

THERMAL ANALYSIS OF ISRAELI PHOSPHORITES

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Abstract. Thermal analysis of Israeli phosphorites from Nahal Zin and Arad deposits was performed using the TG/DTA method complemented with titrimetric and thermogaschromatographic determination of the evolved gases. The amounts and temperature intervals of H₂O, CO₂, and SO₂ evolution were established, both in the oxygen-containing flow and in the inert gas atmosphere, where additionally the organic compounds were established.

Key words: phosphorites, thermal analysis, evolved gases, thermogaschromatography, Israel.

INTRODUCTION

Differences in the composition and properties of phosphorites of different deposits, sometimes even of different layers of the same deposit, strongly affect their processing. Thermal transformations in phosphorites depend on the peculiarities of the main apatitic mineral and the nature of the accompanying minerals [1–3]. Enrichment of phosphorites by flash calcination has been used in Israel. Thermal changes occurring in this process were investigated using FTIR and XRD methods [1].

Thermal analysis of phosphorites enabled us to specify the changes in their composition and the temperature intervals of the reactions. In this study samples of Israeli phosphorites from the Arad (Zefa) and Nahal Zin deposits [4] were subjected to thermal analysis by thermogravimetric (TG), derivative thermogravimetric (DTG), and differential thermal analysis (DTA) complemented with titrimetric determination of the evolved gases (TGT), which had been used before for studying other phosphorites [2], while thermogaschromatography (ThGC) [5] was used for the first time.

MATERIALS AND METHODS

The chemical composition* of the samples is presented in Table 1. Sample 1 is from the Arad deposit, Sample 2 represents the bituminous variety and Sample 3 the non-bituminous variety of phosphorite from the Nahal Zin deposit. The main constituent of the samples is fluorcarbonateapatite (francolite), while among the admixtures calcite, gypsum, silicates (quartz, opal C-T), and organic matter prevail.* Sample 1 is rich in calcite, Sample 2 in organic matter and silicates.

Table 1. Chemical composition of the samples, %

Constituent	Sample 1	Sample 2	Sample 3
P ₂ O ₅	28.2	29.3	31.1
CaO + MgO	52.2	50.3	53.2
MgO	0.3	0.7	0.3
Fe ₂ O ₃	0.1	0.2	0.1
Al ₂ O ₃	0.1	0.2	0.1
SiO ₂	0.5	2.8	1.0
F	3.3	2.9	3.3
CO ₂	10.1	8.6	7.7
SO ₃	2.2	1.4	2.5
S ²⁻ , ppm	6.0	101.1	60.8
Cl	0.02	0.05	0.03
Organic matter	0.5	2.9	0.3
Mole ratio CO ₂ /SO ₃	8.4	11.4	5.6

For the elimination of calcite Samples 1 and 2 were treated with triammonium citrate solution (pH = 8) [6] and with 2% citric acid solution (pH = 2.1). The treatment of the samples with the solutions was carried out within 6 h at room temperature with 200 mL of solution used for 100 mg of sample. After filtering the residue was carefully washed with water and dried at 100°C. Upon treatment of the sample with citric acid solution, also partial dissolution of the fluorcarbonateapatite took place.

Simultaneous DTA, TG, and DTG analyses were recorded under dynamic conditions in oxygen or an air stream with a Q-Derivatograph (MOM, Budapest). The heating rate was 5°C min⁻¹ and the amount of the ground sample 350–450 mg. The sample holder was an uncovered conventional platinum crucible. Determination of the evolving gaseous compounds (CO₂ and SO₂) was performed by the method proposed by J. Paulik and coworkers [7]. Gases were transported into the absorber vessel in the carrier gas stream at 10 L h⁻¹. Titration was performed with 0.05 M NaOH solution at pH = 4.0 for SO₂ and at pH = 9.3 for CO₂. The pH was measured with a glass-calomel electrode.

* Data on the chemical and mineralogical composition were provided by the Geological Survey of Israel.

