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PHYSICO-CHEMICAL TRANSFORMATIONS DURING HEATING OF PHOSPHORITES

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The thermal behaviour of phosphorites in an oxygen or helium atmosphere was studied by means of simultaneous TG–DTG–DTA-gas titrimetric EGA. Thermal oxidation and/or decomposition steps of the contaminating organic materials, carbonate minerals and pyrite, and of the fluorocarbonate–apatite were identified. The evolution of CO_2 from the latter has its maximum at 750–850 °C and is accompanied by an increase in the lattice parameter a_0.

The physico-chemical transformations occurring the heating of phosphorites from different deposits of the USSR (Table 1) up to 1000° have been studied by thermal, chemical, IR, X-ray diffraction and selective dissolution analysis. the main contaminating minerals are dolomite, calcite, pyrite, siderite, quartz, etc. Simultaneous DTA, TG, DTG and gastitrimetric EGA allow a more accurate determination of the temperature intervals of solid-state transformations of phosphorites, depending on the gaseous atmosphere, and taking place with the evolution of gaseous compounds (CO_2 and SO_2) [1, 2].

It has been established that, when an open crucible is used in an oxidizing atmosphere, the evolution of carbon dioxide starts at 200°; during heating up to 400°, the oxidation of the organic carbon in the phosphorites amounts to 60–75 relative per cent. At 380–400° the evolution of sulphur dioxide starts, it continues up to 800° (Figs 1 and 2). It has the highest rate between 400° and 550°. The evolution of SO_2 takes place only in an oxidizing atmosphere, and is caused by the oxidation of pyrite. During this process, 25% of the total sulphide sulphur content in the phosphorites is evolved. From 400° to 600° CO_2 is evolved in both oxidizing (O_2) and inert (He) atmospheres. During heating of the nonsiderite phosphorites (Nos 1–3) in oxygen, the amount of CO_2 decreases to 17%, while in helium it decreases to 25% of the total amount of CO_2 in the phosphorites.

When the pelletized phosphorite (No. 4), which also contains siderite, is heated the percentage of CO_2 evolved in this temperature interval is 6–7% higher than that resulting from the decomposition of the siderite. This is due to the decomposition of a certain quantity of other carbonates, and to the oxidation of organic material.

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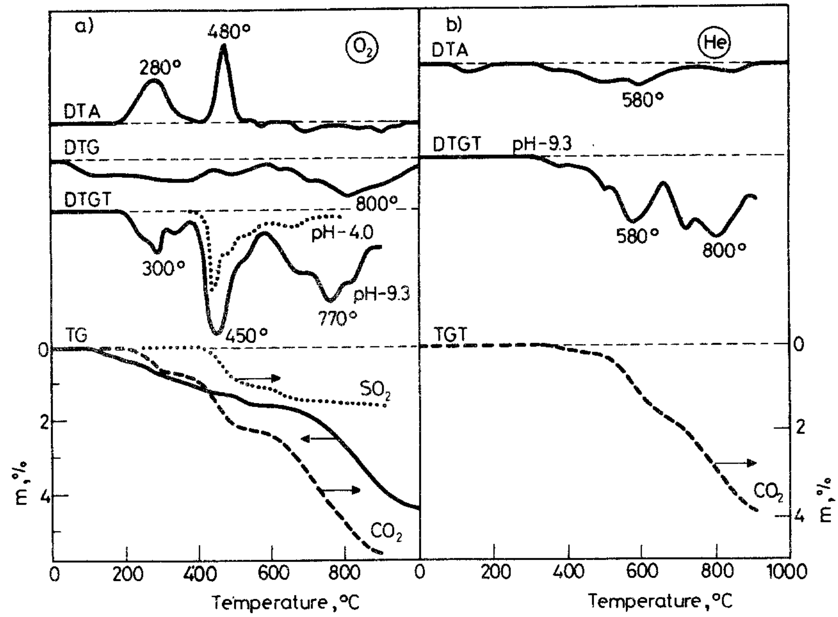

Fig. 1 Thermal curves of Estonian phosphorite No. 1 in a) O_2 and b) He atmosphere. Open crucible, dynamic heating (5 deg min^{-1})

X-ray analyses of phosphorites thermally treated in helium show the appearance of new phases: FeS, $Fe_{1-x}S$, CaS, $CaSO_3$ and in oxygen $Fe_2(SO_4)_3$ and $CaSO_4$. These phases are also stable when the phosphorites are heated to 900–1000°.

