobsite crystals scattered through the ore, while the west side contained lenses of zinc-bearing hausmannite (David Gilbert, private comm.). The kleemanite came from the east side of the fault, and appears to have been formed by leaching of zinc, aluminium, and phosphorus from the surrounding orebody by descending surface waters. Redeposition occurred in cracks and fissures possibly near a former water-table level. The samples examined were free from other phosphate minerals.

Physical properties. Most of the small amount of material available is ochreous in appearance. Examination with a hand lens, however, reveals that it is composed of a very fine, hair-like mass of crystals. In small cavities where crystals are separated and slightly larger and the bright lustre is visible, they are colourless. The fine matted nature of the material makes determination of physical properties difficult. The true hardness was difficult to estimate, but the matted material is quite soft and easily removed with a needle. The crystallites are illustrated in fig. 1.

Optical properties. In transmitted light the crystallites are colourless. Separate fibres frequently appear to be composed of several crystallites parallel to the elongation. Boundaries between crystallites are straight, and inclined extinction of up to 40° in opposite directions in neighbouring crystallites suggests that multiple twinning parallel to the elongation is present. The optics of the crystals indicated that they were either monoclinic or triclinic. Refractive indices were measured by
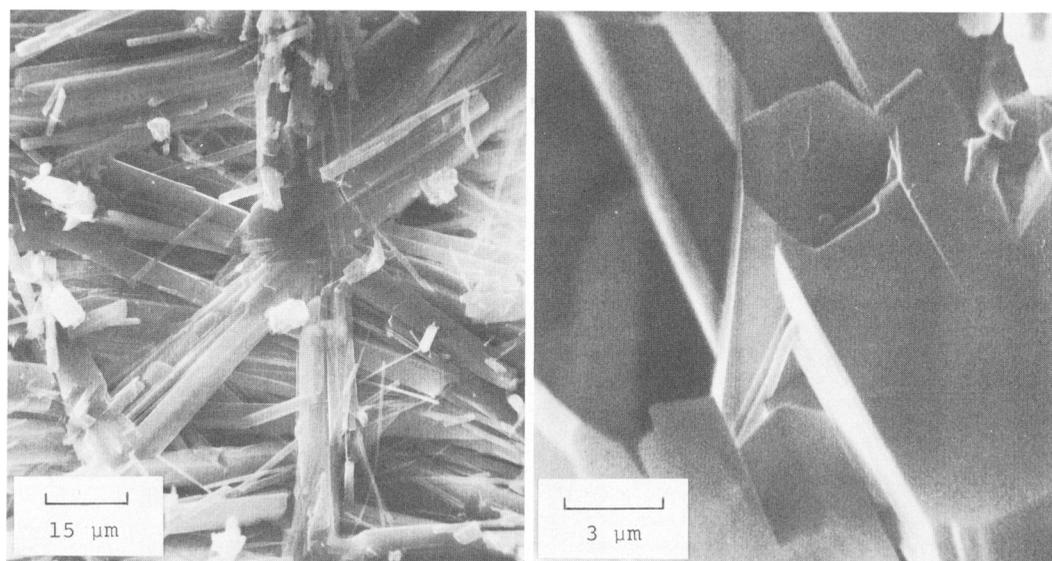
FIG. 1. Scanning electron micrographs of crystallites of kleemanite. Photograph on right shows faces on the ends of the crystals.

the immersion method: $\alpha = 1.598 \pm 0.002$, $\gamma = 1.614 \pm 0.002$. The crystallites, which were about 1 μm in width, were too small for further optical properties to be determined.

Crystallography. The powder diffraction data taken with a Guinier camera with Cu-Kα radiation, using KCl as an internal standard, are recorded in Table I. Intensities were estimated visually by comparison with an empirical standard. The unit cell was determined from single crystal Weissenberg photographs, and was refined from the powder data using the least squares method. The status of the line at 4.73 Å, which is clearly visible on all Guinier photographs taken, is obscure; while it appears to index, although not precisely, as 30$\bar{1}$, such a reflection does not appear on single crystal Weissenberg photographs. Until a detailed structural analysis is carried out, we feel that the data recorded in Table I are most probable.

Chemistry. A preliminary examination in the scanning electron microscope using an energy dispersive analyser showed that the major elements were zinc, aluminium, and phosphorus, with minor amounts of iron and manganese. For quantitative analysis, 73.53 mg of a carefully selected sample was fused in 1.5 g of 1 : 1 mixture of lithium tetraborate and lithium carbonate. The melt was leached in 20 ml of 2N nitric acid and diluted to 100 ml. The concentrations of aluminium, iron, and

TABLE I. *X-ray powder data of kleemanite. Guinier camera Cu-Kα 1.5418 Å. KCl, a = 6.2929, used as an internal standard*

