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, bobierrite, 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 ($AlPO_4$ with α-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.—$AlPO_4 \cdot 2H_2O$, from cherty limestone, Fairfield, Utah. Light green prismatic grains which become lavender on heating slowly to 300° 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° C. The sample heated above 260° C. is still crystalline, but the structure developed has not been identified. A second structure, that of aluminum phosphotridymite ($AlPO_4$ with tridymite structure) is developed upon heating to 1000°C., but there is no indication of this change in the differential thermal curve.

Bolivarite.—$Al_2PO_4(OH)_2 \cdot nH_2O$, 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° C. (Fig. 2, No. 5) is the initial water loss. A sharp secondary endothermic reaction at 430° C. is interpreted as loss of the hydroxyl. Recrystallization is indicated by a weak exothermic reaction at 950° C., and the final sample gave a faint *x*-ray pattern of aluminum phosphocristobalite.

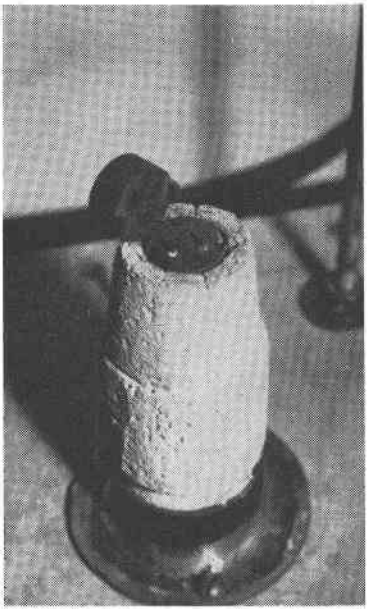

FIG. 1. Detail of removable sample block.

Lazulite.—$R''Al_2(OH)_2P_2O_8$, 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° C., and a second strong endothermic reaction at 780° C. The final reaction is an exothermic peak at 925° C. The final heated product shows an aluminum phosphocristobalite structure with some earlier berlinite structure still showing.

Wavellite.—$Al_3(OH)_3P_2O_8 \cdot 5H_2O$, Montgomery, Arkansas. Light green spherulites. Gives water in closed tube. $\alpha=1.535$, $\beta=1.540$, $\gamma=1.553$; all ± 0.003. No chemical analysis; *x*-ray pattern is very similar to that reported for wavellite by McConnell (1942).

