

## A thermoanalytical study of synthetic carbonate-containing apatites <sup>☆</sup>

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### Abstract

Two series of carbonate-apatites,  $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{F},\text{OH})_2$ , were synthesized by precipitating them from aqueous solutions followed by ripening at the precipitation temperature (20 or 80°C). Initial solutions contained  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  ions; in the second series  $\text{Na}^+$  was added. The samples had low crystallinity but, nevertheless, showed the apatite structure as judged from XRD and IR. Thermal degradation was followed by simultaneous TG/DTA and TG/EGA (evolved gas analysis) methods and by ex situ studies.

The  $\text{NH}_4^+$ -containing samples (A, 20°C and B, 80°C) and two  $\text{Na}^+$ -containing samples (C and D, both at 80°C) were subjected to a detailed study. On the basis of EGA studies of sample A by FTIR, the first two exothermic peaks at 250–300°C could be assigned to the release of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O} + \text{NH}_3$ , respectively; the remaining three at 350–710°C were due to  $\text{CO}_2$  evolution and changes in the apatite structure. For samples synthesized at 80°C, the DTA peaks were smaller than for sample A. The EGA peak due to  $\text{NH}_3$  was missing for  $\text{Na}^+$ -containing samples (C and D). For all samples, the residue at 1000°C had the hydroxy-fluorapatite structure. The TA and XRD data indicate that the crystal structure of the precipitated apatites is relatively labile. After the release of volatiles, however, thermally induced rearrangements take place leading to a more stable and crystalline phase.

*Keywords:* Apatite; Carbonate; Crystallinity; DTA; EGA; TG

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<sup>☆</sup> Presented at the 14th Symposium on Thermal Analysis and Calorimetry, Oslo, Norway, 15–17 June 1994.

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## 1. Introduction

Apatite samples synthesized by the wet route are used as reference materials for biological apatites and for studies of the genesis, metamorphosis and processing of natural phosphates. In addition, they are important for various technical applications such as adsorbents, ion exchangers, catalysts, etc. The chemical activity and thermal stability of these apatites are significantly influenced by substitutions in the crystal lattice [1–4]. Several substitutions in the apatite structure are possible including both cationic and anionic sites. The most common are the substitutions of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  for  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$  and  $\text{HPO}_4^{2-}$  for  $\text{PO}_4^{3-}$ , and  $\text{F}^-$  for  $\text{OH}^-$  [5,6]. Furthermore, in carbonate-apatites (CAp) the carbonate ion can be present at two different sites in the apatite lattice. Thus, in apatites formed at high temperature,  $\text{CO}_3^{2-}$  substitutes for  $\text{OH}^-$  (A-type CAp), while in the precipitated apatites it substitutes mainly for  $\text{PO}_4^{3-}$  (B-type CAp) [7,8]. The incorporation of carbonate and magnesium into the apatite causes a decrease in crystallinity and, as the bonding in the apatite becomes weaker, the chemical reactivity in these apatites is increased [9,10]. However, fluorine and sodium stabilize the crystal structure and effectively compensate for the disorder caused by carbonate inclusion [2,3]. The possibility of incorporation of nitrogen-containing ions into the apatite structure has also been reported [11].

The thermal decomposition reactions of CAp have been mainly studied by the analysis of solid phase composition changes [9,12,13]. In the present work, synthetic apatites with different compositions were studied in order to investigate the role of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  ions in the formation and thermal stability of the CAp structure. Various thermoanalytical methods (simultaneous TG/DTA, evolved gas analysis) were employed together with X-ray powder diffraction and IR spectroscopy in the characterization of precipitated and subsequently calcinated apatite samples.

## 2. Experimental

### 2.1. Synthesis

CAp with partial substitution of  $\text{Mg}^{2+}$  and  $\text{Na}^+$  for  $\text{Ca}^{2+}$  were prepared by precipitation from an aqueous solution at 20 and 80°C. Equal volumes of two solutions, namely 1, containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{NO}_3^-$  ions, and 2, containing  $\text{PO}_4^{3-}$ ,  $\text{F}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{NH}_4^+$  ions, were added, simultaneously and dropwise, over 2 h to an  $\text{NH}_4\text{NO}_3$ – $\text{NH}_4\text{OH}$  solution with an initial pH of 9.7 (Table 1). The pH was maintained between 8 and 10 by the occasional addition of concentrated  $\text{NH}_4\text{OH}$  solution. After that, the suspension was stirred for 3 h at the precipitation temperature in order to improve the homogeneity and crystallinity of the precipitate, and finally kept at room temperature for 24 h when precipitated at 80°C, and for 30 days when precipitated at 20°C. The precipitates were filtered, washed thoroughly with distilled water to free them from soluble salts, and dried at 100°C.

