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THE THERMAL ANALYSIS OF SOME PHOSPHATE MINERALS: STRENGITE, LIPSCOMBITE, CYRILOVITE AND GOYAZITE.

Y. NATHAN, G. PANCZER and S. GROSS
Geological Survey of Israel

ABSTRACT

Four phosphate minerals: strengite, lipscombite, cyrilovite and goyazite were studied by thermal analysis (DTA, TG), X-rays (XRD), electron microscopy (SEM) and infrared absorption. The three hydrous iron phosphates studied behave similarly to hydrous aluminous phosphates. They give endothermic reactions at low and medium temperatures related to the loss of water of crystallization and hydroxyls respectively. This causes a strong decrease in crystallinity. Recrystallization at high temperatures (650 - 800°C) with the formation of $FePO_4$ (α -quartz structure and other polymorphs) appears to be common for hydrous iron phosphates.

INTRODUCTION

An unusual mineral assemblage of iron and aluminum phosphates is found associated with the Mishash-Ghareb Formations unconformity in the Negev (Southern Israel). A recent study [1] has revealed the presence of several minerals which had not previously been identified in Israel.

During the course of the mineralogical investigation it appeared that the thermal data for some of these minerals was incomplete. Four such minerals were chosen for the present study, three iron phosphate minerals: strengite, lipscombite, cyrilovite and one aluminum phosphate mineral: goyazite.

SAMPLES AND ANALYTICAL TECHNIQUES

The samples were hand picked and a preliminary X-ray diffraction done (Philips PW 1050/80). Appropriate samples were then further purified, using nitric acid (4N) to dissolve calcium phosphates. A solution of sodium chloride (100gr/l) was used to wash out gypsum. Each mineral was then checked by XRD and only samples which had no extraneous X-ray lines (apart from the strongest quartz reflection) were taken for further study.

The purified samples were then analysed with a scanning electron microscope (Jeol JSM-840) coupled with an energy dispersive spectrometer (Link EDS 10000). The thermic characteristics were studied by combined differential thermal analysis and thermogravimetry with a Stanton Redcroft 781 apparatus using 30 to 40 mg of the mineral. The heating rate was 20°C per minute.

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All samples were quenched after each thermal event and examined by XRD. An infrared absorption spectrum was done (Nicolet XD5) for the original samples and some of the quenched samples. This was done on pressed pellets (1 mg of sample into 150 mg KBr) from 400 cm^{-1} to 4000 cm^{-1}. The colors of the original and quenched samples given in the text were determined according the US Rock-color Chart [2]

RESULTS AND DISCUSSION

The results of the chemical analysis are given in Table 1. The results are given as obtained and recalculated to a 100%, taking into account the water content as obtained from the TG curves.

TABLE 1: Chemical Analyses

Sample	Strengite		Lipscombite		Cyrilovite		Goyazite	
	EDS %	calc. %	EDS %	calc. %	EDS %	calc. %	EDS %	calc. %
P_2O_5	36.0	36.6	33.5	38.6	22.2	28.6	19.8	24.0
Fe_2O_3	42.0	42.6	43.0	49.5	36.7	47.3	-	-
Al_2O_3	-	-	1.5	1.7	1.7	2.2	30.4	35.5
Cr_2O_3	1.5	1.5	-	-	-	-	-	-
Na_2O	-	-	-	-	5.4	7.0	-	-
CaO	-	-	-	-	0.4	-	3.8	4.5
SrO	-	-	-	-	-	-	14.7	17.0
H_2O	-	19.0	-	10.0	-	15.0	-	19.0
Total		99.7		99.8		100.1		100.0

STRENGITE

Strengite - $Fe^{+3}PO_4.2H_2O$, the Negev species has a pale green color and its hue changes to bluish (600 °C), then yellowish (800°C) and finally gray (1000°C). A typical chemical analysis is given in Table 1 and a SEM picture is given in Plate 1. The X-ray and infrared patterns are almost identical to those given by Arlidge et al. [3].

