

# THE DIFFERENTIAL THERMAL ANALYSIS OF CERTAIN PHOSPHATES

ROBERT L. MANLY, JR., *University of Minnesota,  
Minneapolis, Minnesota.*

## ABSTRACT

Fourteen samples of phosphates were studied by differential thermal analysis, *x*-ray, and petrographic methods. Minerals such as variscite, bolivarite, lazulite, wavellite, evansite, bobierite, vivianite, and zepharovichite (?) give endothermic reactions at low temperatures which indicate the loss of water of crystallization. Smaller endothermic reactions at higher temperatures are correlated with loss of hydroxyl, or possibly fluorine. Recrystallization on heating with the formation of aluminum phosphotridymite, aluminum phosphocristobalite, or berlinite ( $\text{AlPO}_4$  with  $\alpha$ -quartz structure) structures is common for the hydrous aluminum phosphates.

## INTRODUCTION

The method of differential thermal analysis supplies data not easily obtained by ordinary dehydration studies. The most important data pertain to the dissociation and inversion phenomena that various phosphates undergo on being heated rapidly. The number of individual species investigated was limited by the material available which had been previously investigated by chemical or *x*-ray methods. Of the fourteen specimens here reported, the analyzed samples of only two were available. The identity of the remaining twelve samples was established by *x*-ray and petrographic examinations.

## APPARATUS

The differential thermal analysis unit used in this investigation is similar to others described in the literature; the principal difference is in the removable sample block designed by J. W. Gruner (Fig. 1). The sample block is made of "inconel" metal rather than of the usual nickel.

## DESCRIPTION AND BEHAVIOR OF SAMPLES

*Variscite*.— $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ , from cherty limestone, Fairfield, Utah. Light green prismatic grains which become lavender on heating slowly to  $300^\circ\text{C}$ .  $G = 2.52$ ,  $\alpha = 1.565$ ,  $\gamma = 1.595$ . A chemical analysis is not available, but the *x*-ray pattern is very similar to that for variscite from other localities. Petrographic examination shows the material to be homogeneous. Variscite (Fig. 2, no. 4) gives only one broad endothermic reaction with a peak at  $260^\circ\text{C}$ . The sample heated above  $260^\circ\text{C}$ . is still crystalline, but the structure developed has not been identified. A second structure, that of aluminum phosphotridymite ( $\text{AlPO}_4$  with tridymite structure) is developed upon heating to  $1000^\circ\text{C}$ ., but there is no indication of this change in the differential thermal curve.

*Bolivarite*.— $\text{Al}_2\text{PO}_4(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , Ponte Verde, Spain, U. S. National Museum specimen R5594. Light gray-green powdery crust; isotropic,  $N=1.493$ . Amorphous to  $x$ -rays. No chemical analysis. A strong broad endothermic reaction with a peak at  $220^\circ\text{C}$ . (Fig. 2, No. 5) is the initial water loss. A sharp secondary endothermic reaction at  $430^\circ\text{C}$ . is inter-



FIG. 1. Detail of removable sample block.

preted as loss of the hydroxyl. Recrystallization is indicated by a weak exothermic reaction at  $950^\circ\text{C}$ ., and the final sample gave a faint  $x$ -ray pattern of aluminum phosphocristobalite.

*Lazulite*.— $\text{R}''\text{Al}_2(\text{OH})_2\text{P}_2\text{O}_8$ , Graves Mountain, Georgia. Azure-blue monoclinic crystal.  $\alpha=1.604$ ,  $\beta=1.633$ ,  $\gamma=1.639$ , all  $\pm .005$ . Pleochroic;  $X$  colorless;  $Y$  and  $Z$ , azure-blue.  $X$ -ray pattern practically identical with lazulite from Matterhorn, Switzerland.

