

# THE MINERALOGICAL MAGAZINE

AND

## JOURNAL OF THE MINERALOGICAL SOCIETY

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No. 236

March, 1957

Vol. XXXI

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### *Kingite, a new hydrated aluminium phosphate mineral from Robertstown, South Australia.*

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[Read 7 June 1956.]

*Summary.* A new hydrated aluminium phosphate mineral, *kingite*, from phosphate workings near Robertstown, South Australia, has an idealized formula  $\text{Al}_2\text{O}_3 \cdot \text{Al}(\text{OH})_3 \cdot \text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ , with some replacement of OH by F. The specific gravity is 2.2 to 2.3, refractive index 1.514, and percentage chemical composition  $\text{Al}_2\text{O}_3$  31.92,  $\text{P}_2\text{O}_5$  28.63,  $\text{H}_2\text{O}$  37.93. The three strongest lines on the X-ray diffraction pattern are 9.1, 3.45, and 3.48 Å. Kingite changes to a less hydrated phase between 154° C. and 163° C., which is also considered to be a new aluminium phosphate (*meta-kingite*) with idealized formula  $\text{Al}_2\text{O}_3 \cdot \text{Al}(\text{OH})_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ . The strongest lines of its X-ray diffraction pattern are at 7.4, 5.02, and 3.19 Å.

**D**URING an investigation of phosphate minerals in connexion with soil phosphate studies being carried out by us, Mr. D. King, Geologist, of the Department of Mines, South Australia, obtained for us phosphate rocks from various localities. A sample from the Fairview phosphate workings, Robertstown, South Australia, especially noted by Mr. King, proved to be a new hydrated aluminium phosphate mineral. It has been named kingite.

*Occurrence.* The mineral occurs in a fairly pure state as nodules in the phosphate deposits near Robertstown (central province, section 225, hundred of Bright, county Burra, 13 miles north of Robertstown and 20 miles east of Burra). The nodules are white and may be up to 2 inches in diameter; when removed they are coated with a brown powder which

also runs through the nodules in very thin veins. Specimens of the mineral can easily be prepared free from the brown powder and these are found to be pure kingite except for a trace of sodium chloride. X-ray powder diffraction analysis shows that the brown powder is talc, quartz, and sodium chloride, with possibly a little gypsum and hematite or goethite or both. The phosphate deposits near Robertstown are described in a paper by D. King and W. H. Knapman<sup>1</sup> who state that other phosphates present have been identified as vivianite, fluorapatite (collophane), and leucophosphite. The phosphates are associated with Cambrian and Upper Precambrian limestones. They are probably of supergene origin and have been deposited from meteoric waters in fault zones and breccias during Tertiary times. T. W. E. David<sup>2</sup> states that 'in close proximity to the lime phosphates there are deposits of hydrous aluminium phosphates due, apparently, to replacements of slates and shales'.

Since the completion of the work on the original specimen, Mr. D. King has found another deposit of kingite, occurring in the same nodular form in Precambrian sediments at the same stratigraphic level as the original deposit (Torrensian series of dolomites and magnesites). The deposit occurs in an old ironstone quarry near the Clinton phosphate workings, in the hundred of Clinton, section 350, and is about 64 miles west-south-west of the first deposit. The diffraction patterns of kingite from the two localities were identical, except that the Clinton sample showed a trace of goethite.

*Physical, chemical, and X-ray diffraction data.* The nodules are composed of a soft white powder that is too fine-grained for detailed microscopic examination. The mean refractive index is 1.514. The density was determined on lumps and on powdered material; although the pycnometers were evacuated to remove entrapped air, the results were variable, presumably due to the fine porous nature of the material. The following values for specific gravity were obtained: 2.21, 2.30, 2.30.

Weight loss and changes in the X-ray powder diffraction pattern on heating were studied. The weight-loss curve is shown in fig. 1. The mineral loses 10 % of its oven-dry (98° C.) weight at 120° C. and a new phase (meta-kingite) begins to appear. At 160° C., with a weight loss of 20 %, the formation of the second phase appears to be complete, and this decomposes to give an amorphous phase. The cristobalite form of  $\text{AlPO}_4$  begins to form at 410° C. and its crystallization continues with a

<sup>1</sup> Mining Review, Dept. of Mines, South Australia, 1956, no. 99, p. 25.