Table 1  
The conditions for synthesis and chemical composition of precipitated apatites, dried at 100°C

	A	B	C	D
Initial mole ratios of components in solution				
Ca <sup>2+</sup>	8	8	6	6
Mg <sup>2+</sup>	2	2	2	1
Na <sup>+</sup>	–	–	2	3
PO <sub>4</sub> <sup>3-</sup>	6	6	6	6
F <sup>-</sup>	2	2	2	2
CO <sub>3</sub> <sup>2-</sup>	2	2	4	5
Chemical composition of products in wt%				
CaO	38.3	38.4	41.4	46.7
MgO	11.7	11.5	10.1	5.9
NH <sub>3</sub>	1.6	1.2	–	–
Na <sub>2</sub> O	–	–	0.8	1.2
P <sub>2</sub> O <sub>5</sub>	42.5	43.5	42.6	41.3
F	2.9	2.9	3.2	2.9
CO <sub>2</sub>	2.0	1.3	1.4	2.0
H <sub>2</sub> O	6.5	6.1	5.6	3.8

Synthesis conditions: A, 20°C, 30 d; B, 80°C, 24 h; C, 80°C, 24 h; D, 80°C, 24 h.

## 2.2. Analysis

The synthesized apatites were analysed for Ca, Na, Mg, P and F. The chemical composition was determined by using flame spectrophotometry (Na, analytical error  $\pm 3\%$ ), atomic absorption spectrometry (Mg,  $\pm 3\%$ ), colorimetry (P,  $\pm 2\%$ ) and titration with MnO<sub>4</sub><sup>-</sup> (Ca,  $\pm 2\%$ ). The fluorine content was determined by an ion-selective electrode from the solution obtained by hydrothermal destruction of the sample and the subsequent absorption of evolved HF into the water (analytical error  $\pm 3\%$ ). CO<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub> contents were obtained from thermogravimetric (TG) and evolved gas analysis (EGA) measurements carried out with a Bomen TG/Plus instrument consisting of a DuPont 951 thermobalance coupled to a Bomen MB 102 FTIR analyser. The samples (100 mg) were heated in a helium flow of 900 ml min<sup>-1</sup> up to 105°C at the rate of 10°C min<sup>-1</sup> where the temperature was held for 5 min. Thereafter the temperature was increased at the same rate to 1000°C. The evolving gases were analysed and measured quantitatively by the FTIR spectrometer. The specific area of the samples was determined by the BET method using an EMS-53 sorptometer.

The X-ray powder diffraction patterns were recorded by a Philips MPD 1880 diffractometer using copper K $\alpha$  radiation. The X-ray diffractograms were recorded for the precipitated apatites dried at 100°C and for samples heated up to 1000°C. The FTIR absorption spectra (4000–400 cm<sup>-1</sup>) were obtained in a Nicolet Magna-IR 750 instrument using the KBr pellet technique. Simultaneous TG and DTA measurements in the temperature range up to 1000°C were carried out in a Seiko