ThGC is temperature-programmed pyrolysis coupled with gas chromatographic analysis, which provides information depending on two variables – temperature and chromatographic separation of the evolved gases [5]. It was shown to be a reliable tool for obtaining information on the composition and thermal stability of salts [8] and synthetic carbonateapatites [9, 10].

The experiments were carried out in the temperature interval 70–600°C at a heating rate of 10 deg min⁻¹ in the He flow. The evolving species were separated using a capillary column (NSW-PLOT HNU Nordion, Finland) and detected by a thermal conductivity detector. A chromatograph Carlo-Erba 4200 with 450 HWD and FID detectors was used. As the PLOT column used has limited separation possibilities (retaining organic compounds with higher molecular masses), the information obtained was mostly on the evolution of water, carbon dioxide, and light organics.

The sample mass was 20–70 mg and experiments were repeated at least twice. The results are presented as mean values. The mass loss of the sample during the heating from 70 to 600°C was measured by weighing the sample before and after heating. The amount of the evolved products was measured from the peaks on the thermochromatogram using standards to calibrate the chromatographic detector.

RESULTS AND DISCUSSION

The results of the ThGC study in an inert gas atmosphere are presented in Figs. 1 and 2. Figure 1 presents the immediate outputs of thermochromatograms for Samples 1 and 2. The mass losses and the amounts of compounds evolved are shown in Table 2.

Table 2. Mass loss and evolution of volatile compounds by ThGC, %

Sample No.	Mass loss	H ₂ O	CO ₂	Light organics	Heavy organics
1	3.0	1.34	0.68	0.81	0.17
2	5.0	0.88	0.52	1.44	2.16
3	5.3	0.87	0.47	0.78	1.18

The adsorbed water is loosened at 100–160°C. Evolution of the constitutional water from the minerals and the water from the pyrolysis reactions occurs in a wide temperature interval up to 500°C, with maximum around 320°C. This overlaps with the evolution of CO₂, which is also a product of pyrolysis and occurs at temperatures up to 600°C, with maximums around 350 and 500°C. This is clearly seen in case of Sample 2. For Samples 1 and 3, where the content of organic matter is 0.3–0.5%, the amount of gases evolved due to pyrolysis is much smaller. At temperatures above 550°C, evolution of CO₂ is also caused by the beginning of decomposition of carbonates, particularly of dolomite.

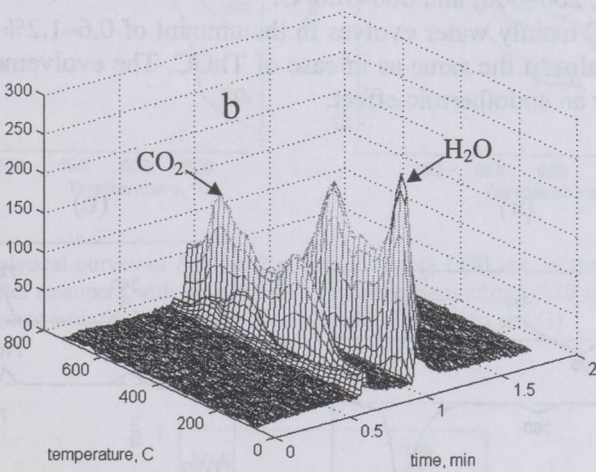
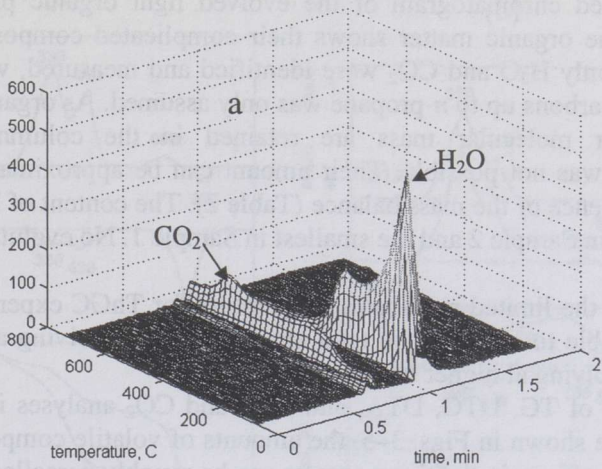


Fig. 1. Thermochromatograms of phosphorite samples on calcination from 70 to 600 °C at heating rate 10° min⁻¹ in the helium flow. a, Sample 1; b, Sample 2.