The DTA's of the strengite samples examined in the present study show three thermal events (Fig. 1). The first is a strong endotherm with a peak at about 240 °C. A previous study [3] has already recorded this event and attributed it to dehydration; we concur with this interpretation. The weight loss - 16.6% - (TG curve - Fig. 1) related to this event and the disappearance of the strong absorption H-O band at 3560 cm^{-1} in the IR spectra confirm that practically all the structural water is expelled in this event. The lines of the X-ray pattern of a sample quenched after 350°C are weak and

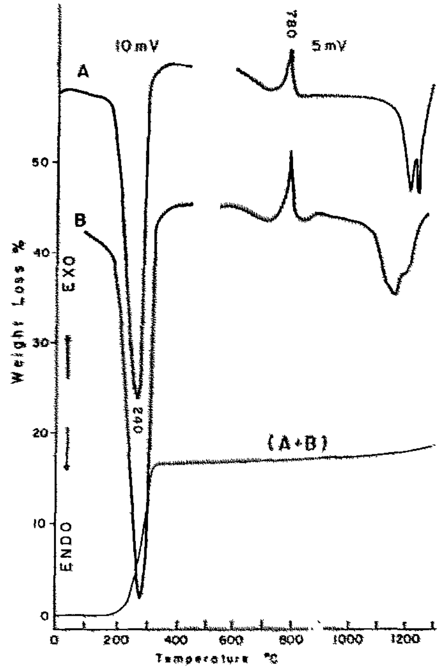

Fig. 1: DTA (A under air, B under Nitrogen) and TG curves of strengite.

diffuse, indicating the formation of a semi-amorphous phase after dehydration. The second event is a medium exotherm at about 780°C which probably represents the recrystallization to the low-quartz type $FePO_4$. X-ray of the sample quenched at 800 °C gives almost only this pattern (JCPDS 29-0715). A SEM picture of this product is given in Plate 1. The third event, which is a broad complex endotherm with multiple peaks between 1000 and 1200°C represents decomposition and melting of the sample. X-ray patterns of the quenched products consist of mixtures of various polymorphs of $FePO_4$ together with some strong lines which could not be identified with certitude but might be related to a condensed phosphate (Fe-pyrophosphate?); these lines in descending order of intensity are at 2.98, 2.95 and 2.52 Å.

A SEM picture of some of the melting products is given in Plate 1. There is a slight difference between DTA's run under N_2 and those run under air. The third thermal event occurs at a slightly higher temperature under air (Fig. 1). There are no differences in the TG curves and therefore only the TG curve under air is given (Fig. 1).