Table 2

Calculated molecular formulae of the synthesized apatites, dried at 100°C

Sample	Molecular formula
A	$\text{Ca}_{6.37}\text{Mg}_{2.70}(\text{NH}_4)_{0.88}(\text{HPO}_4)_{0.56}(\text{PO}_4)_{5.02}(\text{CO}_3)_{0.42}\text{F}_{1.43}(\text{OH})_{0.57} \cdot 3.08\text{H}_2\text{O}$
B	$\text{Ca}_{6.45}\text{Mg}_{2.70}(\text{NH}_4)_{0.67}(\text{HPO}_4)_{0.75}(\text{PO}_4)_{4.97}(\text{CO}_3)_{0.28}\text{F}_{1.44}(\text{OH})_{0.56} \cdot 2.82\text{H}_2\text{O}$
C	$\text{Ca}_{7.01}\text{Mg}_{2.37}\text{Na}_{0.25}(\text{HPO}_4)_{0.69}(\text{PO}_4)_{5.01}(\text{CO}_3)_{0.30}\text{F}_{1.58}(\text{OH})_{0.42} \cdot 2.60\text{H}_2\text{O}$
D	$\text{Ca}_{8.00}\text{Mg}_{1.40}\text{Na}_{0.36}(\text{HPO}_4)_{0.41}(\text{PO}_4)_{5.16}(\text{CO}_3)_{0.43}\text{F}_{1.45}(\text{OH})_{0.55} \cdot 1.83\text{H}_2\text{O}$

320 TG/DTA instrument using a heating rate of  $10^\circ\text{C min}^{-1}$  in a dynamic nitrogen atmosphere.

### 3. Results and discussion

#### 3.1. Stoichiometry and structure

The results of chemical analysis of the samples dried at 100°C are given in Table 1. The calculations of the molecular formulae of the apatite samples are based on a B-type CAp structure and the fact that the sum of P and C atoms equals six (Table 2). The  $\text{HPO}_4^{2-}$  content was calculated from the deficit of cations, and the  $\text{OH}^-$  content was calculated according to the electroneutrality principle.

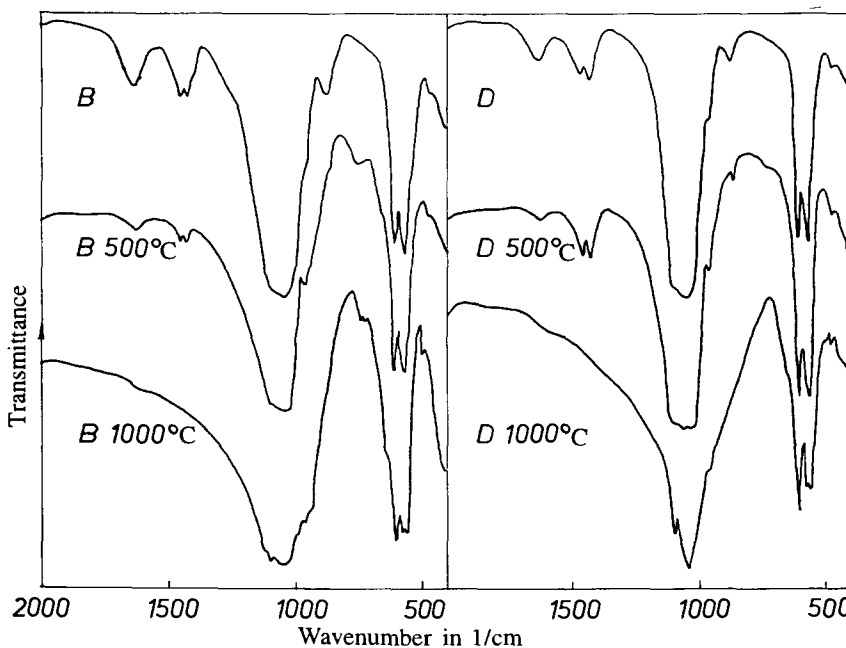


Fig. 1. FTIR absorption spectra of apatite samples B and D, dried at 100°C (upper curve); and heated up to 500° and 1000°C (lower curve).

Table 3  
Specific area ( $\text{m}^2 \text{g}^{-1}$ ) of apatite samples

Sample	Temperature/ $^{\circ}\text{C}$		
	100	500	1000
A	197	114	0.1
B	128	70	0.9
C	172	105	<0.1
D	100	56	<0.1

The apatite sample precipitated at  $20^{\circ}\text{C}$  (A) contains more ammonia, carbonate and water than the apatite precipitated at  $80^{\circ}\text{C}$  (sample B), although the concentrations of components in the initial solutions were equal. The ratio of cations in the apatites also differs from that in the initial solutions. In Ca–Mg apatites (samples A and B), the Mg/Ca mole ratio is higher than in solution (0.42 and 0.25 respectively). In Ca–Mg–Na apatites (samples C and D), the Mg/Ca ratio is almost the same and the Na/Ca ratio is smaller than in solution; in sample C, they are 0.34 and 0.04, respectively, while in the initial solution they were both 0.33. In sample D, the Mg/Ca and Na/Ca ratios are 0.18 and 0.05, while these ratios in solution were 0.17 and 0.5, respectively. This can be explained by the stabilizing effect of sodium on the structure of apatite which hinders the penetration of other cationic substitutes into the apatite lattice.

