

Peisleyite, a new sodium aluminium sulphate phosphate

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ABSTRACT. A new sodium aluminium sulphate phosphate has been named peisleyite. It has the ideal formula $\text{Na}_3\text{Al}_{16}(\text{SO}_4)_2(\text{PO}_4)_{10}(\text{OH})_{17} \cdot 20\text{H}_2\text{O}$. It occurs as fine-grained, compact, brittle, white material on dumps at Tom's Phosphate Quarry, near Kapunda, South Australia. Strongest X-ray diffraction lines are 12.63 Å (100) 010, 7.82(35) 11 $\bar{2}$, 5.41(35) 004, 7.59(30) 111. Unit cell parameters are a 13.31 ± 0.006, b 12.62 ± 0.006, c 23.15 ± 0.01 Å, β 110.0° ± 0.03°, Z = 2.

SMALL rock phosphate deposits occur in phosphatic limestone beds of Upper Precambrian and Lower Cambrian age in the southern part of South Australia. They outcrop intermittently over a distance of some 500 km, and have been quarried on a small scale in several places for fertilizer. From one of these quarries (Moculta, see Segnit *et al.*, 1981), the new mineral aldermanite was recently described (Harrowfield *et al.*, 1981). Another of these quarries, called 'Tom's Quarry' is situated some 8 km ESE of the town of Kapunda. The quarry has not been operated for some years, but the dumps have been a fertile area for the collection of a number of secondary phosphate minerals.

Recently, a white earthy material from this quarry was found to have a distinctive X-ray diffraction pattern, and subsequent chemical analysis confirmed it to be a new mineral species. The mineral has been named for Mr Vincent Peisley of Brahma Lodge, South Australia, who has collected very painstakingly from these quarries for a number of years, and has brought to light interesting suites of minerals, including this new species, peisleyite (pronounced 'peež-lee-ite'). Prior to publication the name and data for the mineral were approved by the IMA Commission on New Minerals and Mineral Names.

A holotype specimen has been lodged with the National Museum of Victoria (Cat. No. M35630).

Occurrence. The geological setting of the phosphate rock at Tom's Quarry was first described by Jack (1919), with later observations by Dickinson

(1943). This deposit is one of a series formed by localized concentration of phosphorus at the base of the Brighton (Upper Precambrian) limestone. At Tom's Quarry, extensive weathering has taken place, and the rock phosphate is associated with masses of limonitic clay. The phosphate rock itself has a high content of Fe and Al, and the most recent quarrying operations (over 30 years ago) yielded ore that was used for the production of high phosphorus pig iron. The remaining reserves of phosphate at this locality appear to be negligible.

Most of the phosphate minerals found in this deposit in recent years have been from the old dumps. These reflect ample evidence of alteration and secondary redistribution of phosphorus by the extensive surface weathering. Wavellite is widespread, sometimes massive, sometimes as radiating, transparent, colourless crystals projecting into small cavities. Other minerals frequently identified are apatite, fluellite, and cacoxenite, and, less commonly, minyulite and leucophosphite.

On one end of an isolated block on the dumps was a white, brittle, compact material looking like earthy alunite. It contained a few thin veinlets of wavellite, seldom more than 0.1 mm in width, but otherwise showed no other mineral associations. There was no evidence as to the original location of the block in the quarry, and the mineral has not yet been identified *in situ*.

Chemistry. The chemical analysis of the sample is given in Table I. For analysis, two stock solutions were prepared to permit the conditions for the determination of each constituent to be optimized. Test portions were weighed from material that had been ground to minus 100 μm and pre-equilibrated with the laboratory atmosphere. Hygroscopic moisture content was determined by heating at 105°C to constant mass to permit the correction of all analytical values to a dry basis.

One test portion was dissolved in dilute sulphuric, evaporated to fumes, and silica determined gravimetrically. From the filtrate, aliquot portions were used to determine Al titrimetrically using

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TABLE I. Chemical composition of peisleyite. wt. % on dry basis. Hygroscopic water 14.3%

	wt. %	Loss on ignition:	
SiO ₂	0.83	at 300°C	17.7
Al ₂ O ₃	35.03	600°	4.2
Fe ₂ O ₃	0.17	1000°	7.9
MgO	0.02(4)		
CaO	0.71		29.8
Na ₂ O	3.83	less SO ₃	7.26*
K ₂ O	0.03(3)		
SO ₃	7.33	water	22.54
P ₂ O ₅	29.10		
H ₂ O (+110°C)	22.54		
Total	99.60		

* Total SO₃ 7.33%; residual SO₃ in sample at 1000° was 0.07%; (NH₄)₂O was sought but not detected.