Lazulite (Fig. 2, no. 6) gives a moderate endothermic reaction with a peak at  $220^\circ\text{C}$ ., and a second strong endothermic reaction at  $780^\circ\text{C}$ . The final reaction is an exothermic peak at  $925^\circ\text{C}$ . The final heated product shows an aluminum phosphocristobalite structure with some earlier berlinite structure still showing.

*Wavellite*.— $\text{Al}_3(\text{OH})_3\text{P}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$ , Montgomery, Arkansas. Light green spherulites. Gives water in closed tube.  $\alpha=1.535$ ,  $\beta=1.540$ ,  $\gamma=1.553$ ; all  $\pm 0.003$ . No chemical analysis;  $x$ -ray pattern is very similar to that reported for wavellite by McConnell (1942).

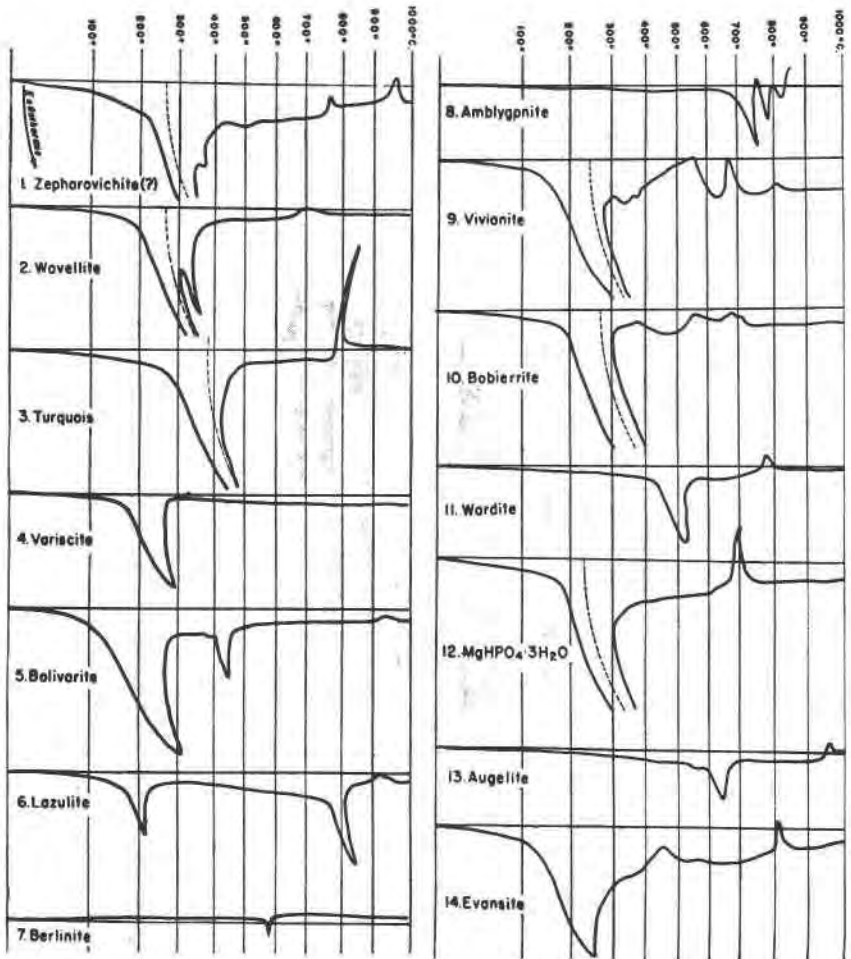


Fig. 2. Differential thermal curves. (Dashed arcs give temperature of broken peaks)

Wavellite (Fig. 2, No. 2) shows a strong endothermic reaction at 275° C. followed immediately by a second smaller endothermic peak at 315° C. An exothermic reaction is developed at 710° C. which may be related to recrystallization with the formation of aluminum phosphotridymite. A second sample of wavellite from an unknown locality shows the various reactions described above, but an additional exothermic peak is developed at 770° C. which is more pronounced than the exothermic reaction at 710° C. When cooled and  $x$ -rayed this second sample

also showed a phosphotridymite structure.\* The optical properties of the second sample of wavellite did not differ appreciably from the first sample, but a closed tube test showed the presence of fluorine in the mineral, and possibly this element is responsible for the variation in the differential thermal curve.

