The high energy milling effect on positional redistribution of CO_3-ions in the structure of sedimentary apatite

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Different types of isomorphic substitutions in the apatite structure are well known, as the substitution of PO_4 by CO_3-ion is the most common. This specifies the existence of various members of the apatite isomorphic series.

Carbonate-hydroxyl-flour apatite sample (B-type with Ca/P ratio >1.67) from Tunisia sedimentary phosphorite ore deposit are investigated.

The high energy milling is an environmentally friendly technological alternative for ore processing, to the conventional acid leaching methods. The high energy milling creates defects in the apatite structure with simultaneous accumulation of mechanic energy. The impact of the mechanical forces over the solids is mostly revealed through the changes of the quantities being related to the energetic stability and reactivity of the solid phase. Under high energy milling process the isomorphic substitution increases mainly ~~of~~ on the account of CO_2 and partly of water vapor.

Thermal with gas-mass analysis in the temperature interval 600–900 °C in air medium has been used to evaluate the achieved effect of the high energy milling on the positional redistribution of CO_3-ions and the structural phase-transformations occurring in the investigated sample. The experimental analysis shows liberation of CO_3-ions in three temperature stages with varying mass losses. Peaks intensities are determined from the high energy milling effect, the high temperature heating and the gas medium during the measurements.

Key words: high energy milling, apatite, structure.

INTRODUCTION

Different types of isomorphic substitutions in the apatite structure are well known. The end members of the apatite (Ap) isomorphic series are hydroxyl-apatite (HAp), flour-apatite (FAp) and chlorine-apatite (ClAp) [1–3]. Two types of substitutions are the most common: (i) PO_4 by CO_3-ions in tetrahedral position (B-type position of CO_3) and (ii) F^- by OH^- (Cl^-) and and vice versa in the channels located nearby the hexagonal crystallographic axes [2]. This specifies the existence of various members of apatite isomorphic series: carbonate-flour apatite (CFAp), carbonate-chlorine apatite (CClAp), carbonate-hydroxyl-flour apatite (CHFAp), etc. Under high energy milling process the isomorphic substitution increases mainly through incorporation of CO_2 and partly of water vapor [2, 4, 5].

Previously we investigated the phase transitions of sedimentary apatite ores from Tunisia and Syria, using Infra-Red spectroscopy (IR) and powder X-Ray Diffraction (XRD), and the results show the isomorphic transitions from B- to A-type apatite through positional migration of CO_3^{2-}-ions (from tetrahedral B-type to channel A-type position of CO_3, where CO_3 occupy the OH^-/F^- position in channels located nearby the hexagonal crystallographic axes [2]) and F^- additional incorporation of CO_2 from the air during the high energy milling [2, 4–6]. The incorporated CO_2 occupy the A-type position of CO_3. The high energy milling activation also leads to decreasing of samples particle size and formation of highly defective nano-particles with high degree of reactivity. The obtained nano-samples are undersized (amorphous) for investigation with powder XRD, so the identification of the phase composition is not possible by this method.

The aim of the study is to evaluate the achieved effect of the high energy milling on the possitional migration of CO_3-ions and the structural phase-transformations occurring in the investigated sam-

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ple – natural fluorine-apatite (FAp) from Tunisia using thermogravimetric and differential thermal analyses with attendant mass-spectrometer analysis of the gas phases.

MATERIALS AND METHODS

We investigated FAp (with Ca/P ratio >1.67) from Tunisia sedimentary phosphorite ore deposit [8, 9]. The chemical composition of the material includes (main components): 29.6% $P_2O_5^{total}$; from which assimilated (ass.) is 6.9% $P_2O_5^{ass}$ (by 2% citric acid); 3.5% F; 46.5% CaO; 0.55% R_2O_3 (R = Al, Fe); 1.1% SO_3; 1.9% SiO_2; 0.35% MgO; 0.05% Cl; 6.6% CO_2; moisture content 3.14% and a granulometric size of the particles of 0.8 mm. There are different forms of P_2O_5 – water-soluble, assimilable, and insoluble in water. They are reflected in the application of P_2O_5 as a phosphate fertilizers. The assimilable forms of $P_2O_5^{ass.}$ are insoluble in water but are soluble in soil solutions. Evaluation of the forms of P_2O_5 is performed on the basis of their solubility in the so-called conditional solvents – solution of ammonium citrate or 2% solution of citric acid. The choice of the reagent is based on its similarity with the soil solutions. In the resent years greater advantage is given to the assimilable fertilizers because their solubility is slower than that of the water-soluble ones and thus they feed the plants for a longer time. The method used for high energy milling is intended to enhance the transformation of the insoluble forms of P_2O_5 in $P_2O_5^{ass.}$.