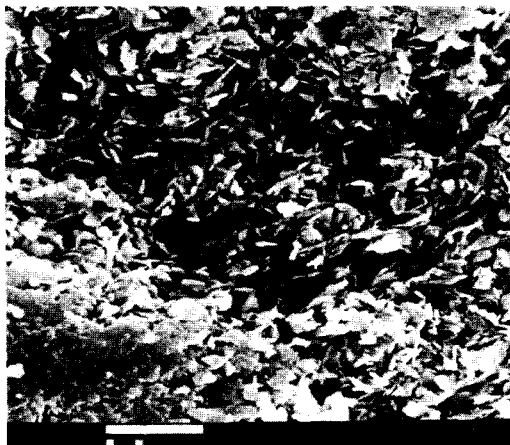


FIG. 1. Scanning electron micrograph of peisleyite, showing platey habit of crystallites. Scale bar represents 10 μm .

EDTA, with phosphorus being determined gravimetrically after precipitation as ammonium phosphomolybdate. A further test portion was fused in high purity lithium tetraborate and leached in hydrochloric acid. The solution was used for the determination by atomic absorption spectrometry of Na, K, Ca, Mg, and Fe. Also in this solution sulphate was determined gravimetrically as barium sulphate using a specially developed method to avoid interference from phosphate.

The value for combined water content was obtained from the corrected value obtained for loss on ignition at 1000°C after a further correction for the oxides of sulphur evolved. For this purpose the small amount of residual sulphate in the ignited residue was determined with a LECO combustion apparatus.

There was a very small residue on dissolution in mineral acid. The main cations of this residue were Ca and Si, but there was sufficient to account for the amounts of these cations in the chemical analysis. There was no evidence of the presence of any mineral contaminant except wavellite, which occurs in discrete veinlets that were easily separated. Si and Ca have therefore been included in the calculation of the formula by considering ($\text{Ca}^{2+} + \text{Si}^4$) as equivalent to ($\text{Na}^+ + \text{P}^{5+}$). This yields the structural formula: $(\text{Na}_{2.88}\text{K}_{0.01}\text{Mg}_{0.01}\text{Ca}_{0.30})\Sigma_{3.20}(\text{Al}_{16.00}\text{Fe}_{0.05}^{3+})\Sigma_{16.05}(\text{SO}_4)_{2.13}(\text{PO}_4)_{9.55}(\text{SiO}_4)_{0.32}(\text{OH})_{17.45} \cdot 20.40\text{H}_2\text{O}$, calculated on the basis of $\text{S} + \text{P} + \text{Si} = 12$. The ideal formula may thus be regarded as $\text{Na}_3\text{Al}_{16}(\text{SO}_4)_2(\text{PO}_4)_{10}(\text{OH})_{17} \cdot 20\text{H}_2\text{O}$.

Physical and optical properties. The peisleyite was a massive, chalky material, light in weight, and quite brittle. The crystallites were too small to be clearly observed with an optical microscope, but appeared in the scanning electron microscope as very small flakes about 2 μm in diameter, and

probably no more than 0.1–0.2 μm thick (fig. 1). Their small size made determination of optical properties difficult. The median refractive index was close to 1.510, and the birefringence low. No other optical properties could be determined.

The density, measured by loss of weight in water, was 2.12; this compares favourably with the density calculated from the formula and unit cell of 2.11, and from the Gladstone–Dale relationship of 2.3. The hardness of the compact material is about 3. It is soluble in mineral acids.

Thermal analysis. DTA and TGA curves are reproduced in fig. 2. The notable features are: (a) low temperature endotherm at 90°, due to loss of water of hydration; the corresponding weight loss up to 145°C is 13.4%; (b) double endotherm at 190–215°, which can be ascribed to loss of hydroxyl water; the corresponding weight loss to 640°C is 19%; (c) two small, sharp exotherms at 575° and 635°; these can probably be attributed to structural rearrangement and recrystallization of the components; (d) the lack of a significant endotherm corresponding with the weight loss between 900° and 1000° is difficult to explain. The weight loss (~7.5%) is clearly due to loss of SO₃. The apparent exothermic reaction may be due in part to change in thermal character of the sample due to shrinkage, and partly due to recrystallization and formation of AlPO₄, the presence of which in the residue was confirmed by X-ray diffraction.

Crystallography. The powder diffraction data shown in Table II were recorded using both a Philips diffractometer at a scanning rate of 1°/min., and a Guinier focusing camera with KCl ($a_0 = 6.2929 \text{ \AA}$) as an internal standard with CuK α radiation. The use of both of these techniques was

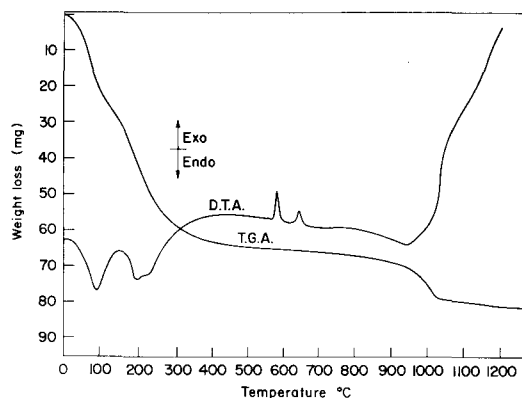


FIG. 2. Thermal analysis curves of peisleyite (sample weight 820 mg).