*Evansite*.— $3\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$ , Goldberg, Idaho, U. S. National Museum specimen #86180. A brown resinous crust. Isotropic,  $N=1.483$ . Amorphous to  $x$ -rays, the sample was identified by optical means. Evansite (Fig. 2, No. 14) gives a large endothermic reaction with a peak at  $190^\circ\text{C}$ . A second endothermic reaction at approximately  $350^\circ\text{C}$ . and a third at approximately  $525^\circ\text{C}$ . are poorly defined. Recrystallization takes place at  $840^\circ\text{C}$ . as indicated by a well-developed sharp exothermic reaction. The structure at  $1000^\circ\text{C}$ . is phosphocrystalite.

*Bobierrite*.— $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , from a fossil mammoth tusk from a gravel pit near Edgerton, Minnesota (Gruner 1943). White prismatic aggregate.  $G=2.2$ ,  $\alpha=1.51$ ,  $\beta=1.52$ ,  $\gamma=1.543$ . The sample gives an  $x$ -ray pattern very similar to that of pure  $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  (Eimer and Amend Chemical Co.). A dehydration curve for bobierrite is shown in Fig. 3. The sample was heated and weighed at intervals of  $50^\circ\text{C}$ . A part of the sample was removed at temperatures of appreciable water loss for  $x$ -ray study. Bobierrite (Fig. 2, no. 10) gives a strong endothermic reaction with a peak at  $280^\circ\text{C}$ . at which temperature the mineral loses five molecules of water. A broad secondary endothermic reaction with a peak at  $470^\circ\text{C}$ . indicates the loss of the remaining three molecules of water. The  $x$ -ray pattern of the sample after heating to  $300^\circ\text{C}$ . shows little loss of structure although 60 per cent of the water has been removed; however, on heating to  $470^\circ\text{C}$ . with loss of three remaining molecules of water, the structure is destroyed. Recrystallization to  $\text{Mg}_3(\text{PO}_4)_2$  takes place at  $565^\circ\text{C}$ . as is also indicated by a sharp exothermic reaction. Two lesser exothermic reactions are recorded at  $675^\circ\text{C}$ . and  $710^\circ\text{C}$ .

There are important differences between the static dehydration curve and the differential thermal curve. The static dehydration curve (Fig. 3) shows that five molecules of water are lost between  $100$ – $150^\circ\text{C}$ .; two molecules of water are lost between  $150$ – $350^\circ\text{C}$ .; and the final molecule of water is lost above  $350^\circ\text{C}$ . Similar results were obtained by earlier investigators. De Schulten (1903) states "das Hydrat  $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  gibt bei  $120^\circ$  fünf Moleküle Wasser ab." Klement (1936) found that two

\* The distinction between tridymite and cristobalite structures is difficult in several of the films. The most intense lines of the two structures are almost identical. In many cases if heating is continued long enough at  $1000^\circ\text{C}$ . the earlier tridymite structure will be followed by a cristobalite one. If such a change is arrested too early both structures will show in the film and cause confusion especially since the lines are diffused.

molecules of water were lost at 300° C. and the last molecule at 400° C. The differential thermal curve shows an endothermic reaction with a peak at 280° C. corresponding to a loss of five molecules of water and a second peak at 450° C. for the remaining three molecules of water. The difference of behavior of the mineral is the result of the rate of heating; rapid heating in the differential thermal analysis apparatus gives two breaks; whereas only one distinct break is shown on slower heating in the static dehydration method.