The high energy milling activation was carried out in a planetary mill Pulverisette-5, Fritsch Co (Germany), for activation times 120 and 150 min, milling bodies of unalloyed steel, diameter of the milling bodies of 20 mm, and a sample weight 0.020 kg.

Thermogravimetric and differential thermal analyses (TG-DTG-DTA) were performed on a SETSYS2400 thermal analyzer (SETARAM, France) in the temperature range 20–950 °C in air medium, with a heating rate of 10 °C.min⁻¹ combined with an OmniStar mass-spectrometer.

RESULTS

Our previous powder XRD studies on untreated phosphorite ores from Tunisia have given evidence that the sample contains the following mineral phases: FAp, calcite and traces of quartz [10]. Our earlier IR measurements have confirmed that the investigated FAp actually is CHFAp B-type, where two types of isomorphic substitution take place: PO_4^{3-}-group by CO_3^{2-}-ions and F^- by OH^--ions [5, 11, 12, 13]. The thermal decomposition mechanism of untreated sample is described in details elsewhere [9, 11–13]. In this work we are focused on the thermal reactions in the temperature interval 600–900 °C only, where decarbonization of CO_3-ions from the CHFAp-structure and impurity carbonate-containing phases occurs.

The obtained results of the present thermal investigations are shown on Figs 1–3 and in Table 1.

Table 1 shows the results from the thermal experiments (temperature data for the inflex points) together with calculated mass losses for the three samples: untreated (TF0), high-energy milled for 120 min (TF120) and for 150 min (TF150), respec-

Table 1. Multi-peak fitting of dTG-curves for untreated and high energy milled samples within the temperature interval 600–850 °C

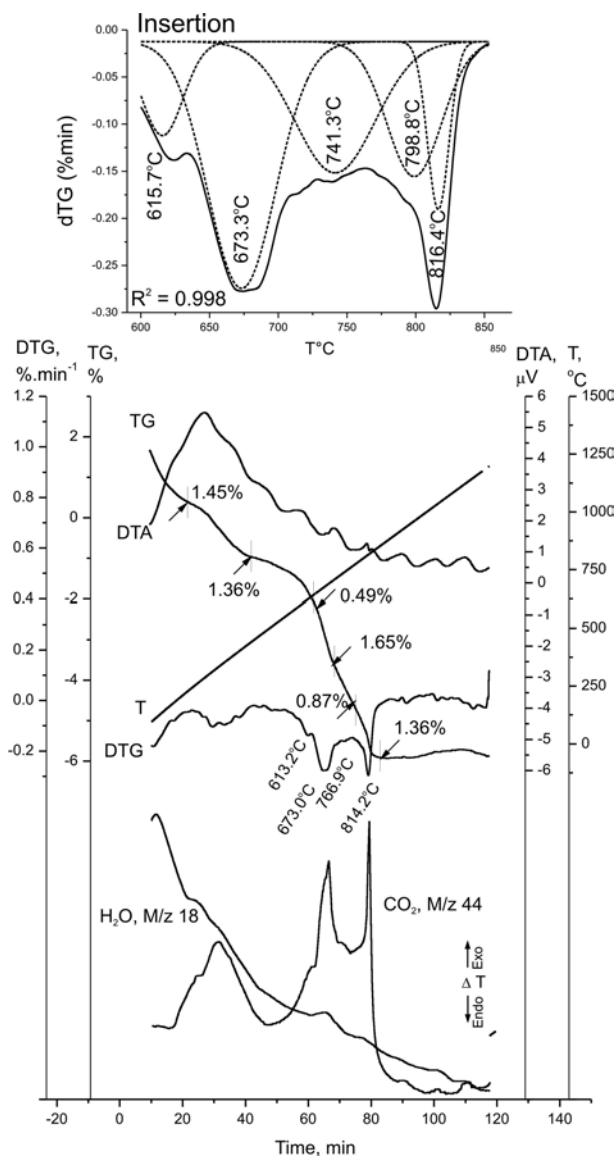| Thermal decomposition of mineral phases	Activation time (min)								
	Untreated apatite (TF0)			120 (TF120)			150 (TF150)		
	Peak position, T °C	Peak area	ML*, %	Peak position, T °C	Peak area	ML, %	Peak position, T °C	Peak area	ML, %
A-type CHFAp		–	–	613.73	–3.73	0.49	630.32	–3.82	0.52
B-type CHFAp	701.2	–18.54	1.70	673.28	–16.22	1.65	692.16	–14.45	0.84
							720.16	–1.10	0.50
CaMgCO₃ (dolomite)	724.0	–1.68	0.80	741.32	–10.19	0.87	741.97	–4.70	0.70
CaCO₃ (calcite)	773.7	–8.47	1.66				770.67	–5.81	0.91
A-B type CHFAp	–	–	–	798.85	–7.14	0.55	810.1	–3.8	0.46
				816.40	–3.50	0.81	828.5	–5.2	0.86
		Sum	4.23		Sum	4.37		Sum	4.06