I	d_{obs}	d_{calc}	hkl	I	d_{obs}	d_{calc}	hkl
6	9.09	9.15	001	4	3.04	3.04	21$\bar{2}$
1	6.91	6.85	100	1	3.01	3.01	112
1	6.68	6.70	10$\bar{1}$	1	2.89	2.89	201
5	5.66	5.65	011	2	2.81	2.81	203
2	4.91	4.95	110	1	2.62	2.62	21$\bar{3}$
2	4.85	4.90	11$\bar{1}$	1B	2.396	$\begin{cases} 2.398 \\ 2.397 \end{cases}$	30$\bar{2}$ 030
10	4.76	4.75	101	1B	2.329	2.328	023
3	4.73*			1B	2.309	2.306	20$\bar{4}$
4	3.97	3.96	111	1B	2.278	2.280	300
5	3.88	3.88	11$\bar{2}$	$\frac{1}{2}$	2.276	2.275	31$\bar{2}$
5	3.64	3.64	20$\bar{1}$	$\frac{1}{2}$	2.213	2.214	22$\bar{3}$
1	3.42	3.42	200	1	2.193	2.196	21$\bar{4}$
5	3.33	$\begin{cases} 3.35 \\ 3.34 \end{cases}$	20$\bar{2}$ 021	1	2.175	2.173	310
				1	2.142	2.141	131
6	3.30	3.31	102	1	1.950	1.950	23$\bar{2}$
8	3.09	3.09	210	2	1.744	1.743	41$\bar{1}$
2	3.06	3.05	003				

* Superlattice reflection?

$a = 7.290 \pm 0.006$ Å; $b = 7.194 \pm 0.006$ Å; $c = 9.762 \pm 0.009$ Å; $\beta = 110.20 \pm 0.04°$.

Space group: $P2$, $P2_1$, $P2/m$ or $P2_1/m$; $Z = 2$; $\rho_{calc} = 2.76$ g/cm^3.

manganese were determined by atomic absorption. A nitrous-oxide-acetylene flame was used to minimize interferences, the standards being prepared as a closely matched mixture in a solution of pure flux. Zinc was determined also by atomic absorption after 20 × dilution. Phosphorus was determined on a 50-ml aliquot of the stock solution using a gravimetric phosphomolybdate method. Standards were prepared from pure metals and potassium dihydrogen phosphate. Water was determined on a separate sample as the weight loss on a thermogravimetric curve (see below). The loss occurred at around 300 °C, so would be unlikely to be fluorine, nor was any gas evolution detected when the mineral was attacked with acid.

TABLE II. *Chemical analysis of kleemanite*

	Wt%	Cation atoms
ZnO	20.7	1.01
Al_2O_3	24.4	1.90
P_2O_5	35.7	2.00
Fe_2O_3*	1.1	0.06
Mn_2O_3*	1.3	0.07
H_2O†	18.2	8.07
Total	101.4	

* Fe and Mn calculated as Fe_2O_3 and Mn_2O_3.
† Total water calculated from weight loss on TGA curve.

The analytical results are given in Table II. Iron and manganese are reported as Fe_2O_3 and Mn_2O_3, as this seems appropriate to the depositional environment of the mineral. Recalculation of the analysis thus leads to the empirical formula:

$$Zn_{1.01}(Al_{1.09}Fe^{3+}_{0.06}Mn^{3+}_{0.07})$$
$$(PO_4)_2(OH)_{2.08}(H_2O)_{2.98}$$
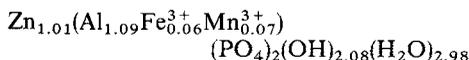
This corresponds closely with the idealized end-member composition of:

$$ZnAl_2(PO_4)_2(OH)_2 \cdot 3H_2O$$
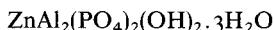
Thermal analysis. DTA and TGA curves of kleemanite are given in fig. 2. A broad endotherm at 265° corresponds to the greater part of the weight loss, and probably represents the molecular water in the structure. A break in the slope of the TGA curve at a little over 300° appears to correspond to the sharp endotherm at 315°; this may represent the loss of water corresponding with the hydroxyl

groups. The small endotherm at 650° is probably caused by the recrystallization of the poorly ordered anhydrous mineral. X-ray diffraction of the DTA calcine showed it to contain mainly $AlPO_4$ and $Zn_3(PO_4)_2$.

Discussion. Zinc phosphates are rare minerals. Only some eight or nine have been recorded, and only one of these was a zinc aluminium phosphate. This is faustite, $ZnAl_6(PO_4)_4(OH)_8 \cdot 5H_2O$, the zinc analogue of turquoise (Erd *et al.*, 1953). Kleemanite is chemically distinct from faustite in having a much higher Zn/Al ratio. It is also distinctive in appearance and X-ray diffraction pattern. There seems to be no mineral isotype of kleemanite. Other phosphate minerals having a $R^{2+}:R^{3+}:P$ ratio of 1:1:1 are either anhydrous or contain more water.
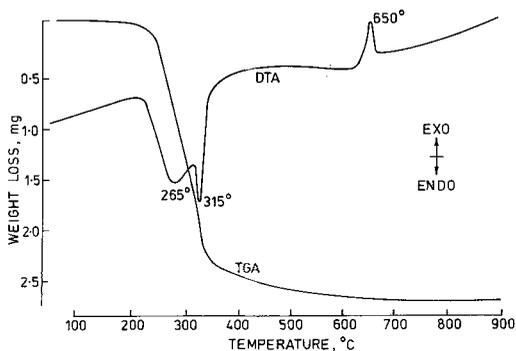
FIG. 2. Thermal analysis curves of kleemanite. Sample weight, 15.34 mg; heating rate, 10 °C/min.

It might be noted in passing that one of the most striking occurrences of zinc phosphate minerals also occurred in South Australia at Reaphook Hill (Hill and Milnes, 1974). Magnificent specimens of scholzite, as well as tarbuttite and parahopeite, were found at this locality.

REFERENCES

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