MINERALOGICAL MAGAZINE, SEPTEMBER 1974, VOL. 39, PP. 802–6

Are vashegyite and kingite hydrous aluminum phyllophosphates with kaolinite-type structures?

DUNCAN McCONNELL

The Ohio State University, Columbus, Ohio 43210, U.S.A.

SUMMARY. In contrast with some other hydrous aluminum phosphates, vashegyite is crystalline. Simultaneous application of several assumptions leads to the hypothesis that it has a structure analogous to that of kaolinite, and thus contains tetrahedral sheets, $n[X_2O_5]$, where X is both P and H_3 (in lieu of Si). Thus, the theory involving $[H_XO_4]$ is extended from phosphates with isolated tetrahedral groups $[XO_4]$ and framework linkages $[XO_2]$ to sheet linkages $[X_2O_5]$. Kingite also may have a kaolinite-like structure.

ONE might assume, in view of the multiplicity of minerals containing structural sheets $n[Si_2O_5]^{2-}$, that similar sheets $n[AlPO_5]^{2-}$ could exist. One might assume further that protons might comprise an integral portion of such a sheet in order to produce $n[H_3PO_5]^{2-}$ sheets, i.e. a sheet $n[X_2O_5]^{2-}$ or $n[XYO_5]^{2-}$ where $X = P$ and $Y = H_3$.

In defence of such speculation one must consider the substitution in hydrogrossular $[SiO_4] \rightarrow [H_4O_4]$, and in griphite $[SiO_4]$ by both $[PO_4]$ and $[H_4O_4]$ (McConnell, 1942). Further, one notes that such substitution takes place in the framework structure of analcime to give viséite (McConnell, 1952), wherein there is sharing of four apices of $[XO_4]$ groups and substitution of X by P and H_3. Thus, it seems reasonable to search for a phyllophosphate inasmuch as both orthophosphates with structures analogous to orthosilicates and a framework structure involving prominent amounts of $Si \rightarrow P$ and H have been recognized.

Where does one look for such a mineral [hydrated phyllophosphate]? There are several highly hydrated aluminum phosphates about which very little is known. Some of these substances are glassy—amorphous, or virtually so, with respect to X-ray diffraction.

If one were to discover such a substance that produced a reasonably good powder diffraction pattern, how would he recognize it? Unfortunately, this necessarily requires the association of a series of assumptions. Depending upon the degree of hydration, the density should be comparable with a clay mineral, i.e. less than 2·6, possibly as low as 1·8. The mean refractive index might be expected to be between 1·55 and 1·46, and the birefringence low to very low (0·020 to 0·001). In the absence of iron, one would be interested in a white powdery substance, a microcrystalline aggregate resembling kaolin. At least one such substance occurs at Vashegy, Slovakia (ČSSR).

Vashegyite—experimental data. Part of the problem involves nomenclature among these poorly crystallized hydrated aluminum phosphates; discussion of this topic will be given in a separate paper.

We are accepting as vashegyite a portion of a specimen from the Roebling collection from the type locality, U.S. National Museum R 5617, which produces a diffraction pattern similar to that of British Museum 1910,101, a cotype specimen received from Zimányi. Its powder diffraction pattern (Table I) is distinctly different from other hydrated aluminum phosphates. It seems to be essentially a single crystalline phase, virtually devoid of impurities.

Koch and Sarudi (1963) re-examined vashegyite from Železnik (= Vashegy); this report contains two electronmicrographs (at ×30 000 and ×20 000), which are interpreted as showing 'no crystalline structure'. Our interpretation, however, is different: these photographs show either growth layers or cleavage planes, which are steplike in nature, and thus imply micaceous characteristics. Their report includes a chemical analysis by Rózsa, a d.t.a. curve, and refractive indices ($n = 1·544–1·547$) as well as an indication that the crystallites have positive optical elongation. Combining their data with those of Ulrich (as reported by Koch and Sarudi, 1963) yields mol. ratios $Al_2O_3:P_2O_5:H_2O$ approximately 2:1·5:12·5.