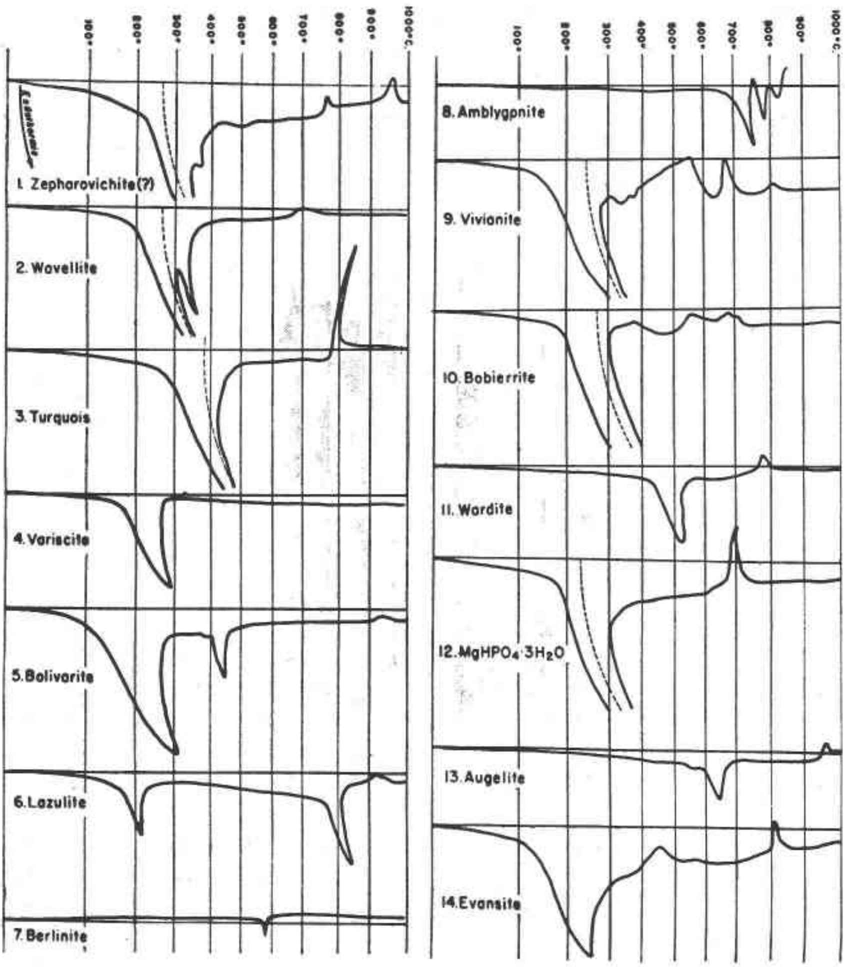

FIG. 2. Differential thermal curves. (Dashed arcs give temperature of broken peaks)

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 phospho-tridymite. 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.—$3Al_2O_3 \cdot P_2O_5 \cdot 18H_2O$, 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° C. A second endothermic reaction at approximately 350° C. and a third at approximately 525° C. are poorly defined. Recrystallization takes place at 840° C. as indicated by a well-developed sharp exothermic reaction. The structure at 1000° C. is phosphocristobalite.

Bobierrite.—$Mg_3(PO_4)_2 \cdot 8H_2O$, 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 $Mg_3(PO_4)_2 \cdot 8H_2O$ (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° 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° C. at which temperature the mineral loses five molecules of water. A broad secondary endothermic reaction with a peak at 470° C. indicates the loss of the remaining three molecules of water. The *x*-ray pattern of the sample after heating to 300° C. shows little loss of structure although 60 per cent of the water has been removed; however, on heating to 470° C. with loss of three remaining molecules of water, the stucture is destroyed. Recrystallization to $Mg_3(PO_4)_2$ takes place at 565° C. as is also indicated by a sharp exothermic reaction. Two lesser exothermic reactions are recorded at 675° C. and 710° 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° C.; two molecules of water are lost between 150–350° C.; and the final molecule of water is lost above 350° C. Similar results were obtained by earlier investigators. De Schulten (1903) states "das Hydrat $Mg_3(PO_4)_2 \cdot 8H_2O$ gibt bei 120° fünf Moleküle Wasser ab." Klement (1936) found that two

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* 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° 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.

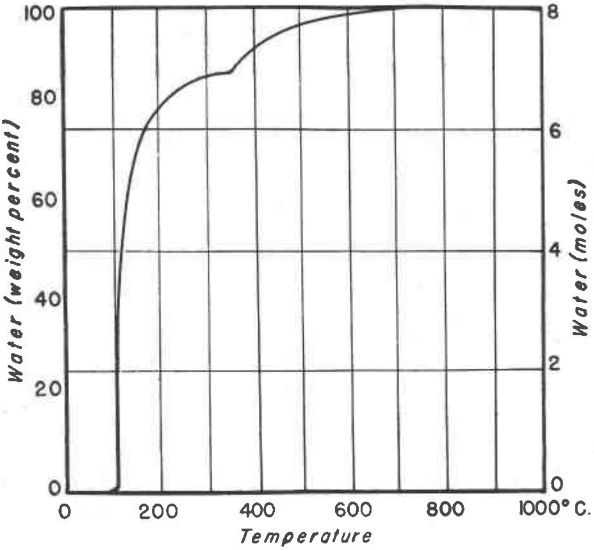


FIG. 3. Dehydration curve.