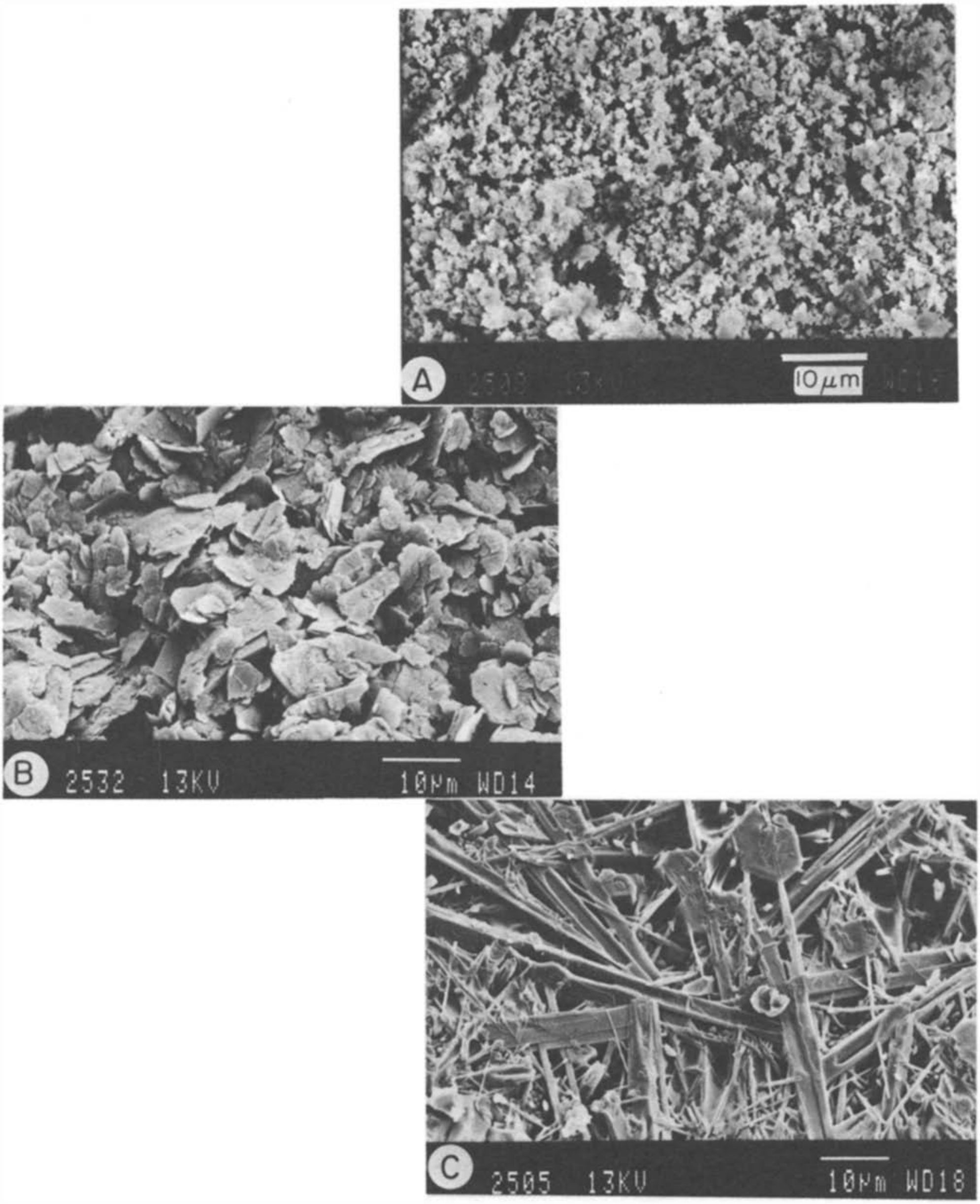

Plate 1: SEM photographs of strengite; A - original sample, B - after heating to 800°C, C - after heating to 1200°C.

LIPSCOMBITE

Lipscombite - $Fe^{+2}Fe_2^{+3}(PO_4)_2(OH)_2$, this mineral occurs in the Negev without any discernable Mn substitution, similar to the synthetic product [4]. A chemical analysis is given in Table 1. The previous mention of a natural occurrence [5] was of a manganoan lipscombite. The X-ray pattern is similar to the one given by Gheith [4]. The mineral is grayish-green turning to dark yellowish-green (200 °C) and to brownish-green (400°C), getting darker (brown and dark brown) with increasing temperature.

The DTA's show at least four thermal events (Fig. 2B). The first is a strong endotherm at about 200°C in which the mineral looses only 0.5% of its weight, the X-ray pattern remaining unchanged. The second is a very broad complex endotherm between 330 and 570°C, with badly defined peaks at 355, 410, 510 and 560°C, this is accompanied by a weight loss of about 9% (complete dehydroxylation). The X-ray pattern still shows the characteristic peaks of lipscombite though weaker and more diffuse. The third event at about 800°C is a very weak exotherm probably representing a phase transition. The X-ray pattern of a sample quenched at 850°C shows three phases: low-quartz type α-$FePO_4$, hematite Fe_2O_3, and an unidentified phase, similar to the one described in the thermal products of strengite. The fourth event is a sharp endotherm at about 1020 °C. X-ray of the product shows the presence of the cristobalite type polymorph of $FePO_4$ together with the unidentified phase which becomes stronger.