In the inert atmosphere, a certain amount of sulphur formed during the reaction

$$FeS_2 \rightarrow FeS + S \tag{1}$$

Table 1 Chemical constituents of phosphorites

Constituent, %	Estonia No. 1	Estonia No. 2	Karatau No. 3	Yegoryevsk No. 4
P_2O_5	28.2	27.8	23.8	18.7
CaO	41.0	41.7	35.8	30.6
MgO	0.9	1.1	2.5	0.6
R_2O_3	3.5	1.9	2.2	12.2
Fe_2O_3	3.3	1.8	1.0	8.2
C, organic	0.3	0.3	0.2	0.7
F	2.8	2.5	2.4	1.8
SO_3, sulphide	5.0	1.5	0.8	2.3
SO_3, sulphate	0.6	0.4	1.8	1.1

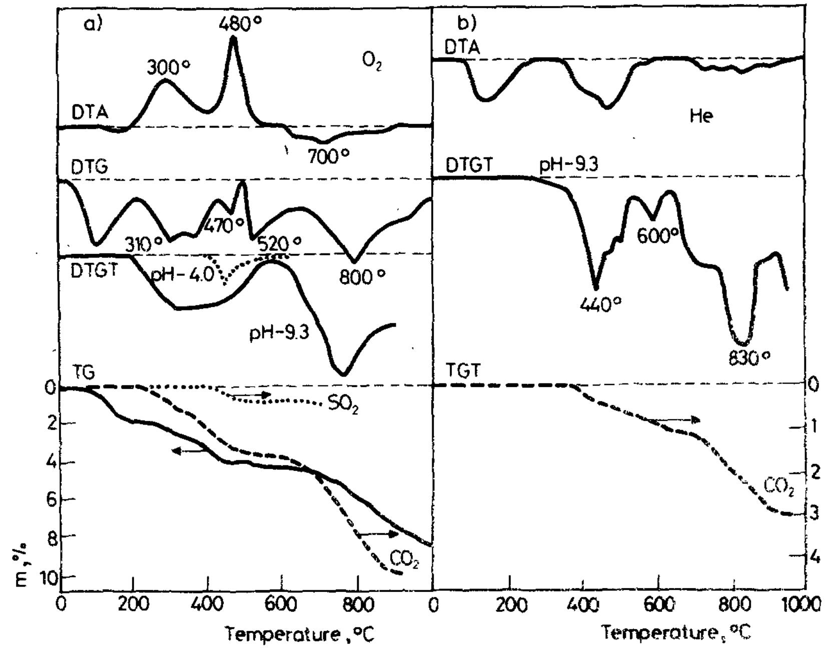

Fig. 2 Thermal curves of Yegoryevsk phosphorite in a) O_2 and b) He atmosphere. Open crucible, dynamic heating (5 deg min^{-1})

reacts with calcite:

$$3\,CaCO_3 + 3\,S \rightarrow 2\,CaS + CaSO_3 + 3\,CO_2 \qquad (2)$$

In oxygen, FeS is partially oxidized to $Fe_2(SO_4)_3$. The formation of $CaSO_4$ is possible after the preceding reaction (2):

$$CaSO_3 + 1/2\,O_2 \rightarrow CaSO_4 \qquad (3)$$

$$CaS + 2\,O_2 \rightarrow CaSO_4 \qquad (4)$$

or after the oxidation of sulphur to SO_2:

$$CaCO_3 + SO_2 + 1/2\,O_2 \rightarrow CaSO_4 + CO_2 \qquad (5)$$

As a result of the decomposition of dolomite, one more new phase is present, MgO, which is preserved up to 900–1000°. MgO proves to be less active than calcium oxide under the conditions of the experiment.

The total amount of CO_2 evolved from 550–600° to 900° in oxygen exceeds the amount evolved in helium by 7–17%. This is a result of oxidation of the organic

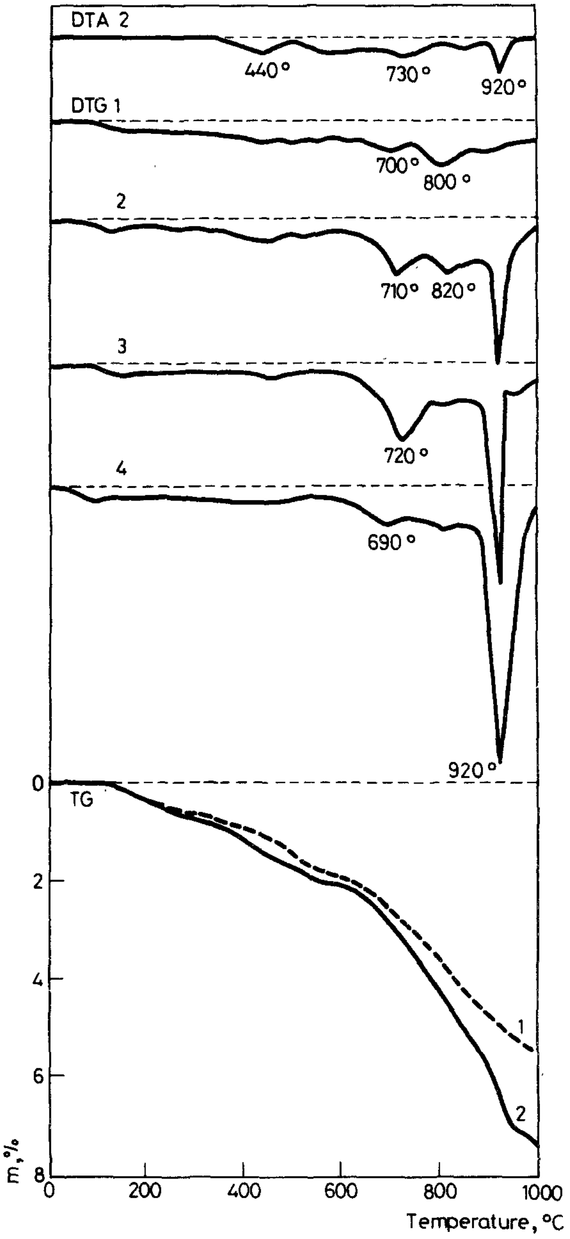

Fig. 3 Thermal curves of Estonian phosphorite No. 2 processed with triammonium citrate (TAC) (1), phosphorite concentrate (2), and its mixtures with dolomite (3) and calcite (4). Labyrinth crucibles, dynamic heating (10 deg min^{-1}) in air.

