Aldermanite, a new magnesium aluminium phosphate

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ABSTRACT. A new magnesium aluminium phosphate mineral with the ideal formula ${\rm Mg_5Al_{12}(PO_4)_8(OH)_{22}} \cdot n{\rm H_2O}$ ($n\simeq32$) has been named aldermanite. It occurs as minute talc-like flakes, partly as an alteration product of fluellite, thinly coating cracks and cavities in a brecciated metamorphosed rock phosphate at Moculta, South Australia. Strongest X-ray diffraction lines are 13.40 Å (100) 002, 7.98 Å (80) 011, 5.55 Å (60) 210; unit cell parameters $a=15.00\pm0.007, b=8.330\pm0.006, c=26.60\pm0.01$ Å, Z=2.

ROCK phosphate was discovered in South Australia in 1903 and has since been mined from numerous small deposits (Jack, 1919; Dickinson, 1943a, 1943b). While commercially not of great importance, some of the deposits have produced some interesting mineralogy.

One of these deposits, exposed in the Moculta quarry, is situated close to the town of Angaston, some 60 km north-east of Adelaide. On several specimens from this locality, minute pearly flakes occurred overlying transparent colourless crystals of fluellite. The X-ray diffraction pattern of the flakes could not be correlated with any recorded mineral, and this, with the elemental composition determined by energy-dispersive analysis, confirmed that it was a new mineral.

The mineral has been named for the late Arthur Richard Alderman, Professor of Geology and Mineralogy at the University of Adelaide from 1953 to 1966. The name and data for the mineral have been approved prior to publication by the IMA Commission on New Minerals and Mineral Names. A type specimen has been deposited with the National Museum of Victoria (No. M34778).

Occurrence. The Moculta rock phosphate deposit lies near the base of Lower Cambrian limestone. It is one of a series of such small deposits, but is unique in that it has been metamorphosed, resulting in hardening of the rock and recrystallization of the apatite. Subsequently there has been

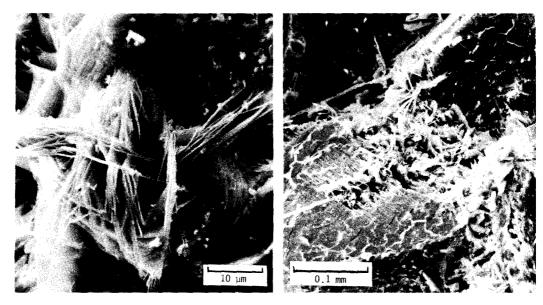
brecciation, and circulating water, probably at shallow depths, has resulted in the redistribution of some of the phosphorus. Brecciated material has been recemented, largely by apatite, but is replaced by iron and aluminium phosphates. In cavities, a number of other phosphate minerals have been deposited, usually finely crystalline, but sometimes as larger crystals visible with a hand lens. The phosphates identified to date include, as well as apatite, the following: beraunite, cacoxenite, childrenite, crandallite, cyrilovite, dufrenite, fluellite, gorceixite, leucophosphite, minyulite, rockbridgeite, variscite, and wavellite.

Physical and optical properties. The aldermanite occurs as minute very thin talc-like crystallites, which, with care, can be scraped off the fluellite with little contamination. The habit of these crystallites is shown in fig. 1. The crystals are generally less than 0.1 mm across and only about 0.1–0.2 μ m thick. Hardness is probably no more than 2. The mineral is soluble in mineral acids.

Their small size made determination of optical properties difficult. In transmitted light the mineral was colourless. The very thin platelets were elongated in one direction, with a simple ensate termination. No interference figure could be obtained. However, the crystals appeared to have straight extinction so that the crystals appeared orthorhombic. Birefringence was very low, and the one measurable refractive index was close to 1.500 (\pm 0.005). Using the data of Mandarino (1976), the Gladstone-Dale relationship indicates a figure of 2.0 for the density.

