

Evolved gas analysis of apatite materials using thermochromatography

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Abstract

Evolved gas analyses of model inorganic compounds and apatites are described. The measurements are performed on the system – a ‘thermochromatograph’ (ThGC) – with a low-volume, thermal furnace, interfaced to a capillary gas chromatograph (GC) via a computer-controlled, pneumatic sample inlet device in the 70–600°C region. The ‘information content’ performance of this inherently simpler system is comparable to that of TG/GC/MS and TG/GC/IR systems when similar materials are analyzed. © 1998 Elsevier Science B.V.

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1. Introduction

An ideal evolved-gas analysis (EGA) instrument would provide a time- or temperature-based record of the appearance and disappearance of all evolved compounds together with their identification. Most recently, thermogravimetry-mass spectrometry (TG-MS) and thermogravimetry-infrared spectrometry (TG-IR) instruments have become available [1,2].

Although the current instruments can continuously monitor the evolved products with scan speeds of fractions of a second, their complete capability may only be required when the evolved gas composition is a truly complex mixture. Even then, better resolution, in terms of non-collinear information content, might be achieved by a thermogravimetry–gas chromatography–spectrometry (TG-GC-MS/IR) system [3]. Weight-

loss curves can be readily reconstructed from EGA curves (taking care that all evolved components are detected, and that detected responses to all components are known). On the other hand, many EGA applications – especially those for inorganic samples – have relatively simple and predictable evolved gas composition and the justification for spectrometric identification tools is not clear. In addition to a high cost per sample, these seemingly more sophisticated approaches add several problems: (a) relatively large TG furnace volume can degrade system performance for narrow EGA peak shapes; (b) potential sample component loss in interconnecting lines between TG and IR or MS instruments because of condensation of tars and other high-boiling products; and (c) unwanted selective detection (e.g. not all evolved components are IR active).

Despite its many attractive features, using gas chromatography (GC) as an EGA detector introduces at least two more problems. Firstly, the detection of

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the evolved compounds in the case of samples which release only small amount of gas during their heating (relative to their total mass) as is the case for many inorganic samples. Secondly, separation of the evolved components requires careful selection of the GC column to avoid selective trapping in the column.

In EGA by GC, where the reactor size is optimised according to needs of chromatography, the result is set of chromatograms of the gases released at the corresponding (sampling) temperatures, i.e. a particular sample temperature can be associated with each chromatogram. If the temperature interval between two chromatograms is small and a set consists of numerous recorded chromatograms, it is straightforward to form an EGA response surface with axes: sample temperature at injection time vs. chromatographic runtime. By analogy to other hyphenated analytical techniques and because of the axis names, this method is called *thermochromatography* (ThGC), and the corresponding surface plots are known as *thermo(gas)chromatograms*. If there are several independent reactions occurring in the sample during the entire course of heating, then the corresponding thermochromatogram is 'a linear combination of the thermochromatograms of individual processes'.

The goal of the present work was to demonstrate ThGC performance in the case where evolution of gas phase materials occurs from inorganic materials, and to show ThGC ability to provide much information for a better understanding of thermal decomposition of apatites.

2. Experimental

2.1. Furnace, sampler and chromatograph.

A schematic of the overall system is presented in Fig. 1. The quartz tube furnace which replaces the injection port of the chromatograph has a volume of 4 ml and the sample is located therein. The furnace/reactor temperature is controlled by a separate, stand-alone temperature programmer with an operating range of 70–600°C, at heating rates of 1–25°C/min. In our experiments, a heating rate of 10°C/min was used in the temperature region from 70° to 600°C, for all the samples. Automatic injection of the evolved gas

onto the GC column must be achieved at relatively-high temperatures. Most commercially available, mechanical sampling valves exhibit accelerated mean-time-to-failure when maintained at the higher temperatures needed to avoid condensation and to match common GC column inlet operating conditions. An alternative is to have sampling done with a pneumatic sampling valve with no moving parts, but at the expense of some further sample dilution. Such samplers operate on the principle of carefully balancing the pressures in the sample stream and the carrier gas flow, first described by Deans [4], and is used in this system to introduce the aliquots of sample head space into a capillary column. A complete description of the sampler is given in an earlier work [5]. The chromatograph is a Carlo Erba 4200 GC with a thermoconductivity detector (mod.430) and a porous layer column 0.53 mm i.d and 25 m in length {NSW-PLOT (HNU Nordion Oy, Finland)} was used to separate gaseous products of decomposition.

