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Crystallinity among some hydrous aluminium phosphates

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SUMMARY. Compositions of nine hydrous aluminium phosphates are considered with respect to the Al, P, and H contents per 8 oxygens, and it is suggested that when the ratio (Al.P)/H is less than 0·11 (or $(Al.P^2)/H^2$ is less than 0·01) such compositions do not crystallize. Examples are bolivarite and evansite.

IT is realized, of course, that the tendency to crystallize is thermodynamically dependent upon the crystal energy in accordance with the Born–Haber relations, but this tendency may be overwhelmed by kinetic considerations, more often than not. Geologically speaking this means: the *time* during which the crystal was exposed to a particular temperature and pressure, the magnitude of temperature and pressure, and their rates of change—given a particular composition. Little is known about such factors in connection with the series of hydrous aluminium phosphates under consideration; we know merely that they are secondary minerals.

Here, the tendency to crystallize will be shown to be related to the compositions through empiricism. Account must be taken of coordination numbers, as well as the activities [concentrations] of the ions involved. It should be indicated, of course, that the bonding of simple water of hydration requires far less energy than is required for OH (in variscite and metavariscite the water is liberated at 160 °C, according to Schaller, 1912).

Admitting that we are concerned with more than one series, nevertheless, it is assumed that bolivarite and evansite might be capable of crystallization, were their compositions appropriate. The appropriateness of the compositions is assumed to be directly related to some function of the aluminium content multiplied by some function of the phosphorus content and inversely to some function of the water content. In this work we have compared (Table I) (Al.P)/H with $(Al.P^2)/H^2$, but without deciding which produces the better correlation. In the second ratio, the greater effect is supposed to be related to $[P^{5+}]$ and $[H^+]$ activities.

It is assumed that an energy barrier exists that resists reduction to a lower energy state and that such a barrier is related to functions of the component ions, the concentrations of which are expressed on a relative basis (8 oxygens) with respect to the volumes. Moreover, it is found that certain glassy phosphates can be induced to crystallize by heating—presumably with reduction of the water content.

TABLE I. *Relations among some hydrous aluminum phosphates*

	Al*	P*	H*	Al/P	Vol.* (in Å^3)	$\frac{\text{Al.P}}{\text{H}}$	$\frac{\text{Al.P}^2}{\text{H}^2}$	Ref. and status
Variscite	1·33	1·33	5·3	1·0	133	0·334	0·0838	McConnell (1940)‡
Metavariscite	1·33	1·33	5·3	1·0	137	0·334	0·0838	McConnell (1940)‡
Redondite	1·33	<1·33	>5·3	>1·0	137	<0·334	<0·0838	A. Kato (1965)§
Senegalite	2·00	1·00	5·0	2·0	141	0·400	0·0800	Z. Johan (1975)‡
Kingite	1·20	0·80	8·4	1·5	145	0·114	0·0109	T. Kato (1970)‡
Wavellite	1·50	1·00	6·5	1·5	146	0·231	0·0355	Araki and Zoltai (1968)
Vashegyite	1·23	0·92	7·7	1·3	167	0·147	0·0176	McConnell (1974)‖
Bolivarite	1·36	0·68	8·5	2·0	(163)†	0·109	0·0087	Van Tassel (1960)‡
Evansite	1·50	0·50	9·0	3·0	(162)†	0·083	0·0046	Manly (1950) and this study§

* per 8 oxygens.

† The volume is indeterminate for an amorphous substance, but is estimated from the crystalline relation: Vol.* = wt.*/0·596G, by taking the specific gravity (G) to be 2·0 for both bolivarite and evansite. (Actually these values are minima inasmuch as they do not take into account the lack of structural organization.)

‡ Holotype or cotype. § Topotype. ‖ Cotype.

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APPENDIX

In the series $(Al,Fe)PO_4 . 2H_2O$ the following species are recognized;

	Al	(Al,Fe) *or* (Fe,Al)	Fe
Orthorhombic	Variscite Redondite	Barrandite (Redondite)	Strengite —
Monoclinic	Metavariscite	Clinobarrandite	Phosphosiderite

Lucinite and peganite are synonyms of variscite. 'Messbach-type variscite', paravariscite (Gevorkyan *et al.*, 1974) and 'variscite' from Candelaria, Nevada, are redondite. Metastrengite and klinostrengite are synonyms of phosphosiderite.