The IR spectra indicate that the precipitated apatites have fluorapatite structure with  $\text{CO}_3^{2-}$  substituting at the  $\text{PO}_4^{3-}$  position (B-type CAp). The absorption bands of carbonate are found in accordance with the proposed structure at 878–867, 1433–1430 and 1468–1458  $\text{cm}^{-1}$  (Fig. 1). The small differences in the frequencies between the different samples are mainly caused by the other substitutions which distort the apatite lattice. Furthermore, the position of the peaks at 878–867  $\text{cm}^{-1}$  are influenced by  $\text{HPO}_4^{2-}$ , which has absorption bands in the same frequency range and at 1645–1639  $\text{cm}^{-1}$  [8,14].

The precipitated materials are weakly crystalline fine powders with large specific areas (Table 3). The diminishing of the specific area from 100–200  $\text{m}^2 \text{g}^{-1}$  to 0.1  $\text{m}^2 \text{g}^{-1}$  upon heating from 100 up to  $1000^{\circ}\text{C}$  shows a rapid growth of apatite crystals accompanied by partial structural rearrangements and a weight loss of 6–10%.

The X-ray diffractograms were recorded for all samples, first when they were dried at  $100^{\circ}\text{C}$  and then after heating to  $1000^{\circ}\text{C}$  (Fig. 2). The precipitated apatites give relatively broad and diffuse X-ray diffraction patterns, which indicate that the materials consist of very small crystals. During thermal treatment, the crystal size of the products increases. In the samples heated up to  $1000^{\circ}\text{C}$  the peaks were sharp and well-resolved, indicating a well-formed hexagonal structure characteristic of the hydroxy-fluorapatite.

### 3.2. Thermal analysis

The results of thermal measurements are shown in Fig. 3. The main products evolved during the heating of precipitated apatites are water and carbon dioxide formed by the decomposition of  $\text{CO}_3^{2-}$ , as well as ammonia from the decomposition of  $\text{NH}_4^+$  which is hypothetically incorporated into the apatite structure from the  $\text{NH}_4^+$ -containing solution in the absence of sodium ions. Because the thermally induced changes in the synthetic apatites are rather complex, involving overlapping reactions with release of several gaseous species, it is not possible to resolve the reactions from the rather monotonous TG curves alone; additional information must be sought from DTA and EGA curves as well as from ex situ IR measurements.

Water is evolved stepwise mainly before  $500^\circ\text{C}$  with sharp DTG peaks at around  $150$ ,  $175$  and  $215^\circ\text{C}$  for all samples. For sample A, which contains more water and

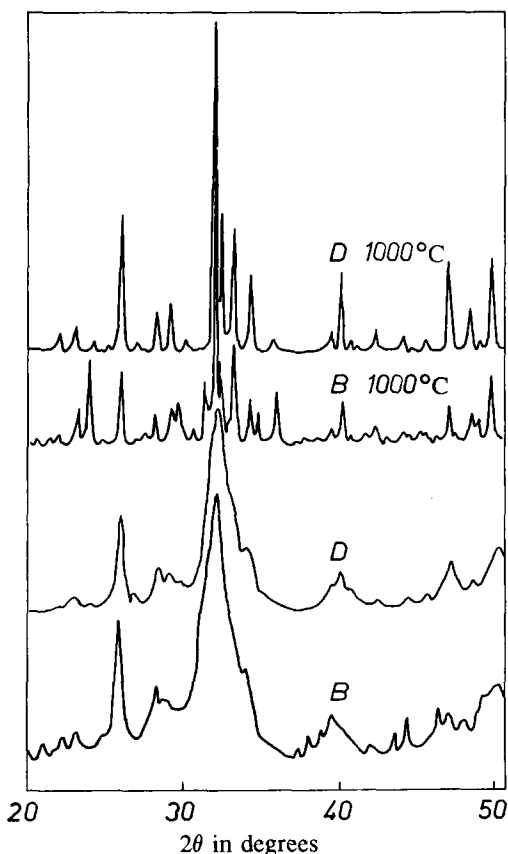


Fig. 2. X-ray diffractograms of apatite samples B and D, dried at  $100^\circ\text{C}$  (lower curves) and heated up to  $1000^\circ\text{C}$  (upper curves).

