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# THE EFFECT OF THERMAL TREATMENT ON THE PROPERTIES OF SOME NATURAL PHOSPHATES

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The properties of Tunisian phosphorite and Kola-apatite were studied after thermal treatment up to 1000°C. It was established that they preserved their reactivity unchanged during acidic treatment to give phosphoric acid and phosphoric fertilizers under the investigated experimental conditions.

The preliminary thermal treatment and grinding of natural phosphates are necessary stages in their effective treatment to give mineral fertilizers. It has been shown [1] that the heating of natural phosphates is a promising procedure for the removal of detrimental impurities. During the preliminary thermal and mechanical treatment, some of the properties, the structure and the phase composition are changed.

The aim of the present work was to establish some of the changes occurring during the thermal and mechanical treatment of Tunisian phosphorite and Kola apatite.

## Experimental

The thermal treatment was performed under isothermal conditions at 500 and 1000°, and the mechanical treatment was carried out in a planetary mill under conditions determined as optimal in previous investigations [2, 3]. The treated phosphates were chemically analyzed by methods of X-ray, differential thermal analysis and IR spectroscopy.

The soluble $P_2O_5$ was determined by extraction with 2% citric acid ($P_2O_5$*) and Peterman solution ($P_2O_5$**), and the reactivity (*R*) was measured in 30% $H_2SO_4$ solution. The electrokinetic parameters were determined by using a Z-potentiometer [4]. The particles of the initial phosphorite were below 0.063 mm, and the chemical composition was as follows:

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29.58% $P_2O_5$, 1.07% $B_2O_3$, 3.58% $SO_3$, 48.40% CaO, 1.88% $SiO_2$, 0.47% MgO, 1.38% $Na_2O$, 0.072% $K_2O$, 2.74% F, 0.056% Cl, 6.98% $CO_2$ and 1.79% insoluble residue.

## Results and discussion

The IR, X-ray and DTA results are presented in Figs 1-5. The intensity of the adsorption bands of the crystal water molecules at 3600 cm$^{-1}$ diminished with the increase of temperature, and those at 1440 cm$^{-1}$ characteristic of the carboxylic groups disappeared after thermal treatment at 1000°. The disappearance of $CaCO_3$ as an independent phase was confirmed by the powder diffraction data (Figs 3 and 4). With X-ray and IR methods, no changes were found in the structure of the main phases of hydroxyl- and fluorapatite for either phosphate.

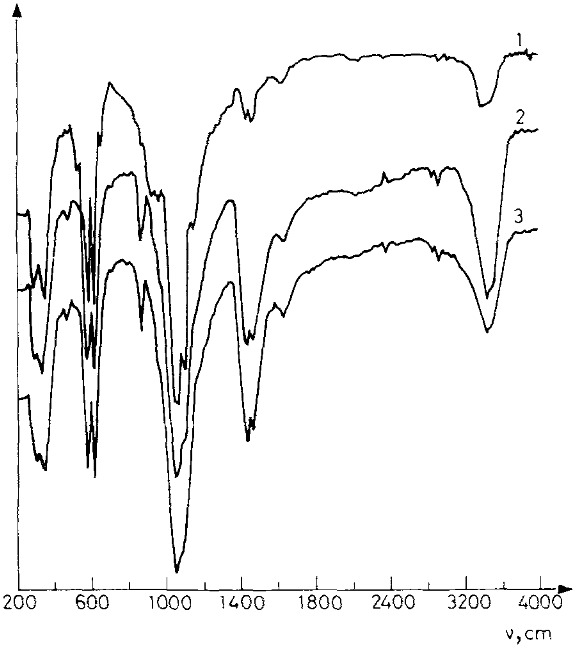

Fig. 1 IR of Tunisian phosphorite; 1 - 1000°C, 2 - 500°C, 3 - starting natural phosphate

The DTA of mechanically treated Tunisian phosphorite showed definite differences in the thermal properties in relation to the starting material