material (90% relatively of the organic carbon) when the phosphorites are heated to 900°. In helium, the amount evolved in 25–60%, possibly due to constituent oxygen of the organic materials. In this temperature range, the evolution of CO_2 is caused by the decomposition of dolomite and calcite and the oxidation of organic material. When heated to 900°, 10–20% of the total amount of CO_2 remained in the phosphorites.

To specify the evolution of CO_2 from the structure of fluorocarbonate–apatite, a series of experiments was carried out in labyrinth crucibles. With the use of these, the effects of evolution of CO_2 from different minerals aee better differentiated. For sample No. 3 there are three endotherms with weight losses, at 710°, 820° and 920° (Fig. 3, curve 2). If 10% calcite is added to the sample (curve 4), the intensity of the endotherm at 920° increases abruptly, while the addition of 10% dolomite enhances the endotherms at 720° and 920° (curve 3). Both admixtures cause practically no change in the intensity of the endotherm at 820°. Curve 1 characterizes the phosphorite previously processed with a 0.5 *M* solution of triammonium citrate (TAC) (Silverman's method [3] for determination of the amount of CO_2 in the structure of apatites). In this case, the endotherm at 920° disappears, while that at 700° decreases noticeably, but the intensity of that at 800° does not change.

The results of chemical and X-ray analyses and selective dissolution prove that the evolution of CO_2 from the structure of fluorocarbonate–apatite (francolite) starts at 550–600° and continues at above 1000° (Fig. 4). However, it has maximum rate in the temperature range from 750° to 850°. As a result of this, the crystal lattice

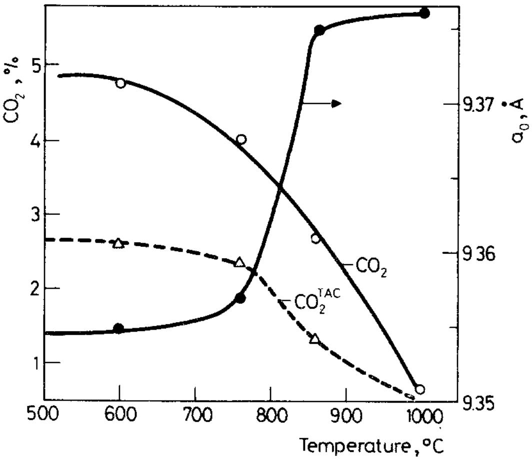

Fig. 4 Changes in the content of CO_2 and the parameter a_0 of the unit cell of Estonian phosphorite No. 2 during the heating. Dotted line: CO_2 loss after processing with TAC

parameter a_0 of apatite for Estonian and Karatau phosphorites increases during heating to 1000° from 9.35 Å to 9.36–9.37 Å, and for pellitized ones from 9.32–9.33 Å to 9.37 Å. The amount of CO_2 in the apatite structure for Estonian phosphorites is 2.0–2.8%, and for pellitized ones is 3.6–4.4%.

Accordingly, simultaneous DTA, TG, DTG and gas titrimetric EGA, in combination with the results of other methods of analyses, permit determination of the mechanisms of thermal transformation occurring during the heating of phosphorites in oxidizing and in inert atmospheres. The evolution of CO_2 from the structure of fluorocarbonate–apatite proceeds in a broad temperature interval; it starts at 550–600° and continues at above 1000°.

References

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Zusammenfassung — Das thermische Verhalten von Phosphoriten in Sauerstoff- oder Heliumatmosphäre wurde durch simultane TG–DTG–DTA–EGA (mittels Gastitrimetrie) untersucht. Thermische Oxidations- und/oder Zersetzungsschritte der Verunreinigungen (organische Materialien, Carbonatminerale und Pyrit) und des Calcium-fluoro-carbonat-apatit wurden identifziert. Die CO_2-Abspaltung aus dem letzteren hat ihr Maximum bei 750–850 °C, sie ist begleitet von einer Vergrösserung des Gitterparameters a_0.

Резюме — Совмещенным методом ТГ, ДТГ, ДТА и газ-титриметрического АВГ изучено термическое поведение фосфоритов в атмосфере кислорода и гелия. Идентифицированы отдельные стадии термического окисления и (или разложения примесных органических веществ, карбонатных минералов, пирита и фторокарбонатапатита. Выделение двуокиси углерода из последнего материала было максимальным при температуре 750–850° и сопровождалось увеличением параметра решетки a_0.