* Mass losses
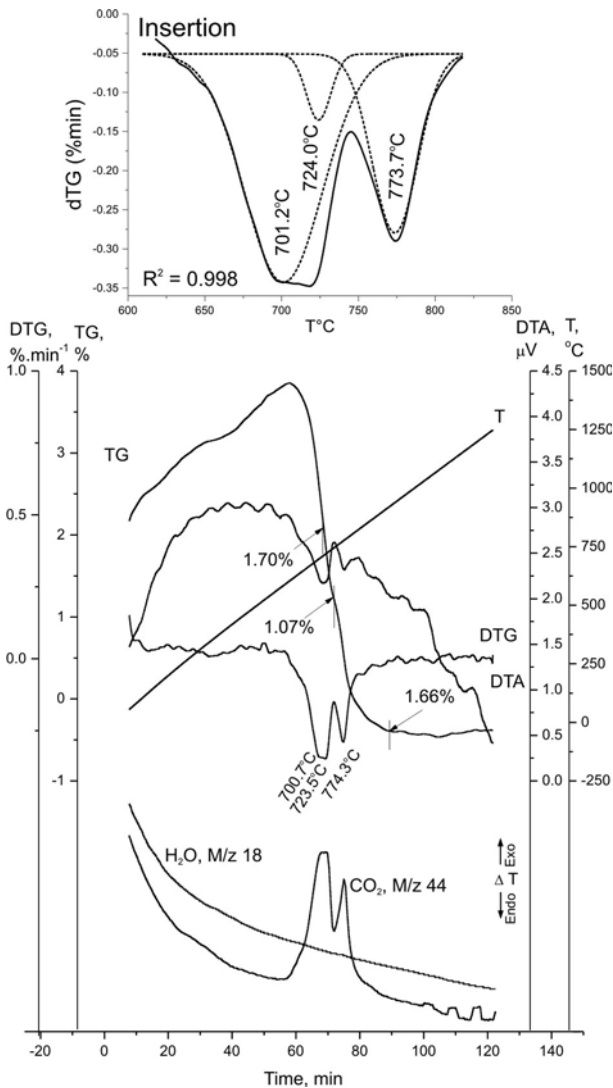
Fig. 1. Thermal with gas-mass analysis of TF0. *Insertion*: Multi-peak fitting (dashed line) of dTG in temperature interval 600–850 °C.

dTG-curves is made and the results are presented as insertions in the figures.

DISCUSSIONS

Within the investigated temperature range (600–850 °C) the decarbonization from CHFAp – B-type, calcite and dolomite occurs [2, 7, 9, 11–13]. For sample TF0 (Fig. 1), peak situated at 701 °C corresponds to decarbonization of CHFAp – B-type positions, the peak at 724 °C – to CO_3 –ions from dolomite and the peak at 773 °C – to CO_3–ions from

tively. There exist three main temperature intervals for TF0, where thermal reactions are accompanied by mass losses as following: 1.70% between 650–720 °C, 1.07% between 720–770 °C and 1.66% between 770–850 °C. At high energy milled samples appear two new temperature ranges 620–650 °C and 770–850 °C. The range 770–850 °C coincides with the third range for the TF0 (770–850 °C) but differs in new thermal reactions proven in a thermal dependencies (TG, dTG, dTA) and mass losses. The analysis of thermal dependencies for TF120 and TF150 shows overlapping of the thermal reactions. The gas-mass analysis shows existence of CO_2 in all samples (Figs 1–3) and H_2O – only for the TF120 (Fig. 3). For more detailed visualization of these processes, the Gauss decomposition of the