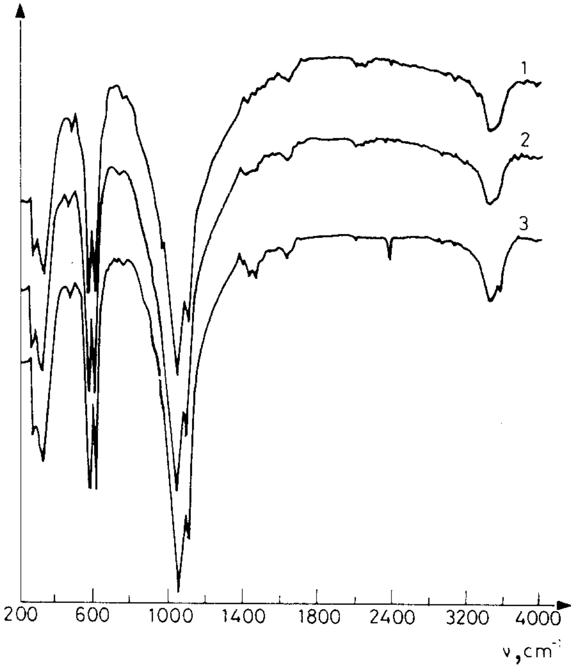

Fig. 2 IR of Kola apatite; 1 - 1000°C, 2 - 500°C, 3 - starting apatite

(Fig. 5). These changes were most marked for the temperature ranges, 200-500° and 700-900° temperature ranges. Obviously, the mechanical treatment caused changes in the structure in favour of the separation of volatile components of phosphorite at lower temperatures (200-300°), but it was probably also the reason for the accumulation of the energy which was discovered with the new-found exothermic effect at 820°.

The Tunisian phosphorite deposit contained more impurities and it was characterized by higher mass losses ($\Delta G$ = 8.8-10.4 weight % at 1000° ) and a fast decrease in the specific sufrace ($S$) with the increase of temperature, from 19.6 $m^2/g$ to 1.26 $m^2/g$. For the apatite, which was of magmic origin, these changes were much less. The mechanically treated Tunisian phosphorite had the highest contents of soluble $P_2O_5$, the highest reactivity ($R_S$), the highest electrical resistance ($r$) and the lowest mobility ($V_\varepsilon$) of the particles in aqueous suspension (Table 1).