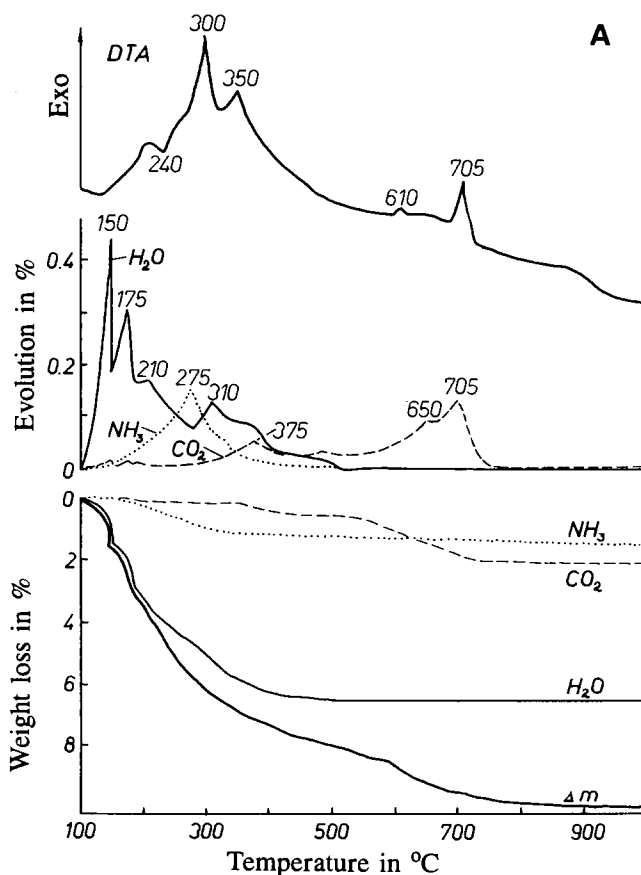
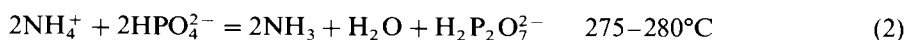


Fig. 3(a).

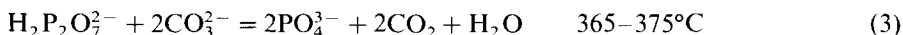
$\text{NH}_4^+$  than the other samples, there is an additional peak at 310°C. In addition to the release of absorbed and structurally incorporated water up to 180°C,  $\text{H}_2\text{O}$  evolution at higher temperatures may be caused by the reactions



The release of water and the reconstruction of the apatite structure are accompanied by exothermic peaks in the DTA curve at 300 and 350°C; for sample A there is an additional endothermic peak at 240°C.

Ammonia evolves in the temperature interval 100–400°C with a sharp peak at 275°C for sample A and with a peak at 280°C for sample B, corresponding to 1.6 and 1.2 wt%  $\text{NH}_3$ , respectively. Although the entry of  $\text{NH}_4^+$  ions into the apatite structure is debatable, the temperature of  $\text{NH}_3$  evolution is too high for the adsorbed ammonia. Therefore, supposing  $\text{NH}_4^+$  ions are incorporated into the

apatite structure, the evolution of ammonia would cause a deficit of cations in the apatite lattice and, together with the increasing temperature, induce the formation of pyrophosphate groups according to reaction (2). The IR absorption band due to the P–O–P bonds is seen at  $751\text{ cm}^{-1}$  for both samples A and B when they are heated up to  $500^\circ\text{C}$ . In samples C and D, where  $\text{NH}_4^+$  was absent, these bands are very weak because there is not a significant deficit of cations during heating. The small amount of  $\text{P}_2\text{O}_7^{4-}$  visible in the IR spectra of samples C and D at  $500^\circ\text{C}$  can only be formed according to reaction (1). On subsequent heating, pyrophosphate ions decompose according to the reactions