Some differences can be noted between our results for a natural sample and those of Gheith [4] for a synthetic sample. The natural sample appears to be better crystallized. The low-quartz type $FePO_4$ in the synthetic sample occurs already at 560 °C, while in the natural sample it occurs only at much higher temperatures (above 650°C). There is no difference between the DTA under air and in an inert atmosphere (N_2). Furthermore, oxidation apparently takes place in both cases (the color changes to brown) confirming Gheith [4] in that the oxidation of the ferrous iron in lipscombite takes place without the addition of oxygen, but by removing the H ions of the OH groups.

CYRILOVITE

Cyrilovite - $NaFe_3^{+3}(PO_4)_2(OH)_4 \cdot 2H_2O$. The mineral is moderate yellow changing to light brown (350°C), then from moderate brown (460°C) to moderate reddish-brown (660°C) and finally to dark reddish brown (1000°C). A chemical analysis is given in table 1.

Five thermal events could be distinguished in the DTA curve (Fig. 2C). The two first weak endotherms at 150 and 325°C are probably not characteristic of cyrilovite. As a matter of fact they occur with stronger intensities in other samples (presumably more impure). Nevertheless these impurities could not be detected by XRD and the TG curve (Fig. 2C) shows that the peak at 325°C is associated with a weight loss of 1.5% and some decrease of the crystallinity is detected in the quenched sample. The first significant event related with certitude to cyrilovite is a double endotherm at 400 and 460°C.

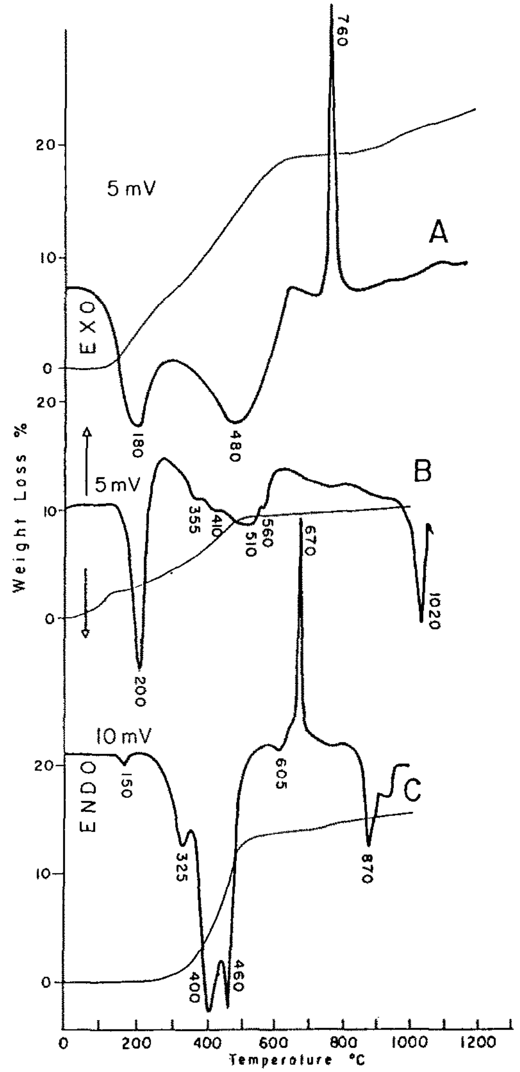

Fig. 2: DTA and TG curves of A - goyazite, B - lipscombite and C - cyrilovite.