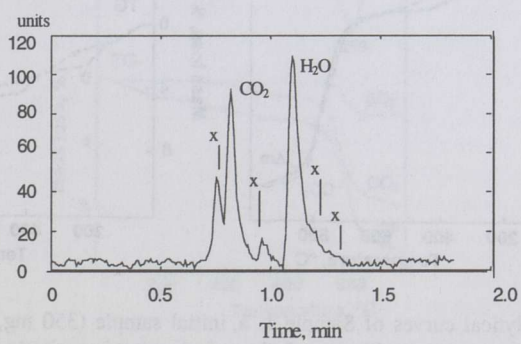


Fig. 2. Chromatogram of the evolved gases from Sample 2 at 375 °C. Unidentified light organic compounds are marked by x.

The detached chromatogram of the evolved light organic products of the pyrolysis of the organic matter shows their complicated composition (Fig. 2). Among them only H₂O and CO₂ were identified and measured, while existence of light hydrocarbons up to *n*-propane was only assumed. As organic compounds with a higher molecular mass are retained in the column, their direct determination was not possible. Their amount can be approximately calculated from the difference of the mass balance (Table 2). The content of heavy organics is the greatest in Sample 2 and the smallest in Sample 1. No evolution of H₂S was fixed.

Because of the limited maximum temperature for ThGC experiment (600°C) it was impossible to estimate the total amount of CO₂ evolving and to measure other gases evolving at higher temperatures.

The results of TG, DTG, DTA, and SO₂ and CO₂ analyses in an oxidizing atmosphere are shown in Figs. 3–5, the amounts of volatile compounds in Table 3. The thermal effects in the thermograms can be roughly parcelled out into three parts: up to 200, 200–600, and 600–980°C.

At 80–200°C mainly water evolves in the amount of 0.6–1.2% of the sample mass, which is almost the same as in case of ThGC. The evolvement of water is accompanied by an endothermic effect.

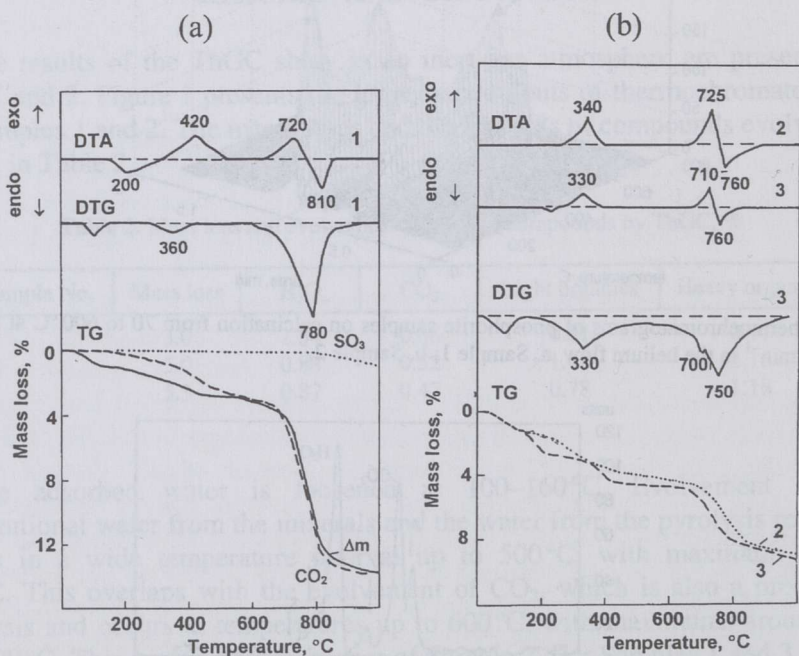


Fig. 3. Thermoanalytical curves of Sample 1. a, initial sample (350 mg, in the oxygen flow) (1). b, solid residue after treatment with the solution of triammonium citrate (450 mg, in air) (2); solid residue after treatment with the solution of 2% citric acid (320 mg, in air) (3).