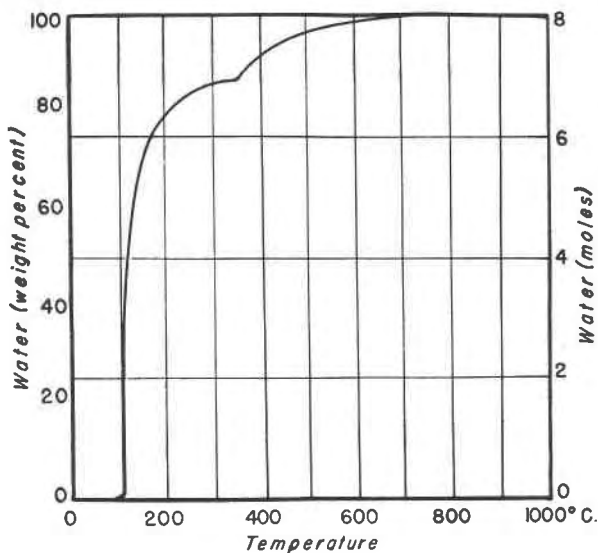


FIG. 3. Dehydration curve.

*Vivianite*.— $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , Keystone, South Dakota. A medium blue, darkening after grinding to a powder.  $G=2.56$ .  $\alpha=1.580$ ,  $\beta=1.605$ ,  $\gamma=1.635$ . Strongly pleochroic:  $X$  = dark blue,  $Y$  = pale yellow,  $Z$  = olive green. The structures of bobierrite and vivianite are closely related as shown by  $x$ -ray patterns.

Vivianite (Fig. 2, no. 9) shows a strong endothermic reaction with a peak at 260° C. corresponding to the loss of five molecules of water in bobierrite. A second endothermic reaction is smaller with a peak at 330° C. during which two molecules of water are lost. The last molecule of water gives a small endothermic reaction with a peak at 380° C. The amplitudes of the endothermic peaks are roughly proportional to the water loss. A poorly defined exothermic reaction takes place at 550° C. This reaction is related to the oxidation of ferrous iron. Differential thermal curves for vivianite are hard to reproduce because of the ferrous

iron which is easily oxidized. Prolonged grinding may result in oxidation of sufficient ferrous iron to change the curve. Studies of minerals such as vivianite probably are best made in an atmosphere of an inert gas.

*Augelite*.— $\text{Al}_2\text{PO}_4(\text{OH})_3$  from Laws, California, U. S. National Museum, specimen #97576. Cream colored crystalline crust.  $G=2.7$ . Biaxial (+),  $\alpha=1.575$ ,  $\gamma=1.588$ ; both  $\pm .003$ . The  $x$ -ray pattern is similar to one published by Peacock (1941) for augelite from White Mountain, California, and the optical data are essentially the same.

Augelite (Fig. 2, no. 13) gives a strong endothermic reaction with a peak at  $680^\circ\text{C}$ . This supports the conclusion of Peacock that augelite contains hydroxyl. There is no endothermic reaction at a low temperature which might indicate the presence of water of crystallization. A sharp exothermic peak is recorded at  $970^\circ\text{C}$ . After heating the residue of augelite to  $1000^\circ\text{C}$ . a structure is developed as shown by  $x$ -ray patterns, which is unlike any of the aluminum phosphates noted previously.

*Wardite*.— $\text{CaNa}_4\text{Al}_{12}(\text{PO}_4)_8(\text{OH})_{18}\cdot 6\text{H}_2\text{O}$ , Lewiston, Utah. A light gray-green dull mineral in nodules resembling turquoise in appearance.  $G=2.78$ . Tetragonal:  $\epsilon=1.600$ ,  $\omega=1.591$ . The optical constants are essentially the same as those given by Larsen (1942) for wardite from Fairfield, Utah. Wardite (Fig. 2, no. 11) gives a strong endothermic reaction with a peak at  $510^\circ\text{C}$ ., and a moderate exothermic reaction with a peak at  $780\text{--}800^\circ\text{C}$ .  $X$ -rays show recrystallization to aluminum phosphocristobalite.