Carbon dioxide evolves more or less continuously, with a few small bursts. The EGA curves presented in Fig. 3 reveal that the evolution of  $\text{CO}_2$  is complete by

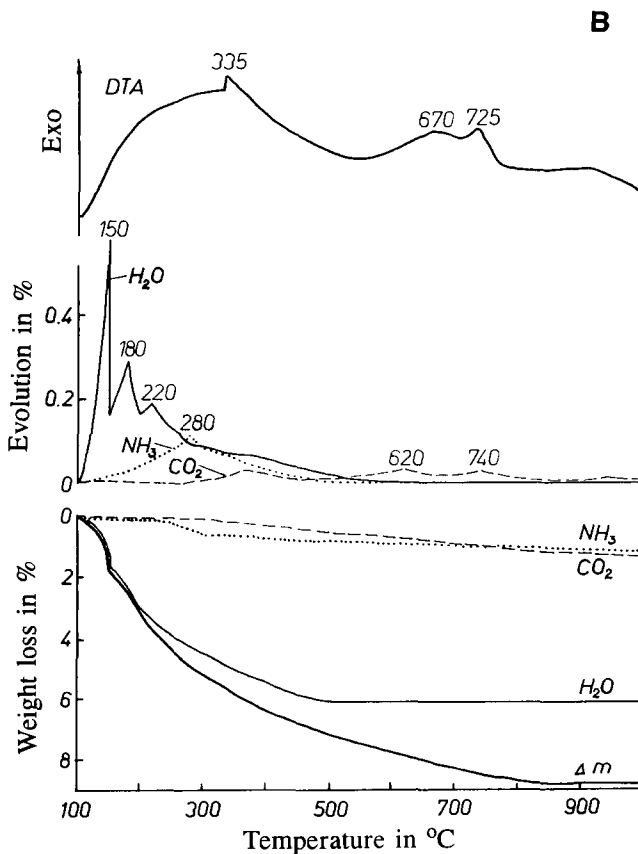


Fig. 3(b).



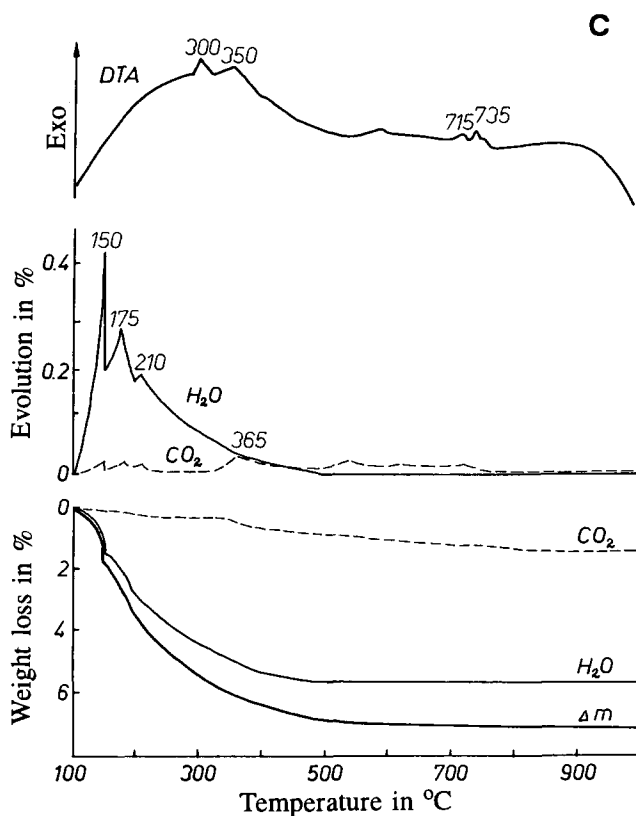


Fig. 3(c).

760°C for samples A and C but for samples B and D a temperature of some 200°C higher is needed. The strength of CO<sub>3</sub><sup>2-</sup> incorporation into the apatite structure is obviously influenced by the precipitation temperature as well as by sodium substitution. In sample A, 55% of the total CO<sub>2</sub> is released in the temperature range between 650 and 705°C, also indicated by exotherms in the DTA curve and thus involving rearrangements in the crystal structure. Similar behaviour is exhibited by sample D, where the sharp release of CO<sub>2</sub> (23% of total content) appears in the same temperature range with a maximum at 715°C. In sample B, as well as in sample C, carbon dioxide is evolved at an even rate.