<sup>2</sup> The Geology of the Commonwealth of Australia, London, 1950, vol. 1, p. 350.

gradual loss of water until the only phases present are  $\text{AlPO}_4$  and a little corundum. The ignition products are  $\text{AlPO}_4$  (cristobalite form) and corundum.

The results of the chemical analysis of kingite are given in table I. A

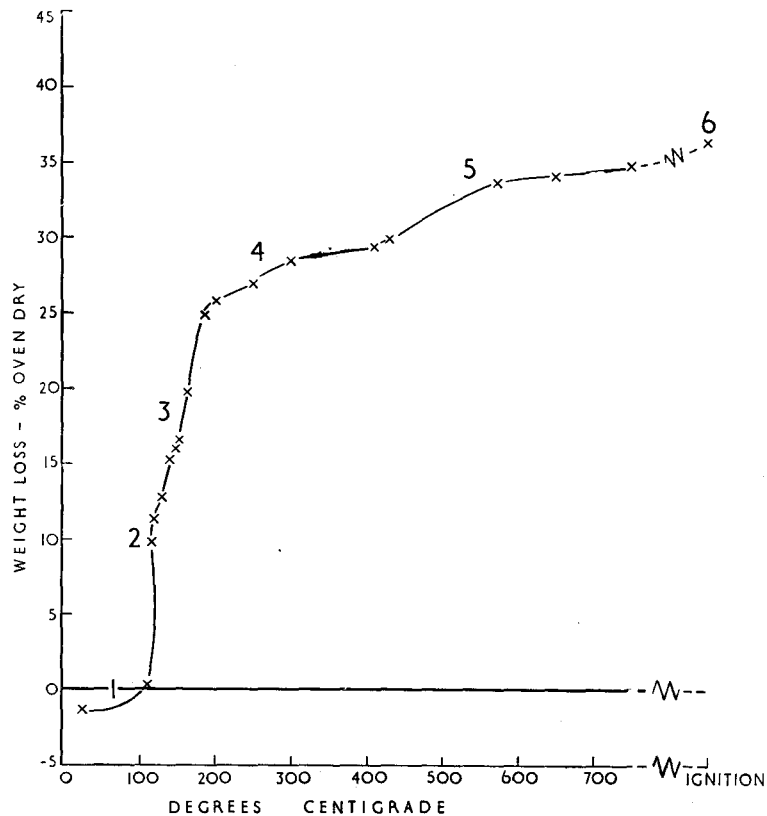


FIG. 1. Weight-loss of kingite with temperature. X-ray photographs show that the phases present in the several regions are: 1, kingite. 2, kingite + meta-kingite. 3, meta-kingite. 4, amorphous. 5, amorphous +  $\text{AlPO}_4$ . 6,  $\text{AlPO}_4 + \text{Al}_2\text{O}_3$ .

trace of chlorine was found and it has been associated with the small amount of sodium, as sodium chloride is a known trace contaminant. (Sodium chloride was recognized in the X-ray diffraction powder photographs by the spotty nature of its lines and also from the persistence of these lines in the diffraction pattern of the material after it had been heated to 200° C.) As part of the water loss at 110° C. may be structural

water, for the purpose of calculating the chemical formulae  $H_2O-$  has been taken as the loss at  $98^\circ C$ . Calculated from the data in table I, the idealized formula of kingite is  $Al_2O_3 \cdot Al(OH)_3 \cdot P_2O_5 \cdot 9H_2O$ , with some replacement of OH by fluorine. The calculation of the exact formula

TABLE I. Chemical analyses of kingite and meta-kingite. The columns headed Calc. give the theoretical compositions for  $Al_3(PO_4)_2(OH)_3 \cdot 9H_2O$  and  $Al_3(PO_4)_2(OH)_3 \cdot 4H_2O$ .