*Turquoise*.— $2\text{Al}_2\text{O}_3\cdot\text{P}_2\text{O}_5\cdot 5\text{H}_2\text{O}$ , New Mexico. Dull-azure-blue, highly fractured. The  $x$ -ray pattern is comparable to that of other samples of of turquoise. A very sharp endothermic reaction with peak at  $380^\circ\text{C}$ . and an extremely sharp exothermic reaction with peak at  $840^\circ\text{C}$ . are characteristic of the relatively simple differential thermal curve of turquoise (Fig. 2, no. 3). The residue shows an aluminum phosphocristobalite structure. Not all of an earlier berlinite structure has disappeared but probably would on longer heating.

*Amblygonite*.— $\text{LiAl}(\text{F}, \text{OH})\text{PO}_4$ , Black Hills, South Dakota. A bluish-white cleavable mass.  $G=3.0$ . Biaxial positive.  $\alpha=1.605$ ,  $\gamma=1.627$ . The optical data (Winchell, 1926) indicate a composition of amblygonite  $\text{LiAl}(\text{F})\text{PO}_4$ , 20 per cent and montebasite  $\text{LiAl}(\text{OH})\text{PO}_4$ , 80 per cent. Amblygonite (Fig. 2, no. 8) gives an endothermic reaction with a peak at  $740^\circ\text{C}$ . followed by an exothermic reaction with a peak at  $760^\circ\text{C}$ . A second endothermic peak occurs at  $780^\circ\text{C}$ . which is followed by a second exothermic reaction at  $800^\circ\text{C}$ . The sample fused at  $850^\circ\text{C}$ .

*Zepharovichite* (?).— $\text{AlPO}_4\cdot 3\text{H}_2\text{O}$ , Bohemia, U. S. National Museum specimen #84339. Grayish-white powder.  $G=2.34$ .  $\alpha=1.525$ ,  $\gamma=1.544$ ,

$\pm .003$ . The sample gives a sharp endothermic reaction at  $270^{\circ}$  C. with a second endothermic reaction at  $355^{\circ}$  C. There are two exothermic (Fig. 2, no. 1) reactions; the first with a peak at  $790^{\circ}$  C., and a second at  $970^{\circ}$  C. The  $x$ -ray pattern of the heated residue shows aluminum phosphocrystalite with some phosphotridymite.

Zepharovichite is not a valid mineral species. Winchell (1927) noted the similarity of the optical data to that for wavellite, and McConnell (1942) pointed out that the  $x$ -ray pattern of zepharovichite is almost identical with that of wavellite. These findings are supported by the differential thermal curve; the temperatures of the endothermic peaks for

Name & Composition	Temperature									
	100	200	300	400	500	600	700	800	900	1000°C.
Wavellite $Al_2(OH)_2P_2O_7 \cdot 5H_2O$			V V					•	•	
Zepharovichite $AlPO_4 \cdot 3H_2O$			V	v				•		•
Bolvavite $Al_2PO_8(OH)_2 \cdot nH_2O$			V		v					•
Variacite $AlPO_4 \cdot 2H_2O$			V							
Lozulite $R^+ Al_2(OH)_2P_2O_7$			v					V		•
Turquoise $2Al_2O_3 \cdot P_2O_5 \cdot 5H_2O$					v				•	•
Evansite $3Al_2O_3 \cdot P_2O_5 \cdot 18H_2O$			V							•
Bobierite $Mg_3(PO_4)_2 \cdot 8H_2O$				V		v	•	•	•	
Vivianite $Fe_2(PO_4)_2 \cdot 8H_2O$			V	v v		•	•	•	•	
$MgHPO_4 \cdot 3H_2O$			V				•	•		
Augelite $Al_2PO_8(OH)_2$							V			•
Wardite $CaNa_4Al_2(OH)_2(PO_4)_5 \cdot 5H_2O$						v		•		
Amblygonite $LiAl(F,OH)PO_4$								V	V	•
Berlinite $AlPO_4$						v				

Symbols: (V) = Endothermic; (•) = Exothermic

FIG. 4. Summary of differential thermal data.

zepharovichite agree with those for wavellite, and the first exothermic reaction is found in wavellite. The second exothermic reaction at  $970^{\circ}$  C. was not recorded for wavellite.