Fig. 2. Thermal with gas-mass analysis of TF120. *Insertion*: Multi-peak fitting of dTG in temperature interval 600–850 °C.
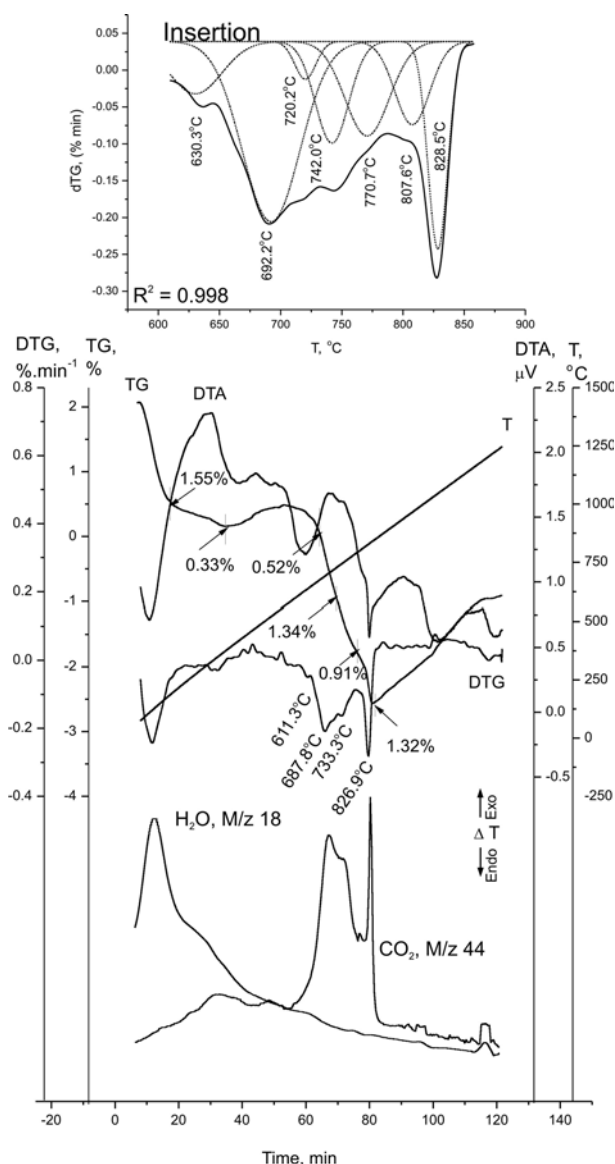
Fig. 3. Thermal with gas-mass analysis of TF150. *Insertion*: Multi-peak fitting of dTG in temperature interval 600–850 °C.

calcite (Table 1). The decarbonization of B-type position proceeds at lower temperatures because of the weak chemical bonds in CHFAp, predetermined by isomorphism of PO_4 by CO_3, as the ionic radii of PO_4-group is bigger than that of CO_3-ion [2].

The high-energy milled samples changed the temperature of decarbonization in comparison to TF0:

– for the ions of B-type position: in TF120 temperature decreases, whereas in TF150 the temperature increases and splitting of dTG-peaks is observed (Table 1, Figs 2–3);

– for calcite and dolomite: in TF120 the temperature decreases, and falls down in the area where overlay of the process is observed; in TF150 the temperature increases and splitting of the dTG-peaks is observed (Table 1, Figs 2–3).

The sum of the peaks areas and mass losses are nearly constant which is determined from the permanent quantities of the mineral phases in the experiment. The temperature changes during the decarbonization process can be explained with the alterations of the particle sizes of the samples after the high energy milling activation. At the beginning of the milling stage, the particles reach nanosize [4, 6, 10], the next stages of milling are followed by particle agglomeration. The increasing level of agglomeration depends contrariwise on the specific surface area and determines: (i) diffusion difficulties in the thermal decomposition and (ii) splitting of the dTG-peaks and increasing of decarbonization temperatures.

During the thermal experiments of high energy milled samples new peaks situated in the two temperature intervals appear: 590–630 °C and 770–850 °C.