	Kingite.				Meta-kingite.		
	% composition.		Atomic ratio to basis P = 2.	Calc.	% composition.		
	Experimental.	Corrected.*			154° C.	163° C.	Calc.
$Al_2O_3$	31.92	32.25	Al = 3.10	32.10	38.67	40.23	38.81
$P_2O_5$	28.63	28.93	P = 2	29.83	35.05	36.46	36.03
$Na_2O$	0.47	—	H = 20.85	—	—	—	—
$K_2O$	0.01	—	O = 20.18	—	—	—	—
F	0.84	0.85	—	—	—	—	—
Cl	trace	—	—	—	—	—	—
Loss on Ign.	36.52	38.32( $H_2O$ +)	—	38.07	26.29	23.30	25.15
Loss at $110^\circ C$ .	2.71	—	—	—	—	—	—
Insoluble	0.02	—	—	—	—	—	—
Total	101.12	100.35	—	—	—	—	—
Loss at $98^\circ C$ .	1.3	Less O } 0.35 for F }	—	—	—	—	—
Total		100.0	—	100.0	100.0	100.0	100.0

\* Loss at  $98^\circ C$ . has been taken as  $H_2O-$ ; and as sodium chloride is a known contaminant, sodium has been associated with chlorine and deducted.

of meta-kingite is difficult; the weight loss curve is very steep in this region, and it is difficult to decide from the X-ray data when, if ever, meta-kingite alone is present as there are resemblances between its powder diffraction data and those of kingite. In addition, meta-kingite decomposes to an amorphous phase which only becomes obvious when large amounts are present. Calculating from the water content at  $154^\circ C$ . and  $163^\circ C$ . (where meta-kingite appears to be pure), the idealized formula for this phase is  $Al_2O_3 \cdot Al(OH)_3 \cdot P_2O_5 \cdot nH_2O$  where  $n$  lies between 3.5 and 4.5 (see table I).

X-ray powder diffraction data for kingite and meta-kingite are given in table II. The powder diffraction photographs for kingite, meta-kingite, wavellite, and wardite are shown in fig. 2. Attempts were made to index the diffraction photograph of kingite but the symmetry proved too low or the unit cell too large to allow indices to be assigned. The mineral does not appear to have cubic, tetragonal, or hexagonal symmetry.

*Differential thermal analysis.* A differential thermal analysis was carried out by Mr. R. M. Taylor, at a heating rate of  $10^\circ C$ . per minute, against a standard of aluminium oxide, and gave the curve shown in

TABLE II. X-ray powder diffraction data for kingite and meta-kingite. Co-K $\alpha$  radiation,  $\lambda$  1.7889 Å.

Kingite.*				Meta-kingite.†	
<i>d</i> Å.	<i>I</i> .	<i>d</i> Å.	<i>I</i> .	<i>d</i> Å.	<i>I</i> .
9.8	9	2.476	7	9.8	40
9.1	100	2.446	5	7.4	100
7.2	6	2.404	1	6.84	60
6.85	24	2.365	1	6.30	30
6.27	14	2.336	5	5.71	30
5.34	28	2.300	7	5.41	30
5.28	52	2.292	2	5.02	90
5.10	24	2.274	2	4.79	60
4.96	4	2.269	3	4.66	60
4.86	5	2.255	1	4.13	20
4.61	18	2.248	3	3.76	20
4.55	5	2.233	7	3.59	60
4.36	8	2.216	4	3.42	30
3.93	15	2.208	4	3.35	20
3.75	1	2.196	3	3.19	80
3.60	6	2.189	1	3.100	60
3.48	65	2.182	1	3.012	60
3.45	80	2.159	2	2.962	60
3.38	27	2.148	2	2.883	10
3.29	2	2.127	3	2.793	10
3.24	2	2.112	14	2.696	50
3.17	39	2.054	3	2.656	20
3.14	15	2.041	1	2.569	5
3.108	30	2.026	6	2.470	20
3.066	14	2.005	2	2.355	20
3.018	10	1.990	8	2.282	50
2.975	24	1.974	13	2.209	50
2.940	4	1.922	3	2.122	20
2.893	2	1.914	1	2.002	20
2.846	9	1.900	5	1.887	20
2.837	6	1.882	1	1.854	5
2.759	7	1.875	1	1.808	20
2.712	3	1.858	3	—	—
2.667	2	1.835	13	—	—
2.640	12	1.814	1	—	—
2.617	9	1.805	3	—	—
2.590	5	1.788	2	—	—
2.568	8	1.772	4	—	—
2.551	4	—	—	—	—
2.529	3	—	—	—	—

Data for kingite obtained with a Philips high-angle diffractometer; intensities given are based on relative peak heights. Data for meta-kingite obtained with 5.73 cm. diameter camera and intensities estimated by eye. Both patterns extend considerably beyond the spacings given but as the lines are very numerous and weak accurate measurement of individual lines becomes difficult.