According to the IR spectra, the CO<sub>3</sub><sup>2-</sup> absorption bands at frequencies 1433–1430 and 1468–1458 cm<sup>-1</sup> are slightly shifted to higher frequencies when the apatites are heated up to 500°C, whereas the bands at 878–867 cm<sup>-1</sup> are shifted towards lower frequencies. The latter feature can be assigned to the disappearance of the HPO<sub>4</sub><sup>2-</sup> peaks resulting from the condensation reactions (1) and (2). At 1000°C, the IR spectra no longer indicate the presence of CO<sub>3</sub><sup>2-</sup> in the apatite structure.

#### 4. Conclusions

Thermal analysis with FTIR–EGA allows an estimation of the water, carbonate and ammonia contents, and also a resolution of the overlapping reactions taking place during the heating of synthetic apatites. Water evolves mainly before 500°C in three or four steps, followed by thermal effects accompanying the rearrangements of the structure. Carbon dioxide is evolved over a wide temperature range, from 100 up to 800–1000°C.

A comparison of apatites synthesized at different temperatures shows that higher temperature of precipitation diminishes the concentration of  $\text{CO}_3^{2-}$  and  $\text{NH}_4^+$  ions in the synthetic apatites. As there are no other established  $\text{NH}_4^+$ -containing phases in the product and because ammonia is absent in the presence of sodium in the apatite samples, this suggests that  $\text{NH}_4^+$  ions may be incorporated into the CAP structure. In this case, the ammonium ions cause the deficit of cations in the structure of apatite during the heating and promote the formation of pyrophosphate at temperatures up to 500°C. The simultaneous evolution of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  accounts

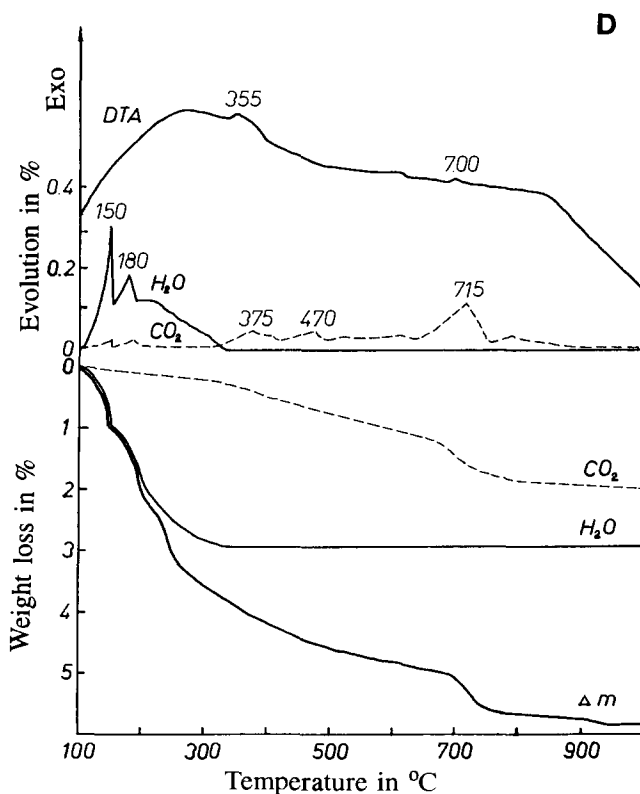


Fig. 3(d).

Fig. 3. Thermoanalytical curves (DTA, EGA, TG) of apatite samples A, B, C and D.

for the formation of relatively small amounts of pyrophosphate in spite of a high content of  $\text{HPO}_4^{2-}$  in the precipitated apatites. Sodium-containing Ca–Mg CAP appears to be thermally slightly more stable than those without sodium.

### Acknowledgements

The authors thank Ms Helgi Veskimäe, M.Sc., for performing the specific area measurements. The work was supported by a scholarship to Kaia Tõnsuaadu from the Finnish Centre for International Mobility (CIMO) and by grants from the Estonian Scientific Foundation and Tallinn Technical University.

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