necessary as the reflections at 12.63 and 10.85 Å were at too low a Bragg angle to be recorded on the Guinier film data. The *d* spacings from the first four reflections in Table II are the average values from the diffractometer and Guinier data; the remaining spacings were measured from the photographic film. The pattern showed some line broadening, which may be attributed to the very thin nature of the crystallites (< 0.2 μm) particularly along the large *c*-axis, which is probably perpendicular to the platelets. The proposed unit cell was determined from a difference synthesis of these data, initially assuming orthorhombic symmetry with the rather broad reflection at 10.85 Å taken to correspond with an 002 spacing. The data was subsequently refined by a least squares method to give a monoclinic cell.

TABLE II. X-ray diffraction data for peisleyite

<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>hkl</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>hkl</i>
100	12.63	12.62	010	12	3.47	3.478	320
15	10.85	10.87	002	10	3.34	3.348	231
35	7.82	7.88	11 $\bar{2}$			3.343	133
30	7.59	7.603	111			3.291	107
15	6.43	6.460	202	5	3.29	3.291	321
		6.435	113			3.288	126
10	6.32	6.310	020	10	3.16	3.159	217
35	5.41	5.436	004			3.155	040
8	5.23	5.239	11 $\bar{4}$	5	3.11	3.113	135
8	4.98	4.994	014			3.108	205
10	4.71	4.714	122	5	3.01	3.011	142
8	4.57	4.575	22 $\bar{1}$			3.009	333
20	4.35	4.351	005			2.934	233
10	4.28	4.279	22 $\bar{3}$	10	2.93	2.933	423
		4.113	015			2.882	142
15	4.11	4.098	215	10	2.88	2.878	411
		4.000	13 $\bar{1}$	10	2.72	2.719	008
5	3.99	3.987	130			2.658	018
5	3.92	3.923	032	5	2.65	2.656	417
5	3.79	3.801	222			2.607	432
5	3.51	3.512	302	5	2.61	2.607	145

Unit cell *a* 13.31 ± 0.006, *b* 12.62 ± 0.006, *c* 23.15 ± 0.01 Å, β 110.0 ± 0.03°, *Z* = 2, *D* 2.11 (calc).

The intensities were determined from the diffractometer data using the average peak heights from two identically prepared specimens. The crystallites were much too small for single crystal data to be obtained, and until larger crystals are found or prepared synthetically, the data given in Table II are the most probable.

Using the experimentally determined density of 2.12, the number of formula units in the unit cell was calculated as 2. The diffraction pattern, indexed on this basis, indicates a unit cell with *a* 13.31, *b* 12.62, *c* 23.14 Å, β 11.0°, *Z* = 2.

Discussion. Unfortunately, the mineral has not yet been found *in situ*. It is clearly a secondary mineral, formed before the deposition of the widespread wavelite of the deposit. The origin of the sulphur is also uncertain, as there is little other evidence of it in this locality, although traces of gypsum and jarosite are present. There are considerable amounts of hard goethite in some parts of the quarry, and it is possible that this has been formed from the oxidation of pyrite, which seems the most likely source of the sulphur. Pyrite, often altering to goethite, occurs in the related Moculta deposit. Reaction of acidic sodium sulphate solutions with colloidal aluminium phosphate could result in the formation of a fine-grained mineral such as peisleyite.

No other mineral of similar composition has been recorded. Three aluminium sulphate phosphates have been described, but are only known from their discovery localities:

kribergite	(du Rietz, 1945)
$\text{Al}_5(\text{PO}_4)_3(\text{SO}_4)(\text{OH})_4 \cdot 2\text{H}_2\text{O}$	
sanjuanite	(de Abeledo <i>et al.</i> , 1968)
$\text{Al}_2(\text{PO}_4)(\text{SO}_4)(\text{OH}) \cdot 9\text{H}_2\text{O}$	
sasaite	(Martini, 1978)
$\text{Al}_{14}(\text{PO}_4)_{11}(\text{SO}_4)(\text{OH})_7 \cdot 83\text{H}_2\text{O}$	

All of these are fine-grained, white, sometimes chalky minerals, but in none is there any significant sodium. All have one or more very strong X-ray diffraction peaks in the 10.5–11.5 Å region. Little data is available on kribergite, although it bears similarities to sanjuanite, which has a microfibrillar habit. An analogy may perhaps be drawn between sasaite and peisleyite, in that they both form platey crystallites. A layer structure has been suggested for sasaite; the same type of structure is likely for peisleyite. Furthermore, if the phosphate and sulphate layers exist as separate entities, it is possible that numerous similar sulphate phosphates with different S/P ratios may exist.

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