

## STRUCTURE AND THERMAL BEHAVIORS OF MOROCCAN PHOSPHATE ROCK (BENGURIR)

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Moroccan phosphate ores have important phosphate reserves, thus makes possible to distinguish three main layers: submittal, principal and basal. A characterization of the ore was carried out to determine the mineralogical and chemical characteristics. Thermal analysis, infrared and NMR techniques were used to study the thermal and structure behaviors of the organic matter in Moroccan phosphate from Bengurir. The TG analysis showed that the investigated mineral exhibited 7 mass% as total mass loss. The calcination-separation enrichment of carbonate-phosphorite ores from Bengurir region (Morocco) has been studied.

**Keywords:** natural phosphate, structure, thermal properties

### Introduction

Phosphate rocks are complex raw materials and mainly used in the manufacture of phosphoric acid and phosphate fertilizers [1–4]. The composition of these rocks varies from one deposit to another, which are primarily composed of the apatite groups in association with a wide assortment of accessory minerals, mainly fluorides, carbonates, clays, quartz, silicate, and metal oxides. Fluoroapatite is a common source of Moroccan natural phosphates, because it is the most stable and insoluble of all calcium phosphates [5, 6]. It occurs in a wide range of substituted forms, both biological and mineralogical. The presence of carbonates and silica in Moroccan phosphate rocks usually requires additional acidulent (sulphuric acid) during the manufacture of phosphoric acid. Much works have been carried to reduce carbonate content of phosphate rocks by flotation and calcination processes [7–9]. Depending on the efficiency of the process, calcination may lead to almost complete disposal of the carbonates present in the phosphate rock, while the silica and other oxides as impurities. The thermal behaviors of natural phosphate of the Morocco depend on its composition. In fact, the association of carbonates with phosphates has been investigated [10–12]. The degree of substitution in phosphates ores affects the stability of the layer and consequently influences the solubility of the mineral in aqueous environments [13]. The present investiga-

tion was conducted to identify the possible environments of carbonate, phosphorus and silicon in Moroccan phosphate using high-resolution MAS-NMR technique, which is representative of the complexity of the problem and of its importance. To study the structural changes, the phosphate mineral was heated at different temperatures and the thermal properties were carried out by TG/DTA analyses. Using the calcination process, it is possible to obtain a phosphate product with high P<sub>2</sub>O<sub>5</sub> recovery, depending on the conditions of the heating as well as the nature and the size of the raw phosphate used for the heating process. The phosphate rock used in this study comes from the Bengurir ores located in the south of Morocco.

### Experimental

Phosphate samples used here come from an extracted ore of Bengurir (Morocco). Prior to use this material requires initial treatments such as crushing and washing. The fraction of 100–400 μm grain size was washed with distilled water several times to remove the soluble matter. Then, the chemical composition was determined as: Ca (37.84%), P (15.03%), F (3.07%), Si (1.78%), S (0.78%), Na (0.79%) and other negligible elements. The resulting solids were characterized using X-ray powder diffraction (Philips PW131 diffractometer).

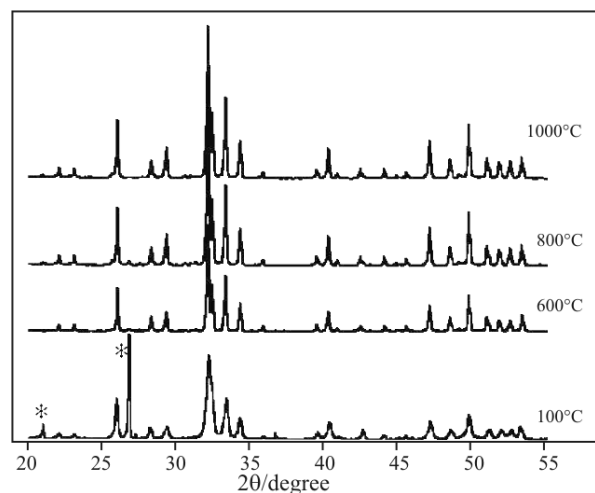
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Infrared spectra were recorded at a  $2\text{ cm}^{-1}$  resolution from  $400$  to  $4000\text{ cm}^{-1}$  on a Brüker IFS 66v Fourier transform spectrometer using KBr pellets.  $^{29}\text{Si}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  MAS-NMR spectra were recorded on a Bruker MSL 300 spectrometer equipped with an Andrew type rotor rotating. Thermogravimetric and differential thermal analyses were carried out simultaneously in airflow using a TA Instruments Netzsch STA-409EP apparatus. The temperature range is from  $30$  to  $1200^\circ\text{C}$  at various heating rates. Scanning electron microscopy was performed on carbon-coated samples using a Cambridge Stereoscan 120 instrument at an accelerating voltage of  $10\text{ kV}$ . Nitrogen adsorption isotherms were recorded at  $77\text{ K}$  using a Micromeritics ASAP 2010 instrument. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method using adsorption data in the relative pressure range from  $0.05$  to  $0.25$  whereas the pore size and volume were estimated using the Barret–Joyner–Halenda (BJH) approximation.