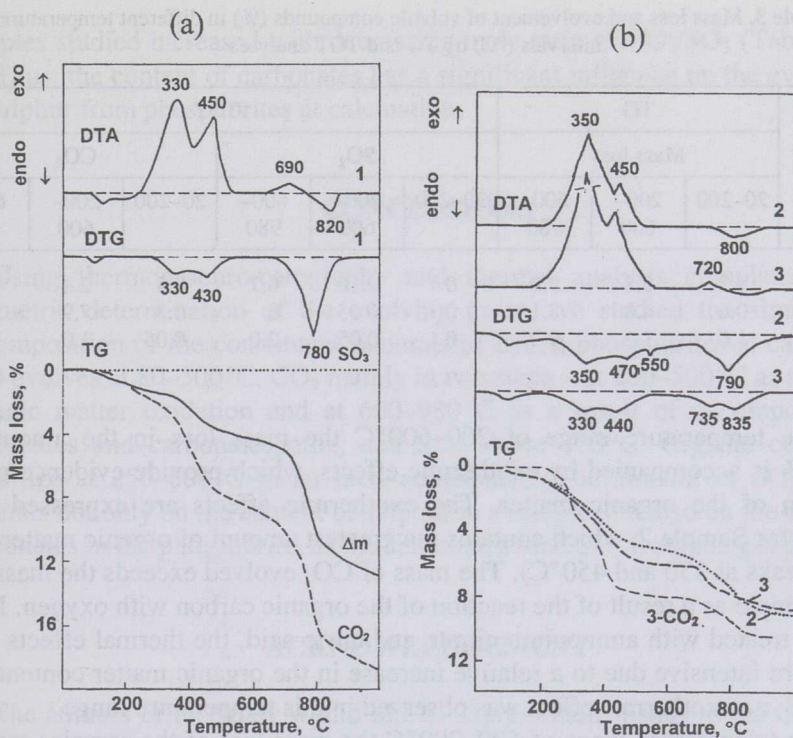


Fig. 4. Thermoanalytical curves of Sample 2. a, initial sample (350 mg, in the oxygen flow) (1). b, solid residue after treatment with the solution of triammonium citrate (320 mg, in air) (2); solid residue after treatment with the solution of 2% citric acid (350 mg, in air) (3).

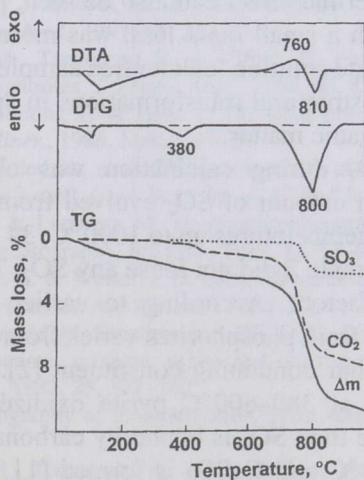


Fig. 5. Thermoanalytical curves of Sample 3 (400 mg, in the oxygen flow).

Table 3. Mass loss and evolution of volatile compounds (%) in different temperature intervals (°C) by TG and TGT analyses

Sample No.	TG			TGT					
	Mass loss			SO ₂			CO ₂		
	20–200	200–600	600–980	20–200	200–600	600–980	20–200	200–600	600–980
1	1.2	2.8	9.8	0	0.10	0.7	0.3	2.4	10.2
2	0.6	4.0	8.1	0	0.05	0	0.8	7.9	9.9
3	1.0	1.2	9.0	0	0.05	2.0	0.05	1.0	5.4

In the temperature range of 200–600°C the mass loss in the amount of 1.2–4.0% is accompanied by exothermic effects, which provide evidence of the oxidation of the organic matter. The exothermic effects are expressed most strongly for Sample 2, which contains the greatest amount of organic matter (two strong peaks at 330 and 450°C). The mass of CO₂ evolved exceeds the mass loss of the sample as a result of the reaction of the organic carbon with oxygen. In the samples treated with ammonium citrate and citric acid, the thermal effects were even more intensive due to a relative increase in the organic matter content. For Sample 3, no exothermic effect was observed in this temperature range.