**Berlinite.**— $AlPO_4$ , synthetic, milky-white crystals.  $G=2.56$ . ( $N_a$ )  $\epsilon=1.535$ ,  $\omega=1.525$ ,  $\pm .002$ . In the  $x$ -ray pattern all the lines are very similar to quartz, except  $d$  1.380 and  $d$  1.375 where the intensities of the berlinite lines are the reverse of the quartz lines.

Berlinite (Fig. 2, no. 7) shows a single sharp exothermic reaction at  $585^{\circ}$  C. which marks the inversion from the alpha to beta form. The inversion point is  $10^{\circ}$  C. higher than the inversion of alpha to beta form of quartz recorded on the same instrument.

**$MgHPO_4 \cdot 3H_2O$ .**—(dibasic magnesium phosphate), Mallinkrodt Chemical Co. A fine-grained white powder.  $G=2.10$ .  $\alpha=1.514$ ,  $\gamma=1.533$ ,  $\pm .003$ .

Dibasic magnesium phosphate (Fig. 2, no. 12) gives a strong endothermic reaction with a peak at 255° C. An exothermic reaction which begins at 620° C. is culminated in a peak at 680° C.

Certain generalizations are drawn from the present study, but as the available data are few, revisions may be necessary with the study of more samples. The differential thermal reactions of the fourteen samples are shown in Fig. 4. In this chart the temperatures of the reaction peaks have been plotted to scale. The relative magnitude of the reaction is approximately indicated by the size of the symbol plotted.

#### ACKNOWLEDGMENTS

This problem was suggested by Professor J. W. Gruner, and the laboratory studies were made under his direction. Valuable assistance was received from Dr. S. S. Goldich and Mr. Lynn Gardiner. Five samples were obtained through the kindness of Dr. William Foshag of the U. S. National Museum.

#### REFERENCES

- DE SCHULTEN, M. A. (1903), Recherches sur le phosphate et L'arsenate trimagnésien. Reproduction artificielle de la bobierite et de la hoernesite: *Bull. Soc. Min. Française*, **26**, 83.
- GRUNER, JOHN W., AND STAUFFER, C. R. (1943), A unique occurrence of bobierite,  $Mg_3PO_4 \cdot 8H_2O$ : *Am. Mineral.*, **28**, 339-340.
- (1946), Isostructural relationship of  $AlPO_4$  and  $SiSiO_4$ : *Am. Mineral.*, **31**, 196.
- KLEMENT, R., AND MOSEBACH, R. (1936), *Zeits. f. anorganische und allgemeine Chemie*, **228**, 236.
- LARSEN, ESPER S., 3rd (1942), Mineralogy of variscite nodules from Fairfield, Utah: *Am. Mineral.*, **27**, 292, and 299.
- MCCONNELL, D. (1937), The substitution of  $SiO_4$ - and  $SO_4$ -groups for  $PO_4$  in the apatite structure: ellestadite, an end member: *Am. Mineral.*, **22**, 977-986.
- (1942), X-ray data on several phosphate minerals: *Am. Jour. Sci.*, **240**, 654.
- PEACOCK, M. A. (1941), On a crystal of augelite from California: *Mineral. Mag.*, **26**, 105-115.
- WINCHELL, A. N. (1926), Relations between properties and composition in the amblygonite-montebrazite series: *Am. Mineral.*, **11**, 248.
- WINCHELL, N. H., AND WINCHELL, A. N. (1927), *Elements of Optical Mineralogy*, Part II, New York, John Wiley and Sons, p. 149.