## Results and discussions

### Structure characterization

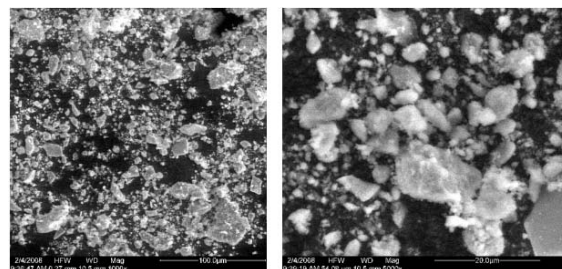
The crystallographical structure of Natural Phosphate from Bengurir- Morocco (noted NP-BM) was examined by XRD patterns at different temperatures of the calcination (Fig. 1). The high intensity of XRD peaks indicates that NP-BM powder has a high crystallinity. Therefore, the diffractograms of raw material show a mixture of two main phases (apatite and  $\text{SiO}_2$ -quartz). We note that no other phases such as calcite, fluorine and dolomite are observed in the NP-BM ores opposite to other Moroccan phosphorites cited in the litera-



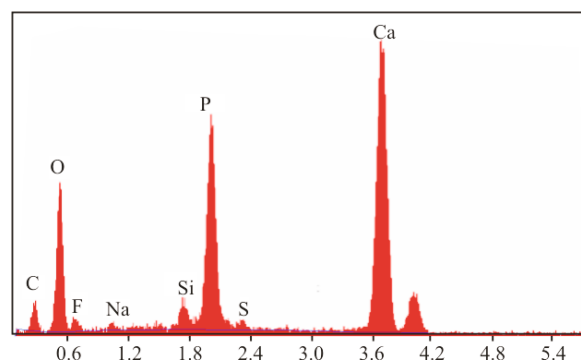
**Fig. 1** XRD patterns of NP-BM mineral showing the evolution of the natural phosphate structure with the calcination temperature

ture [1, 14, 15]. In heating NP-BM sample at the temperature up  $600^\circ\text{C}$ , it shows a single apatite phase and the absence of reflections due to any  $\text{SiO}_2$  crystalline forms. The analysis of the XRD data suggests two possibilities: (i) transformation of quartz to amorphous silica and (ii) silicon substitutes into the calcium phosphate lattice resulting in a silicon-substituted apatite, when the carbonates are leaved from apatite structure at the sintered temperature above  $600^\circ\text{C}$ . This modification of the chemical composition is accompanied by a reorganization of the apatite structure indicating the absence of calcium carbonate  $\text{CaCO}_3$  in raw material, contrary to that reported by Aouad *et al.* [14, 15] that it found many additional phases such as fluorine, calcite and dolomite, which cause very important changes in the thermal characteristics of the phosphate mineral. The significant structural changes were recognized between  $600$  and  $1000^\circ\text{C}$ . The SEM micrographs of the phosphate rock are illustrated in Fig. 2, composed of irregular particles, which have a strong tendency to aggregate. Figure 3 depicts the EDAX analysis of plate-like shaped phosphate, which confirms the previous chemical analyses. The specific surface area is  $21\text{ m}^2\text{ g}^{-1}$  very lower than synthetic apatites [16], whereas there are two types of the pore diameter ranging of  $2\text{--}5$  and  $7\text{--}15\text{ nm}$ .

Fourier transform infrared spectroscopy shows the absorption bands at  $571$ ,  $601$ ,  $962$ ,  $1046\text{ cm}^{-1}$  rela-