Chemistry. Total water content was determined by Mr R. McDonald of the CSIRO Microchemical Laboratory on 0.380 mg of carefully collected material. Loss on ignition at 800 °C was determined, and water evolved was collected and weighed. The former gave 36.1%, and the latter determination 38.9%. Owing to the small weights involved, the errors in the weighing of the absorbed water were likely to be considerably more than

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Figs. 1 and 2: Fig. 1 (left). Scanning electron micrograph of aldermanite crystallites. Fig. 2 (right). Aldermanite forming from the breakdown of fluellite.

those involved in weighing for loss on ignition. The figure of 36.1% is therefore considered to be a truer reflection of the actual water content. No evolution of gas (e.g. CO₂) was seen when the mineral was attacked with acid on a glass slide under the microscope, nor were halides or sulphur detected in the microprobe. It is therefore assumed that loss on ignition represents the water content. The qualitative electron-probe scan also showed that the only cations present in significant amounts were Mg, Ca, Al, and P. Traces of Na and Fe were detected.

Backscattered electron images of a sample prepared for electron-probe analysis showed that the material was less than ideal for this purpose. Minute grains of contaminating mineral, usually Ca-rich, were present, although these could be avoided by selecting targets with the appropriate crystal habit (fig. 1). Also, since these flakes were only a fraction of a micron in thickness, the section did not present a continuous surface to the beam. X-rays were in part generated from material that was covered by plastic and from surfaces that were tilted with respect to the beam. Absorption corrections, which were considerable for the elements present, were therefore subject to some uncertainty. It was therefore not possible to obtain completely reproducible total X-ray counts. Only the ratios of the concentrations of the elements could be determined, and even these were subject to a small degree of uncertainty.

Crystals for analysis were selected using the backscattered electron images as well as X-ray maps. Only the regions of high Mg content as well as expected crystal habit were chosen. In this way, contaminant grains were avoided. Two methods were used to determine the element ratios:

X-ray intensity ratios Mg/Al and Al/P were determined for some twenty-five points and these were plotted against the Mg and Al count rates respectively. It was found that both ratios increased slightly as the count rate increased. This was considered to be due to the lower absorption of Mg and Al X-rays when larger areas of the mineral, less covered by plastic, were encountered. The maxima of the ratios were therefore selected as the most probable values. The ratio of Ca to P count rates was also determined.

X-ray intensity ratios were determined for points selected for maximum P and Mg X-ray count rates, and which appeared to have the largest target areas in the backscattered electron images.

Ratios determined by the two methods agreed within 6%; compositions calculated from these results and the gravimetric water determinations are given in Table I. The above ratios were corrected for absorption using programmes similar to those developed by Frost (1977). The average of these two analyses yields the ratios to forty-three oxygen atoms in the anhydrous part included in Table I, or ideally, $Mg_5Al_{12}(PO_4)_8(OH)_{22} \cdot nH_2O$ where $n \simeq 32$.

TABLE I. Analyses of aldermanite

TABLE II. X-ray diffraction data for aldermanite

	1	2	3	4
MgO	8.5	8.2	8.4	4.53
CaO	1.2	1.2	1.2	0.47
Al_2O_3	28.4	28.4	28.4	12.12
P_2O_5	25.8	26.1	25.9	7.94
H_2O	36.1	36.1	36.1	43.5
	[100]	[100]	[100]	

- 1. Calculated from results of method 1 (see text).
- 2. Calculated from results of method 2 (see text).
- 3. Average analysis, calculated directly from electron-probe results.
- 4. Atomic ratios to 43 oxygen (excl. H₂O).

Crystallography. The powder diffraction data, taken with a Guinier camera with $\text{Cu-}K\alpha$ radiation and using KCl as an internal standard, are recorded in Table II. The unit cell was determined from a difference synthesis of these data and later refined to an orthorhombic cell using a least-squares method. The intensities were estimated visually by comparison with an empirical standard. Until larger crystals are found for detailed single-crystal analysis, the data given in Table II are the most probable.