In addition to the very energetic inflection [endothermic] at about 200 °C (their fig. 2c), there is a small but definite exotherm at about 850 °C. The latter seems to be more or less characteristic of such substances, and supposedly represents the formation of $AlPO_4$ [with the high cristobalite structure?]. This exotherm had a maximum inflection at 845 °C for an 'amorphous allophanoid' containing iron and phosphorus (Levitskii and Vlasov, 1965).

The indexed diffraction pattern (Table I) is then assumed to comprise pseudohexagonal sheets to give an orthorhombic structure comparable with kaolinite, thus:

	a	b	c	α	β	γ	V	Z
Kaolinite:	5·16	8·95	7·42 Å	91·7°	105°	90°	331 Å³	2
Vashegyite:	20·92 = 4×5·23	19·82 = 2×9·91	14·48 = 2×7·24	90°	90°	90°	6000 = 16×375	32

Using the formula proposed by Koch and Sarudi (1963), namely

$$Al_3(PO_4)_3.(AlOOH).12H_2O,$$

and assuming 288 oxygens (16×18) per unit cell, we have the following comparison of structural sites:

Kaolinite	18 O	8 H	4 Al	4 Si
Vashegyite	288	277 (64)	44·3 (64)	33·2 P (64)

The numbers in parentheses are the theoretical requirements for a simple replacement of Si by P in the kaolinite structure and adjustment of H to balance.

Thus of the total sites for P, only about half appear to be filled, the deficiency being met by protons, and about 20 missing Al atoms are similarly compensated by protons. A calculation of the density gives

$$\rho = 1·66(288\times 16+277\times 1·008+44·3\times 26·98+33·2\times 30·98)/6000 = 1·98,$$

which compares with Zimányi's determination of 1·964 (1909). See also Doelter (1918).

TABLE I. *X-ray powder diffraction data for vashegyite*

d_{obs}	d_{calc}	*hkl*	*I*
9·80	9·91	020	vs
9·20	9·25	210	vs
8·55	8·48	201	w
7·71	7·80	211	w
	7·62	121	
7·24	7·24	002	vs
6·80	6·84	102	m
	6·80	012	
5·25	5·23	400	vw
4·40	4·407	421	m
3·46	3·457	043	w
3·15	3·150	260	m
2·96	2·955	710	w
2·90	2·896	452	vs
		005	
		711	
	2·895	144	
2·76	2·763	215	m
	2·762	702	
	2·760	362	
	2·755	125	
2·68	2·676	731	m
	2·674	552	
		305	
	2·673	054	
2·51	2·5129	415	ms
	2·5111	604	
	2·500	045	
2·413	2·4131	742	w
	2·4130	006	
2·127	2·131	291	ms
	2·124	374	
		246	
1·982	1·9829	307	w
	1·9820	0.10.0	
1·533	1·5333	12.6.1	m
	1·5330	419	
	1·5320	558	
1·471	1·4717	828	m
	1·4708	10.0.7	
	1·4704	13.0.4	
1·455	1·4562	867	m
		895	
	1·4549	10.7.5	
		10.2.7	
	1·4546	13.2.4	
	1·4544	12.7.2	
1·371	1·3714	379	w
	1·3713	8.12.2	
	1·3710	398	
	1·3707	659	

The structure is assumed to be orthorhombic. Data represent a composite of patterns prepared by use of filtered copper radiation and unfiltered iron radiation; spacing $< 2·50$ Å were obtained with iron radiation. In addition to the spacings recorded, an uncertain line was observed at about 14·1 Å; possibly it is either 001 or 110, which should have spacings of 14·5 and 14·4 Å, respectively.

Data on kingite. Kingite was described by Norrish *et al.* (1957) and was re-examined by Kato (1970). It is similar to vashegyite except that it is triclinic and has an Al/P ratio of about 1·5. Thus it might be related to kaolinite in the following manner:

Kaolinite	a 5·16	b 8·95	c 7·42 Å	α 91·7°	β 105°	γ 90°	V 331 Å$^{\circ 3}$	Z 2
Kingite	10·00	9·15	7·24 Å	93·6°	98·6°	86·8°	V 652 Å^3	Z 4
Kaolinite	18 O	8 H	4 Al	4 Si				
Kingite	36	37·8 (16)	5·4 (8)	3·6 P (8)				

The numbers in parentheses are, again, the theoretical requirements for a simple replacement of Si by P in the kaolinite structure, and, as with vashegyite, the number of protons is almost equal to thrice the number of vacant Al and P sites.