\* Kingite, Fairview Mine, Robertstown, South Australia. The pattern remains unchanged to 120° C.

† Kingite heated to 163° C.

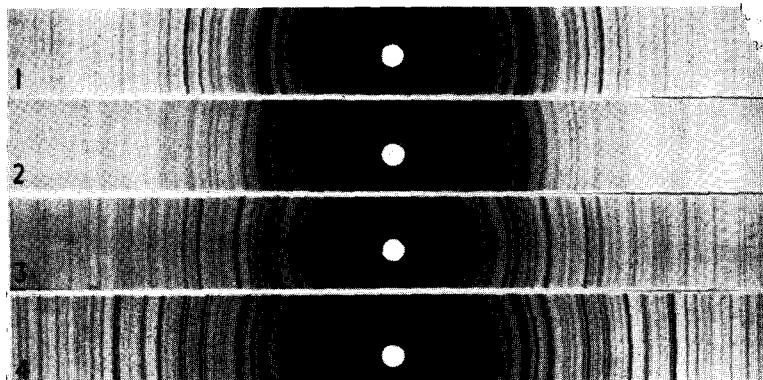


FIG. 2. Powder diffraction photographs, taken with  $\text{Co-K}\alpha$  radiation in a 5.73 cm.-diameter camera; reduced 4:4.7. 1. Kingite, Fairview Mine, Robertstown, South Australia. 2. Meta-kingite. 3. Wavellite, York County, Pennsylvania, U.S.A. 4. Wardite, Fairfield, Utah, U.S.A.

fig. 3. The low-temperature endothermic peak corresponding to the phase changes kingite  $\rightarrow$  meta-kingite  $\rightarrow$  amorphous material shows evidence of being resolved. The broad exothermic reaction (600–700° C.) confirms that the recrystallization of the amorphous material is gradual.

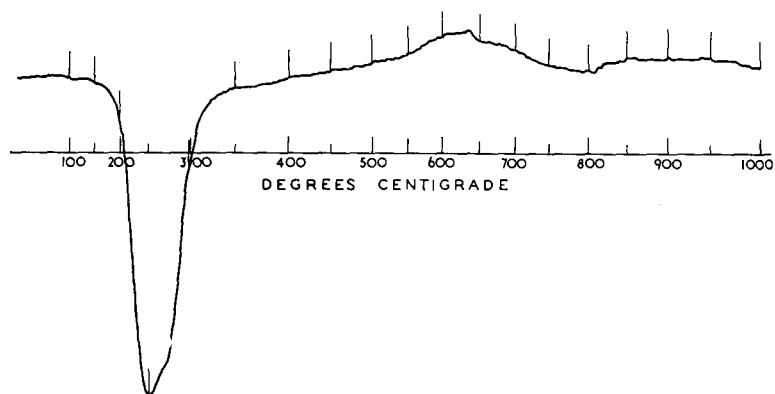


FIG. 3. Differential thermal analysis curve for kingite.

*Discussion.* Initially it was suspected that kingite could have been a mixture containing wardite, but its behaviour on heating and a comparison of its X-ray diffraction data with that of wardite shows that this is not so, although the two minerals have some lines in common.

ner aluminium phosphate minerals with the same  $\text{Al}_2\text{O}_3$  to  $\text{P}_2\text{O}_5$  ratio as kingite are less hydrated (e.g. sterrettite and wavellite) and give different diffraction data. A comparison of the diffraction patterns of meta-kingite and wavellite, fig. 2, shows them to be different structurally, if not chemically. X-ray diffraction and chemical analyses indicate that both kingite and meta-kingite are new hydrated aluminium phosphate compounds.

*Acknowledgements.* The authors wish to thank Dr. C. Frondel for supplying a specimen of wardite and for critically reading the manuscript.

The work described in this paper was carried out as part of the research programme of the Division of Soils, Commonwealth Scientific and Industrial Research Organization, Australia.

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