In the temperature range of 600–980°C the mass loss of the samples reaches its maximum value (8.1–9.8%) due to the decomposition of carbonates and the evolving of CO₂ from carbonateapatite [1, 2]. The mass loss and the mass of the evolved CO₂ are almost equal, except for Sample 3 from which more SO₂ evolved. The endothermic effects at 810–820°C are induced by the decomposition of calcite. In the temperature interval of 680–760°C transformation with an exothermic effect can also be seen, particularly for Sample 1. This effect, together with a small mass loss, was more clearly observed for the samples treated with citrate solution (calcite free samples). The exothermic effect can be explained by the structural transformations in apatite [1] or by oxidation of more thermostable organic matter.

Volatilization of SO₂ during calcination was observed at temperatures 780–800°C. The greatest amount of SO₂ evolved from Sample 3 – 77% of the total sulphur content. At temperatures up to 1000°C, 34 rel. % of sulphur evolved from Sample 1, while Sample 2 did not lose any SO₂. The evolution of SO₂ is influenced by several factors. According to earlier studies the temperature interval of SO₂ emission from phosphorites varies from 300 to 900°C depending on the decomposed sulphur containing constituent [2]. At 300–500°C sulphur-rich organic matter and at 380–600°C pyrite oxidize, at 800–850°C MgSO₄ decomposes. At the same time SO₂ is bound by carbonates and carbonateapatite at temperatures 400–800°C and CaSO₄ is formed [11, 12]. CaSO₄ decomposes above 1200°C. Therefore, the level of SO₂ emission at calcination should depend on the carbonate content in the sample. The amount of SO₂ evolved from the

samples studied increased with decreasing mole ratio of CO_2/SO_3 (Tables 1 and 3). Thus, the content of carbonates has a significant influence on the evolution of sulphur from phosphorites at calcination.

CONCLUSIONS

Using thermogaschromatography and thermal analysis complemented by titrimetric determination of the evolving gases, we studied the simultaneous decomposition of the constituent minerals of Israeli phosphorites at calcination. H_2O evolves at 80–500°C, CO_2 mainly in two steps – at 200–500°C as a result of organic matter oxidation and at 600–980°C as a result of decomposition of carbonates and carbonateapatite, and SO_2 above 780°C. Organic compounds volatilize at 250–600°C in an inert atmosphere. The amount of SO_2 evolved depends not only on the content of sulphur in a sample, but also on the content of carbonates in the phosphorite, as the carbonates bind SO_2 from the gas phase.

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IISRAELI FOSFORIITIDE TERMIILINE ANALÜÜS

Kaia TÕNSUAADU, Mihkel VEIDERMA, Mihkel KOEL ja Yaacov NATHAN

Israeli Nahal Zini ja Aradi (Negev) leiukoha fosforiitide termilisel töötlemisel toimuvate muutuste selgitamiseks tehti nende termogravimeetiline ja diferentsiaaltermiline analüüs. Lisaks sellele analüüsiti eralduvaid gaase titrimetrilisel meetodil hapniku keskkonnas ja termogaaskromatograafia meetodil inertgaasi keskkonnas. Fosforiidi proovides sisalduvate mineraalide samaeelse lagunemise tõttu kuumutamisel lendub veeaur temperatuuril 80–500°C, CO₂ vahemikus 200–500°C orgaanilise aine oksüdeerumise tagajärjel ning vahemikus 600–980°C karbonaatide ja karbonaatapatiidi lagunemise tagajärjel. SO₂ lendub temperatuuril üle 780°C. Inertgaasi atmosfääris lenduvad orgaanilised ühendid vahemikus 250–600°C. Eralduva SO₂ hulk ei sõltu ainult väevli sisaldusest fosforiidis, vaid ka karbonaatide sisaldusest selles, sest karbonaadid seovad SO₂ gaasifaasist.