The first peak of the doublet is associated with a 5.5% weight loss and the second one with 7%. The quenched sample at 500°C is completely amorphous (no X-ray lines). Following a weak endotherm (605°C) a strong exothermic event occurs at 670 °C (the weak shoulder on which the sharp exothermic peak is located, appears to be related to the impurities already mentioned). This event corresponds to recrystallization; four phases can be detected in the X-ray diffraction of the quenched sample (750°C): hematite, low-quartz type $FePO_4$, $Fe_2(PO_4)_2$ and maricite $NaFePO_4$. A broad complex endotherm occurs between 860 and 930°C, with a sharp peak at 870 °C representing decompositon and fusion.

The results are similar to those given by Correia Neves [6], with some differences such as a much better defined doublet (400 and 460°C) and higher temperatures for the exothermic peak and fusion in the Negev mineral.

GOYAZITE

Goyazite.- $(Sr,Ca)\,Al_3(PO_4)_2(OH)_5.H_2O$. The very pale orange mineral is turning to grayish orange at 600°C and finally to light brown at 1000°C. A chemical analysis is given in Table 1.

At least three main events could be observed in the DTA curve (Fig. 2A). A first endotherm occurs at 180°C together with a weight loss of 4.5%, without causing any significant change in the XRD pattern of goyazite. The 14.5% weight loss which is associated with the second endothermic event at 480°C, corresponds to the complete loss of crystallinity. The third event is a sharp exotherm with a peak at 760°C, which marks the beginning of recrystallization. Two phases may be identified in the sample quenched at 800°C: the aluminous isotype of tridymite $AlPO_4$ (20-44 or 20-45) described by Floerke [7], and a Sr-phosphate (fermorite type). A very weak endotherm occurs at 950°C; however the TG curve records at this temperature a weight loss of 3.5% for which we have no explanation. The sample quenched at 1100°C, has not yet melted and gives the same components as at 800°C, plus corrundum Al_2O_3(10-173).

Thesé results are similar to those presented by Capdecomme et al [8] and by Gilkes et al [9]. However, we did not identify the aluminous phosphate isotype of cristobalite, which begins to crystallize at 750 °C according to Capdecomme.

CONCLUSIONS

The results of the present study together with those of previous works [3, 10] show that the thermal behaviour of hydrous iron phosphates is very similar to that of hydrous aluminum phosphates [11]. Endothermic reactions at low and medium temperatures indicate loss of water of crystallization and hydroxyls respectively. This results in a breakdown of the structure. Subsequently an exothermic structural reordering occurs at higher temperatures (650 - 800°C) resulting in the formation of α-$FePO_4$ or one of its polymorphs. Finally decomposition and/or melting occur with the formation of condensed phosphates.

It is interesting to note that the presence of Na in cyrilovite lowers considerably the temperatures of both the exothermic reordering and the melting point.

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REFERENCES

1 G. PANCZER, S. GROSS, Y. SHILONI and Y. NATHAN, Ann. Meet. Isr. Geol. Soc., 'En Boqeq, (1988) 89.
2 Rock-color Chart, Geol. Soc. America, New York, (1951).
3 E.Z. ARLIDGE, V.C. FARMER, B.D. MITCHELL and W.A. MITCHELL, J. Appl. Chem., 13 (1963) 17.
4 M.A. GHEITH, American Mineral., 38 (1952) 612.
5 M.L. LINDBERG, American Mineral., 47 (1962) 353.
6 J.M. CORREIA NEVES, Rev. Estud. Gerais Univ. Mocambique, Ciencias Geol., 3 (1966) 41.
7 O.W. FLOERKE, Zeitschr. fur Kristallogr. 125 (1967) 134.
8 L. CAPDECOMME and M. ORLIAC, Coll. Int. Phosph. Min. Solides, Toulouse, Vol.2 (1967) 45.
9 R. J. GILKES and B. PALMER, Mineral. Mag., 47 (1983) 221.
10 R.L. MANLY, American Mineral., 35 (1950) 108.
11 K.A. RODGERS and G.S. HENDERSON, Thermochimica Acta, 104 (1986) 1.