Using the figure of 2.0 for the density, and allowing for $32H_2O$ in the empirical formula, the number of formula units in the unit cell was calculated as 2.

Discussion. Fluellite and minyulite were usually the last of the phosphate minerals to form at Moculta. Aldermanite, however, is normally associated with the fluellite, which is present as colourless, transparent idiomorphic crystals up to 0.5 mm in size. It occurs in small cavities and on old fracture surfaces overlying dark-green veinlets of beraunite. The aldermanite clearly post-dates the fluellite, and appears, at least in part, to have been formed by the reaction of late fluids with the fluellite crystals (fig. 2). These fluids must have been relatively rich in Mg, and the phosphorus/cation ratio of the new mineral suggests that in these late solutions, the P content was probably decreasing. Aldermanite is the only Mg-bearing phosphate mineral to have been found so far in this deposit. There is no definite indication of the origin of the Mg; traces may have been leached from the neighbouring limestones.

Aldermanite does not appear to have any analogues amongst the known phosphate, arsenate, or vanadate minerals. Three other magnesium aluminium phosphate minerals (disregarding replacement by Fe) are known: lazulite, MgAl₂(PO₄)₂

I	$d_{ m obs}$	$d_{ m calc}$	hkl
100	13.40	13.29	002
80	7.98	7.95	011
30	5.70	5.726	203
60	5.55	5.573	210
30	4.96	4.975	204
20	3.47	3.470	216
		3.393	411
20	3.40	3.390	207
		(3.325	(008
10	3.32	3.318	306
10	3.32	3.314	412
20	3.27	3.270	404
20	3.21	3.270	/ ***
10	3.085	(1 018 316
10	2.989	1 3.083 2.983	501
5	2.930	2.983	502
3	2.930	{ 2.844	(317
50	2.841	/	
		{ 2.843 { 2.776) 503 (030
20	2.776	,	
			421
10	2.757	{ 2.762 2.757	
			127
10	2.720	{ 2.717 } 2.716	{ 032 131
		2.716	/ 0 0 4 0
30	2.660	2.659	$\left\{ \begin{array}{l} 0.0.10 \\ 423 \end{array} \right.$
20	2.159	{ 2.164 2.153	{ 433
			518
5	2.083	2.084	€ 623
J	2.000	2.083	703
		1.903	{ 342
10B	1.901	{ 1.902	721
		1.900	0.0.14
		1.854	631
5 B	1.852	{ 1.853	438
		1.852	536
10 B	1.789	1.790	634
5B	1.748	1.751 1.744	{ 726 5 1 12
313	1.770		
5 B	1.673	1.678	539
10B	1.642	{ 1.642 { 1.641	{ 734 { 0.4.10
1013	1.042		
		{ 1.495	{ 257
5B	1.494	{ 1.494	740
		1.493	4.1.16

Unit cell $a = 15.000 \pm 0.007$ $b = 8.330 \pm 0.006$ $c = 26.60 \pm 0.01$ Å Z = 2D = 2.15 (calc).

(OH)₂, gordonite, MgAl₂(PO₄)₂(OH)₂ · 8H₂O, and souzalite, (MgFe)₃(AlFe)₄(PO₄)₄(OH)₆ · 2H₂O. Lazulite is characteristically a pegmatite mineral, and must form at a higher temperature than the

other minerals. Souzalite appears to be known only from its discovery locality (Pecora and Fahey, 1949), and was formed by the hydrothermal alteration of scorzalite, the Fe-rich analogue of lazulite. Gordonite (Larsen and Shannon, 1930) is also very rare, and has only been described from a pegmatite environment. Aldermanite has probably formed at a lower temperature than these minerals but its stability may also be determined in part by its higher cation/phosphorus ratio as compared with the other magnesium aluminium phosphates.

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