Kato calculated the density as 2·465, basing his model on Norrish's formula $Al_3(PO_4)_2(OH)_3.9H_2O$, with 40 oxygen atoms per unit cell. With reduction of the oxygen content to 36 atoms, we have

$$\rho = 1{\cdot}66(36\times16+37{\cdot}8\times1{\cdot}008+5{\cdot}4\times26{\cdot}98+3{\cdot}6\times30{\cdot}98)/652 = 2{\cdot}23,$$

which agrees better with the experimental value of 2·2–2·3.

Discussion. We have discussed models for vashegyite and kingite based upon the structure of kaolinite in qualitative terms; it remains to show quantitative data relating to comparisons of calculated *v.* observed intensities. Undoubtedly a structural determination involving the location of the oxygens would be most difficult for vashegyite, particularly because of distortion of the shared tetrahedra resulting from the very large number of protons (277 H atoms *v.* 288 oxygens).

In the case of deuterated hydrogrossular, Foreman (1968) made a precise location of the deuterons by neutron diffraction, but this was for a highly symmetrical structure ($Ia3d$). It has been found, based on analytical data for the isotype of analcime (viséite), that x of the (H_XO_4) tetrahedra is 3, rather than 4 (McConnell, 1952).

The appropriate structural formulae proposed are:

Vashegyite $16[(OH)_8(P_{2\cdot1}H_{5\cdot7})(Al_{2\cdot8}H_{3\cdot6})O_{10}]$ with Al/P = 1·33, and

Kingite $2[O_8H_{8\cdot4}(P_{1\cdot8}H_{6\cdot6})(Al_{2\cdot7}H_{3\cdot9})O_{10}]$ with Al/P = 1·5, as compared with kaolinite:

$(OH)_8Si_4Al_4O_{10}$.

Acknowledgements. Among his colleagues, the writer is indebted to Dennis W. Foreman, *Jr.*, for the computation of *d* spacings, using the FORTRAN IV, APOL program of C. J. F. Cole and H. Villiger (Imperial College, London). P. M. Harris, Dan McLachlan, *Jr.*, and R. T. Tettenhorst (Columbus), as well as M. H. Hey (British Museum), F. Permingeat (Toulouse), A. Pabst (Berkeley), and J. J. Finney (Golden, Colorado), supplied constructive criticism of the manuscript.

REFERENCES

DOELTER (C.), 1918. *Handbuch der Mineralchemie*, III, Erste Abt. Leipzig, 465.

FOREMAN (D. W., *Jr.*), 1968. Neutron and X-ray diffraction study of $Ca_3Al_2(O_4D_4)_3$, a garnetoid. *Journ. Chem. Phys.* **48**, 3037–41.

KATO (T.), 1970. Cell dimensions of the hydrated phosphate, kingite. *Amer. Min.* **55**, 515–17.

KOCH (S.) and SARUDI (I.), 1963. The hydrous basic aluminum phosphates of Železnik (Vashegy), Slovakia (ČSSR). *Acta Univ. Szeged.* **16,** 3–10.

{LEVITSKII (V. E.) and VLASOV (V. V.)] Левицкий (В. Е.) и Власов (В. В.). 1965. [Allophanoid containing iron and phosphorus in the Upper Jurassic of the Ul'yanovski region.] Зап. всесоюз. мин. оьщ. (*Mem. All. Union Min. Soc.*), **94,** 465–7.

MCCONNELL (D.), 1942. Griphite, a hydrophosphate garnetoid. *Amer. Min.* **27,** 452–61.

—— 1952. Viséite, a zeolite with the analcime structure and containing linked SiO_4, PO_4 and H_XO_4 groups. Ibid. **37,** 609–17.

NORRISH (K.), ROGERS (L. E. R.), and SHAPTER (R. E.), 1957. Kingite, a new hydrated aluminium phosphate mineral from Robertstown, South Australia. *Min. Mag.* **31,** 351–7.

ZIMÁNYI (K.), 1909. *Math. Termész. Értes.* **27,** 64.

[*Manuscript received 9 October 1973; revised 4 March 1974.*]