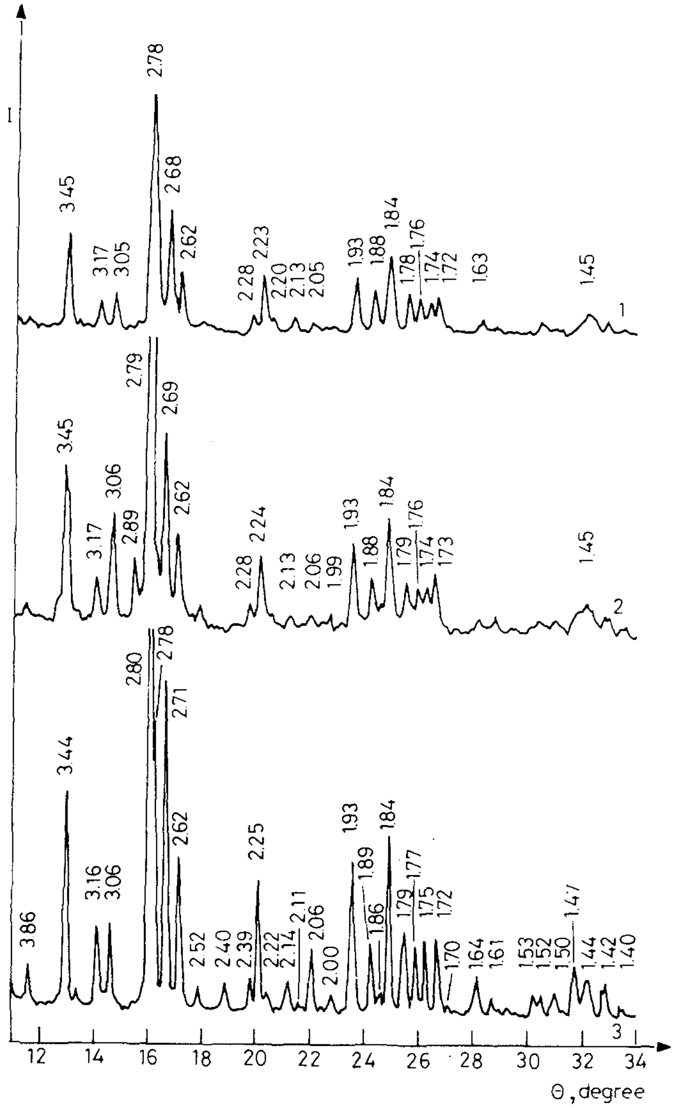

**Fig. 3** X-ray of Tunisian phosphorite; 1 - starting natural phosphate, 2 - 500°C, 3 - 1000°C

The data presented in Table 1 showed that they were strongly influenced by the mineral origin and the composition, as well as by the selected method and the conditions of thermal and mechanical treatment.

**Table 1** Some properties of Tunisian phosphorite and Kola apatite before and after thermal and mechanical treatment

| Param-eters | Dimen-sion | Tunisian phosphorite | | | | Kola apatite | | |
|---|---|---|---|---|---|---|---|---|
| | | NPh* | after 500°C | after 1000°C | NPh** | NPh* | after 500°C | after 1000°C |
| $P_2O_5$* | % | 9.76 | 9.08 | 6.16 | 20.77 | 3.50 | 2.32 | 3.10 |
| $P_2O_5$** | % | 0.30 | 0.27 | 0.27 | 7.78 | 0.33 | 0.29 | 0.27 |
| $\Delta G$ | % | | 3.50 | 8.80 | | | 0.10 | 0.20 |
| $R_s$ | % | 7.88 | 10.75 | 8.98 | 28.77 | 12.12 | 10.03 | 15.33 |
| $S$ | $m^2/g$ | 19.76 | 8.62 | 1.26 | 6.80 | 1.33 | 0.75 | 0.39 |
| $r$ | $\Omega$ | 2015 | 1438 | | 8285 | 21266 | | 21130 |
| $V_\varepsilon$ | $cm^2s^{-1}V^{-1}$ | 0.0112 | 0.0211 | 0.0216 | $3.9\cdot10^{-4}$ | $6.4\cdot10^{-4}$ | | $8.5\cdot10^{-4}$ |

Natural phosphate - NPh* = starting natural phosphate, Natural phosphate - NPh** = phosphate after mechanical treatment

## Discussion

It was obvious that the thermal treatment created a possibility for the removal of some detrimental impurities from the natural phosphates, which favoured their further treatment. When the thermal effect was combined with mechanical impact, the end temperatures were significantly lowered. This was explained by the sharp decrease in the specific surface. The absence of changes in the referred solubility ($P_2O_5$ **) and the real constancy of the reactivity ($R_S$) showed that the thermal treatment involved no changes in the apatite structure. Some changes occurred after the mechanical treatment, as confirmed by the data for $r$, $V_\varepsilon$ and $R_S$. The lower the values of $V_\varepsilon$ and the higher the values of $r$, the higher the solubility of the phosphate complex and its reactivity. The absence of a similar dependence between $S$ and $R_S$ allowed the conclusion that $R_S$ for the investigated phosphates wad directly connected with the internal energy and the crystal defects located on the external surface of the particles. This conclusion was in full agreement with the established correlation between the number of active centres on the internal surface of the particles and the reactivity of Tunisian phosphorite [4]. The magmic origin and the composition of the apatite resulted in relatively small changes in the properties during the process of its heating.