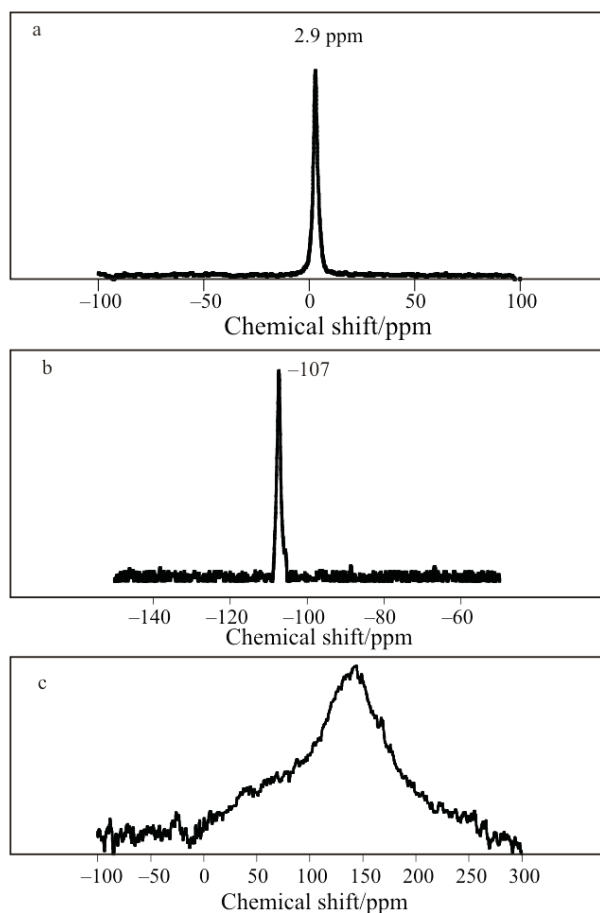


**Fig. 2** MEB images of natural phosphate particles from Bengurir (NP-BM)



**Fig. 3** EDAX analysis of natural phosphate rock from Bengurir (NP-BM)

tive to the  $\text{PO}_4$  groups, in close proximity to those of synthetic calcium fluoroapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$  [3, 9, 17]. FTIR spectrum of NP-BM (not shown) also shows sharp intense peaks at 1458, 1430 and  $871\text{ cm}^{-1}$ , which may be attributed to the presence of the  $\text{CO}_3$  groups. No broad bands around 3600 and  $630\text{ cm}^{-1}$  due to the OH groups are detected, indicating that the NP-BM mineral is a carbonaceous fluoroapatite. However, the appearance of peaks at 1800, 1640, 790, 690 and  $648\text{ cm}^{-1}$  indicates the presence of trace contamination of residual organic matter in NP-BM material as reported elsewhere [18, 19]. At the heating temperature up  $600^\circ\text{C}$ , the bands assigned to organic matter species were disappeared. In order to obtain further information on the conformation and the bonding nature of phosphorus, silicon and carbon in Moroccan phosphate rock, the solid-state MAS-NMR measurements have been performed (Fig. 4). A single peak of phosphorus (vs.  $\text{H}_3\text{PO}_4$ ) at 2.9 ppm is observed (Fig. 4a), which relied to one crystallographic site such as obtained, in synthetic apatite [20, 21]. This result confirms the single phosphate phase (apatite) and no other phosphate phases

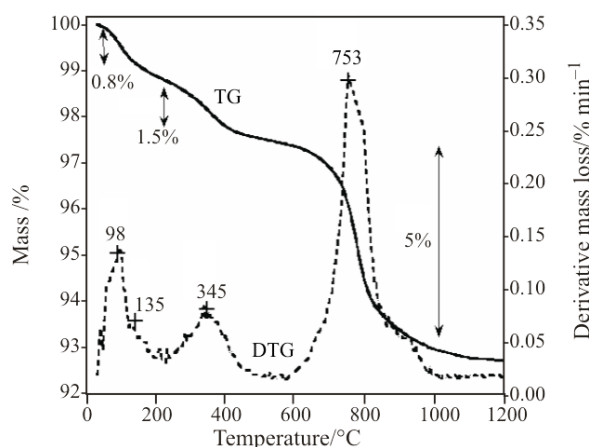


**Fig. 4** MAS-NMR spectra obtained from Moroccan phosphate rock (NP-BM): a –  $^{31}\text{P}$  MAS-NMR, b –  $^{29}\text{Si}$  MAS-NMR, c –  $^{13}\text{C}$  MAS-NMR

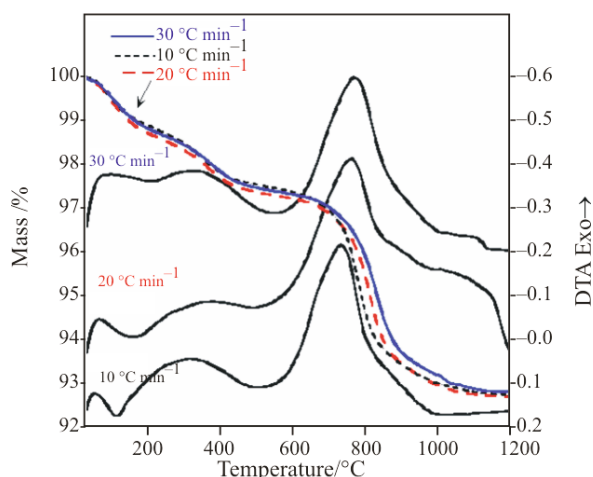
such as  $\text{Ca}_3(\text{PO}_4)_2$ . Other single peak of  $^{29}\text{Si}$  MAS-NMR is observed at  $-107\text{ ppm}$ , characteristic to the presence of quartz [22] in natural phosphate and no other silicate forms containing NP-BM sample (Fig. 4b). The  $^{13}\text{C}$ -MAS NMR spectrum of carbonate-containing NP-BM phosphate is shown in Fig. 4c, which shows many broadening peaks at 40.8, 66, 88, 132, 142.2, 149, 169 and 175 ppm. It appears that several possibilities are provided for the carbonate environments, which can replace phosphates (type B) and/or hydroxide ions (type A). The  $\text{CO}_3$  substituted  $\text{PO}_4$  (type B) may occupy three non-equivalent crystallographic positions related to the occupancy of the four tetrahedral oxygen sites such as reported in bone and synthetic apatite characterization [23, 24]. The peaks 40–150 and 180–240 ppm correspond to the organic carbon environments such as demonstrated by IR spectroscopy.