Vivianite.—$Fe_3(PO_4)_2 \cdot 8H_2O$, 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.—$Al_2PO_4(OH)_3$ from Laws, California, U. S. National Museum, specimen #97576. Cream colored crystalline crust. G=2.7. Biaxial (+), $\alpha=1.575$, $\gamma=1.588$; both ±.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° 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° C. After heating the residue of augelite to 1000° C. a structure is developed as shown by *x*-ray patterns, which is unlike any of the aluminum phosphates noted previously.

Wardite.—$CaNa_4Al_{12}(PO_4)_8(OH)_{18}\cdot 6H_2O$, Lewiston, Utah. A light gray-green dull mineral in nodules resembling turquois 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° C., and a moderate exothermic reaction with a peak at 780–800° C. *X*-rays show recrystallization to aluminum phosphocristobalite.

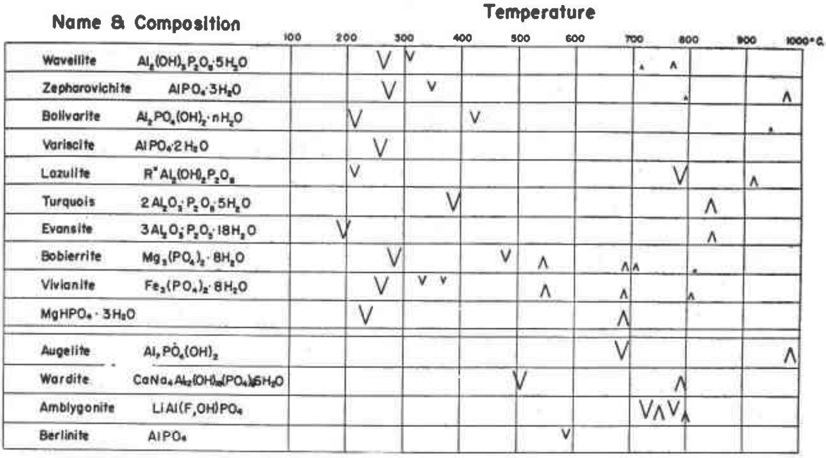
Turquois.—$2Al_2O_3\cdot P_2O_5\cdot 5H_2O$, New Mexico. Dull-azure-blue, highly fractured. The *x*-ray pattern is comparable to that of other samples of of turquois. A very sharp endothermic reaction with peak at 380° C. and an extremely sharp exothermic reaction with peak at 840° C. are characteristic of the relatively simple differential thermal curve of turquois (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.—$LiAl(F, OH)PO_4$, 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 $LiAl(F)PO_4$, 20 per cent and montebrasite $LiAl(OH)PO_4$, 80 per cent. Amblygonite (Fig. 2, no. 8) gives an endothermic reaction with a peak at 740° C. followed by an exothermic reaction with a peak at 760° C. A second endothermic peak occurs at 780° C. which is followed by a second exothermic reaction at 800° C. The sample fused at 850° C.

Zepharovichite (?).—$AlPO_4\cdot 3H_2O$, Bohemia, U. S. National Museum specimen #84339. Grayish-white powder. G=2.34. $\alpha=1.525$, $\gamma=1.544$,

±.003. The sample gives a sharp endothermic reaction at 270° C. with a second endothermic reaction at 355° C. There are two exothermic (Fig. 2, no. 1) reactions; the first with a peak at 790° C., and a second at 970° C. The *x*-ray pattern of the heated residue shows aluminum phosphocristobalite 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 zepharovichite agree with those for wavellite, and the first exothermic reaction is found in wavellite. The second exothermic reaction at 970° C. was not recorded for wavellite.



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

FIG. 4. Summary of differential thermal data.

Berlinite.—$AlPO_4$, synthetic, milky-white crystals. G=2.56. (Na) $\epsilon=1.535$, $\omega=1.525$, ±.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° C. which marks the inversion from the alpha to beta form. The inversion point is 10° C. higher than the inversion of alpha to beta form of quartz recorded on the same instrument.

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

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