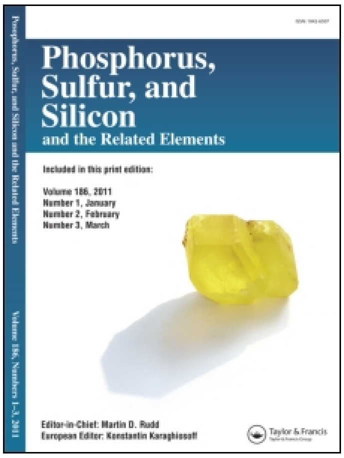

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Thermal Transformations in Systems Based on Natural Apatites

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THERMAL TRANSFORMATIONS IN SYSTEMS BASED ON NATURAL APATITES

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Abstract The mechanisms of thermal transformations in different types of natural phosphates and their mixtures with H_3PO_4 and Na_2CO_3 are discussed.

The changes proceeding at thermal processes for enriching and processing phosphate rock involve transformations in phosphate and impurity minerals, interactions between them and the products of their decomposition, and also introduced admixtures and components of the gas phase.

The phosphate mineral of phosphate rock used in our work was represented by 3 varieties of the apatite group minerals: fluoroapatite (Kola apatite), fluorohydroxyapatite (from the Kovdor deposit), fluorocarbonate apatite (phosphorites from various deposits).

Thermal stability of apatites depends considerably on the spread of anion and cation isomorphism. Kola fluoroapatite in solid state is thermally stable. The loss in mass of fluorohydroxyapatite of the Kovdor deposit when heated up to 1600°C, reaches 1.5% by evolution of water and CO_2. The parameter a of the crystal lattice decreases from 9.405 to 9.395 Å but c increases (from 6.888 to 6.695). The phosphate in the heated product is represented by fluoroapatite with vacancies in the structure and, possibly, by oxyfluoroapatite.

Thermal transformations are most complicated in natural fluorocarbonate apatites being characterized by fine-crystal structure, non-stoichiometry, defectiveness of structure etc. Fig. 1 shows thermograms along with the gas titrimetric curves of Estonian phosphorite I containing 32% P_2O_5. The thermoeffects have been mainly caused by

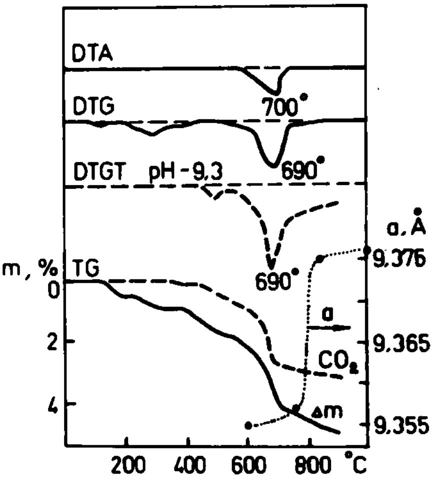

FIGURE 1. Thermal curves and change in the parameter *a* of the apatite unit cell of Estonian phosphorite I (in He atm.).

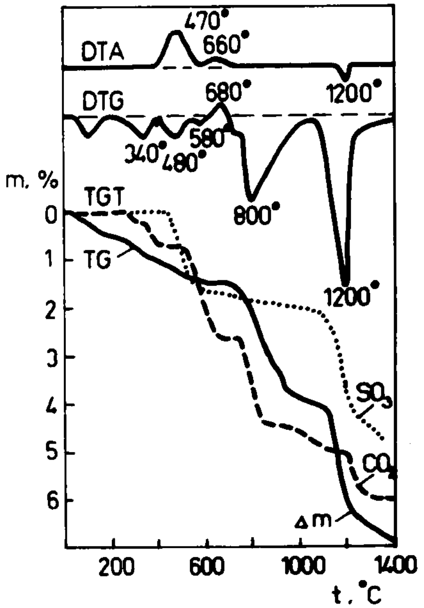

FIGURE 2. Thermal curves of Estonian phosphorite II (in O_2 atm.).

evolution of CO_2 from fluorocarbonate apatite in the range of 700-800°C. In the solid phase new phases of CaO and CaF_2 have been revealed. When fluorocarbonate apatite changes into fluoroapatite, the parameter *a* increases (Fig. 1), the number of P-O-P bridge bonds and hydrogen bonds F...OH on the hexagonal axis characteristic to fluoroapatite, also increases, reaching maximum at the temperature of about 800°C. Contrary to what could be expected, the evolution of CO_2 from carbonateapatite is not completed even at 1000--1100°C and depends on transposition of CO_3^{2-} to the hexagonal axis of the crystal.

The presence of impurity minerals in phosphates strongly complicates the thermal changes as shown in the thermogram of Estonian phosphorite II which contains quartz, pyrites, dolomite, organic matter etc. (Fig. 2). A part of thermal transformations, affecting other minerals in phosphorites, does not affect phosphate mineral: decomposition of carbonates and other minerals, secondary transformations of free oxides with the formation of silicates, oxidation of pyrites and organic matter formation of sulfphates, ferrites etc. The transformations affecting phosphate mineral are evolution of CO_2 from carbonateapatite the entry of ion SiO_4^{4-} and, in case of the presence of pyrites also ion SO_4^{2-}, to the positions made free by the elimination of CO_2.