The peaks in the interval 590–630°C are assigned to be due to decarbonization of weakly bonded ions in the apatite structure. According to literature [2, 3, 14–16] and our previously published data [5, 6, 10] it is known that in this temperature interval the decarbonization of CO_3-ions from the A-type apatite occurs, where these ions substitute OH^--groups in the channels with weak bonds. It is important to note that mass losses are nearly 0.50% and are constant and independent from the activation time of the samples. It could be explained with the incorporation of CO_2 from the air, but in limited quantities, uncontrolled by the activation time.

The peaks situated in the 770–850 °C temperature range are a result from the emission of CO_3-ions, as evidenced by the gas-mass analysis. Until now, it was thought that at these temperatures OH^--groups replacing F^--ions in the apatite structure are released. As it has already been reported [3, 5, 17] these peaks originate from the decarbonization of mixed A-B-type apatite [3, 15]. In mixed A-B-type apatite substitution of PO_4 and Ca-vacancy by CO_3-ions occur. That type isomorphism influences the length of the Ca-O-bonds, and the degree of substitution depends on the activation time (i. e. size of the particles) and water presence [2]. That is why, the mass loses of TF120 are bigger than those ones of TF150. The splitting of the dTG-peak of TF150 could be explained with liberation of CO_3-ions from different crystallographic positions. The diffusion difficulties of TF150 are caused by particle agglomerationas manifested by the increased temperature of decarbonization and the decreased mass loses.

The TG-dTA-dTG analysis of untreated and activated samples (Figs. 1–3) reveals that the decomposition runs after the following main reaction:

- 590–630 °C – decarbonization of CO_3^{2-} from A type positions of CHFAp
- 660–710 °C – decarbonization of CO_3^{2-} from B type positions of CHFAp
- 730–770 °C – $CaCO_3 = CaO + CO_2$
- 770–30 °C – decarbonization of CO_3^{2-} from A-B type positions of CHFAp
- >850 °C – $Ca_{10}FOH(PO_4)_6 = 2Ca_3(PO_4)_2 + Ca_4P_2O_9 + HF$
  $Ca_3(PO_4)_2 + 2CaO + SiO_2 = Ca_3(PO_4)_2.Ca_2SiO_4$

CONCLUSIONS

High energy milling activation causes structural and phase changes in the studied samples.

(i) The gas-phase analysis, clarified the mechanism of chemical reactions and isomorphic substitutions as a result of the high energy milling: all samples absorbed CO_2 from the air, as the TF120 exhibits the highest level of absorption, which is controlled from the specific surface area of the powdered samples and does not depend on the structural type.

(ii) The formation of two new apatite phases – CHFAp-A and A-B-types via isomorphic substitution of CO_2–ionsis detected. Their existence is evidenced by gas-mass analysis.

(iii) The temperature ranges and mass-losses for each particular isomorphously substituted apatite phase are determined and this new information supplements the existing up to now data.

(iv) The isomorphic substitution is a result from the obtained defects and energy-metastable structure condition achieved via high-energy milling.

(v) The activation effect in different samples has no functional dependence with the high energy milling activation time, because of agglomeration processes.

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ЕФЕКТ ОТ ИНТЕНЗИВНО ЕНЕРГИЙНО СМИЛАНЕ
ВЪРХУ ПРЕРАЗПРЕДЕЛЕНИЕ НА КАРБОНАТНИТЕ ЙОНИ
В СТРУКТУРАТА НА СЕДИМЕНТЕН АПАТИТ

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(Резюме)

Изследван е седиментационен карбонат-хидроксил-флуор апатит (B-type) от Тунис. За повишаване на химичната реакционна способност на апатита е използван сух метод за високоенергетична активация в планетарна мелница.

Този метод се прилага като алтернатива на киселинните методи за преработване на фосфатни суровини за получаване на фосфорни торове и неорганични киселини. Под влияние на сухата активация се извършва внедряване на на CO_2 и водни пари от въздуха в в различни кристалографски позиции в подрешетката на апатита – във ваканциите на Ca^{2+} или замествайки частично F. Изоморфните замествания са анализирани чрез термичен метод с анализ на изходящите гозаве с масспектрометър. Доказва се изоморфно заместване на карбонатни йони с образуване на A-type и A-B type и са определени температурните интервали и масови загуби на отделните типове изоморфно заместени фази на апатита.