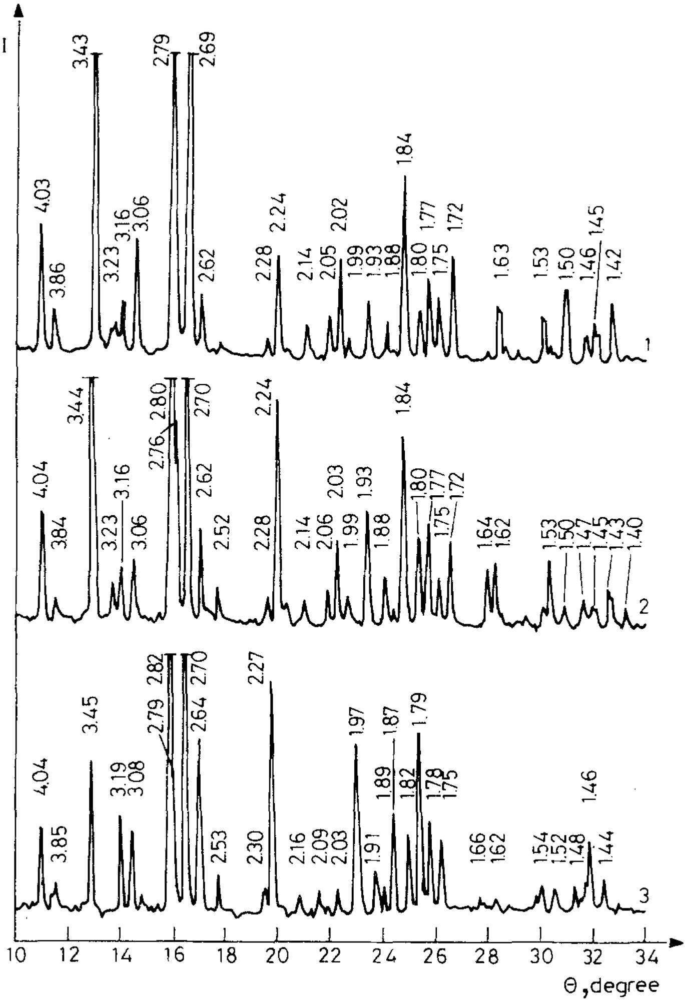

**Fig. 4** X-ray of Kola apatite; 1 - starting apatite, 2 - 500°C, 3 - 1000°C

## Conclusion

This investigation confirmed the possibility of monitoring the reactivity of the natural phosphates by appropriate thermal and mechanical treatment. A higher effectiveness was characteristic of the treatment of phosphates of sedimental origin, and the process depended strongly on their mineral origin.

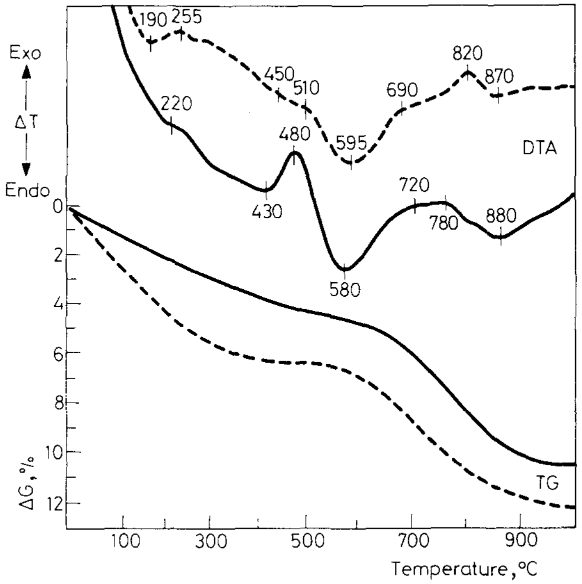

**Fig. 5** DTA and TG curves of sterting (—) and mechanically treated (- - -) Tunisian phosphorite in air with a heating rate of 10 deg/min

## References

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**Zusammenfassung** — Thermische Eigenschaften von tunesischem Phosphorit und Kola-Apatit wurden nach Erhitzen bis 1000°C untersucht. Es wurde festgestellt, daß ihre Reaktivität durch eine Säurebehandlung zu Phosphorsäure und Phosphordüngemitteln unter den untersuchten experimentellen Bedingungen nicht verändert wird.