#### Thermal analyses

Thermal analysis techniques were used to get the further stability properties. The TG and its derivative DTG curves of NP-BM are presented in Fig. 5. Three main thermal effects are observed in TG curves. A small mass loss of 0.8 mass% is observed before  $118^\circ\text{C}$  assigned to water physical desorption, whereas the second from  $118$  to  $420^\circ\text{C}$  (with 1.5 mass% as mass loss) is due to the simultaneous elimination of the chemical water in the structure and the decomposition of organic matter adsorbed onto apatite layer. The final thermal event takes place between  $420^\circ\text{C}$  and  $1000^\circ\text{C}$  with 5 mass% as mass loss, corresponding to which the major of this loss may be due to decomposition of the mineral carbonates present in the sample as indicated by FTIR and  $^{13}\text{C}$ -NMR spectroscopy. These results demonstrate that by raising the temperature, over  $600^\circ\text{C}$ , the mass loss continues and it is not completed



**Fig. 5** TG/DTG curves of phosphate rock (NP-BM) (heating rate at  $10^\circ\text{C min}^{-1}$ )



**Fig. 6** Simultaneous TG/DTA analysis of Moroccan phosphate at various heating rates (10, 20 and 30°C min<sup>-1</sup>)

even at 1000°C. These data confirmed that the optimum temperature interval for calcination of the NP-BM material is 1000°C. The thermal analysis data also confirmed the formation of stable material from the NP-BM sample pre-heated to 1000°C to form calcium fluoroapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub> such as proved by XRD technique (Fig. 1). Figure 6 shows the simultaneous TG/DTA curves of NP-BM sample at the heating rates of 10, 20 and 30°C min<sup>-1</sup>. For given temperature interval, the extent of decomposition is found greater at a slower rate of heating than for a similar sample heated at a faster rate. This small difference is due to the shorter exposure time to a particular temperature at a faster heating rate. We should be noted that although the decomposition temperatures are changed with heating rate, the mass losses remained nearly same. The endothermic peaks in the differential thermal analysis (DTA) curves (Fig. 6) located at low temperature (100–200°C) can be attributed to the evaporation of physically bound water adsorbed onto phosphate surface. The changes that take place with carbonates during calcination of carbonaceous phosphates can be divided into two stages: (1) dehydrated physical and chemical waters and (2) combustion of different type of organic and inorganic carbons to form fluoroapatite such as confirmed by XRD technique. Aouad *et al.* [1, 14, 15] have studied the thermal analysis of sedimentary Moroccan phosphates from Youssoufia deposit, in which the total mass loss has 20.8 mass% using 10°C min<sup>-1</sup> as heating rate, that higher value that obtained, in this study, for Bengurir phosphates (~7%), in which the content of the organic matter varies from one deposit to another. The small content organic matter demonstrated by TG analysis is in good correlation with the absence of some additional components such as calcite and dolomite, which can affect the thermal properties [25, 26]. However, the

little amount of organic matter with unique phosphorite phase can be an advantage for phosphoric acid production. A simple thermal treatment at 600°C can produce a phosphorus gain with no mass production such as found in many sedimentary phosphate ores. These suggestions will be detailed in our future studies on this phosphate ores.

## Conclusions

In this study, structural and textural properties of natural phosphate from Bengurir (Morocco) are presented. We have shown that the NMR spectroscopy can be a helpful adjunct to XRD and IR techniques in ascertaining the state of characterization of natural phosphate. In the examination of this phosphate, the XRD results indicate the presence of two inorganic components (apatite+quartz-SiO<sub>2</sub>), but give no indication for any remaining organic material or of relative amounts. NMR spectroscopy has identified the environments of phosphorus, silicon and carbon elements containing NP-BM material. The thermal analysis has shown that small quantity of the organic component is actually still present (7 mass%) compared to other sedimentary phosphates. Via the thermal treatment of natural phosphate, it was verified that the structure change and the thermal stability can be in relation with the phosphorus (P<sub>2</sub>O<sub>5</sub>) amount and therefore of the solubility in acid solution.

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