Adding reagents to apatites even in small quantities sharply affects the proceeding of the thermal changes. The mechanism of industrial solid phase processes for obtaining thermal fertilizers and feed phosphates is given in literature by the following reactions:

$$2Ca_{10}(PO_4)_6F_2+SiO_2+2H_2O \xrightarrow{1400^\circ C} 6Ca_3(PO_4)_2+Ca_2SiO_4+4HF \quad (1)$$

$$3Ca_{10}(PO_4)_6F_2+2H_3PO_4 \xrightarrow{1200^\circ C} 10Ca_3(PO_4)_2+6HF \quad (2)$$

$$Ca_{10}(PO_4)_6F_2+2H_3PO_4+2Na_2CO_3 \xrightarrow{1200^\circ C} 2[Ca_3(PO_4)_2\cdot 2CaNaPO_4]+$$

$$+\ 2HF\ +\ 2CO_2\ +\ 2H_2O.$$

While the reaction (1) describes the process of hydrothermal defluorination of Kola apatite quite well, the reactions (2) and (3) do not express the real mechanism of the processes. We have shown that the mechanism of the solid phase process (2) when treating Kola apatite is schematically described by the following reactions (at molar ratio $CaO:P_2O_5 = 3$):

$$Ca_{10}(PO_4)_6F_2+14H_3PO_4+10H_2O = 10Ca(H_2PO_4)_2\cdot H_2O+2HF$$

$$nCa(H_2PO_4)_2\cdot H_2O \xrightarrow{200-600^\circ C} [Ca(PO_3)_2]_n+3nH_2O$$

$$Ca_{10}(PO_4)_6F_2+4Ca(PO_3)_2+H_2O \xrightarrow{600^\circ C} 7Ca_2P_2O_7+2HF$$

$$Ca_{10}(PO_4)_6F_2+Ca_2P_2O_7+H_2O \xrightarrow{800^\circ C} 4Ca_3(PO_4)_2+2HF$$

The changes in the content of different forms of phosphates with the increase in temperature are given in Fig. 3.

The mechanism of the process in the case of Kovdor hydroxyfluoroapatite differs considerably. During heating the spread of the hydrogen bonds F...OH increases reaching the maximum at 800°C, and hindering the diffusion along the hexagonal axis of the crystal and defluorination of apatite. The evolution of fluor proceeds non-synchronically with the decomposition of apatite leading to the enrichment of the apatite residue by fluor (Fig. 3). Impurity minerals - carbonates and forsterite, are more reactive and react primarily with polyphosphates, therefore the amount of polyphosphates for reacting with apatite decreases, respectively. The phosphate in the product is represented mainly by β-$Ca_3(PO_4)_2$. New phases of $Ca_4P_2O_9$, calcium silicophosphates and silicates have been found.

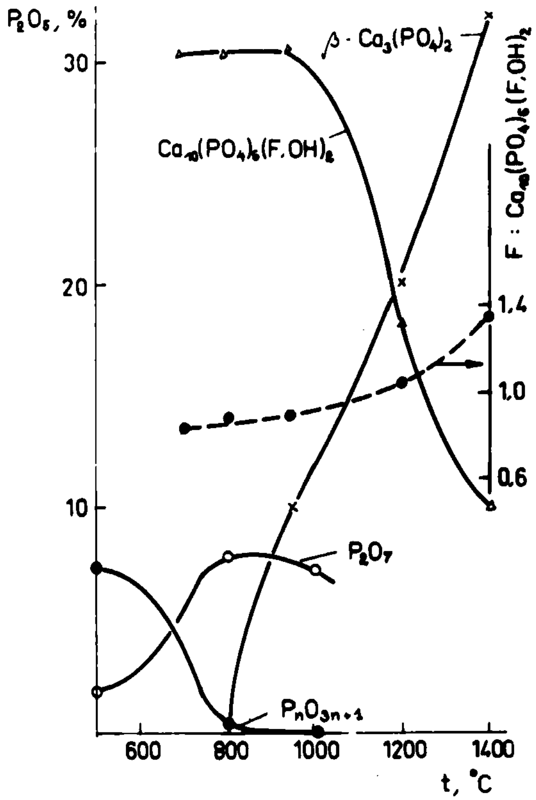

FIGURE 3. Changes in the content of different forms of phosphates and the molar ratio F:apatite in the heating mixtures of Kovdor apatite with H_3PO_4.

To obtain more soluble thermal phosphates as fertilizers, Na_2CO_3 is introduced into the mixtures. During heating a mixture undergoes principally the same stages of the process, but at temperatures above 1200°C an easily-soluble phase of $Ca_3(PO_4)_2 \cdot 2CaNaPO_4$ is formed which remains when quickly cooled.

Phosphorites, as a rule, get defluorinated at lower temperatures or at greater speed than apatite ores. Depending on the kind and quantity of impurity minerals the mechanisms of the process and the composition of the product differ considerably.