2.2. Sampling control and data acquisition

The sampling is controlled by an Apple II computer and a locally made interface card. The sampling events occur at intervals equal to the separation time of the evolved components (total chromatogram runtime in our case was 110 s) and then chromatograms of evolved gases are found at certain predetermined temperatures. The detector signal is converted to digital form by a 23-bit analog-to-digital converter (ECTA, Estonia), received by the Apple II control computer and transferred to a 486-type PC over an RS232 interface for final data processing. At first, image processing methods display such EGA response surfaces as 2D objects either as a contour or mesh plots. Fig. 2 presents the thermochromatogram of magnesium carbonate hydroxide as a mesh plot. Although such plots do not add much to the final presentation of the EGA results – the evolution rates of the released gas components as a function of sample temperature, they provide for the analyst a convenient 'picture' of the thermal events occurring in the sample.

Most of the software used was written by the authors. Equipment control (sampling and data recording) software was written in assembly language. When necessary, the chromatogram pre-processing

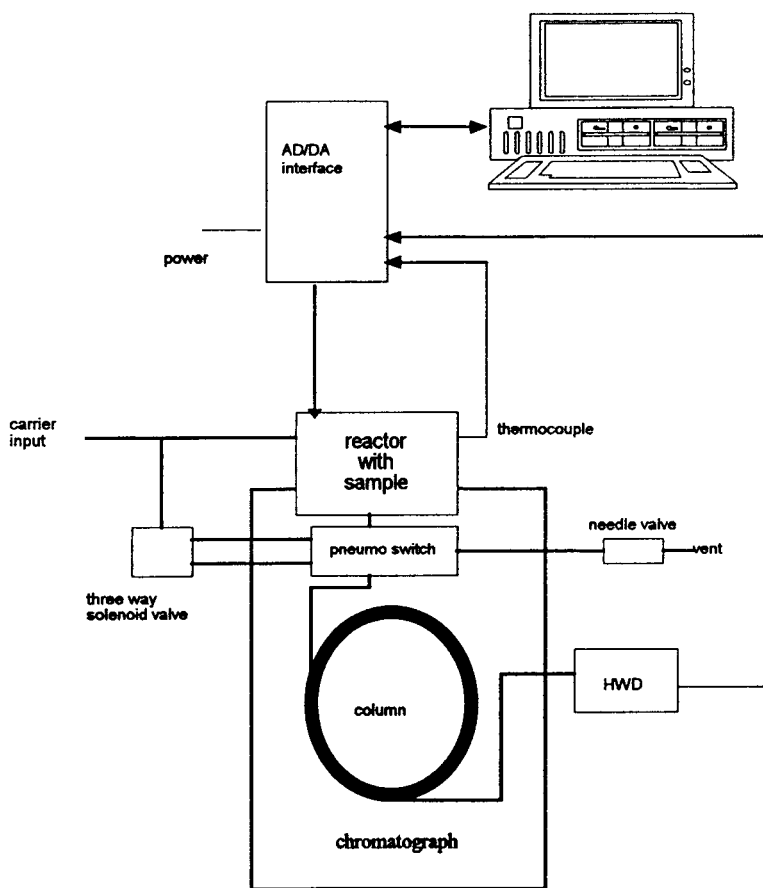


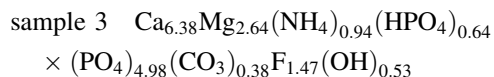
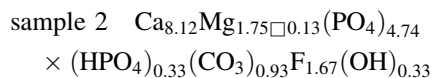
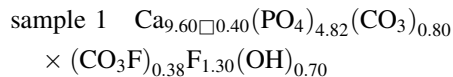
Fig. 1. Schematic of a thermochromatographic experiment.

(base-line correction, spike removal, digital filtering, etc.) was performed, for which software was written in C. The thermochromatogram 2D representation sub-routines are written in MATLAB (Math Works, Natick, USA).

2.3. Samples

Two inorganic reagents, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, Fluka, Germany, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, Reachim, Russia, and three samples of synthetic carbonate apatites, synthesised at the Tallinn Technical University, were studied. The apatite samples were synthesised by the precipitation method described previously [6,7]. The apatites were identified by XRD and IR spectroscopy as B-type carbonate apatites (CO_3^{2-} substituted for

PO_4^{3-}). The formulae of samples calculated by data of chemical analysis, and according to the electroneutrality principle, are as follows:



The samples were placed in a quartz vial inside the reactor and the weight of each sample was ca. 20 mg. Under thermal influence, all the proved samples evolve together with H_2O and NH_3 or CO_2 .

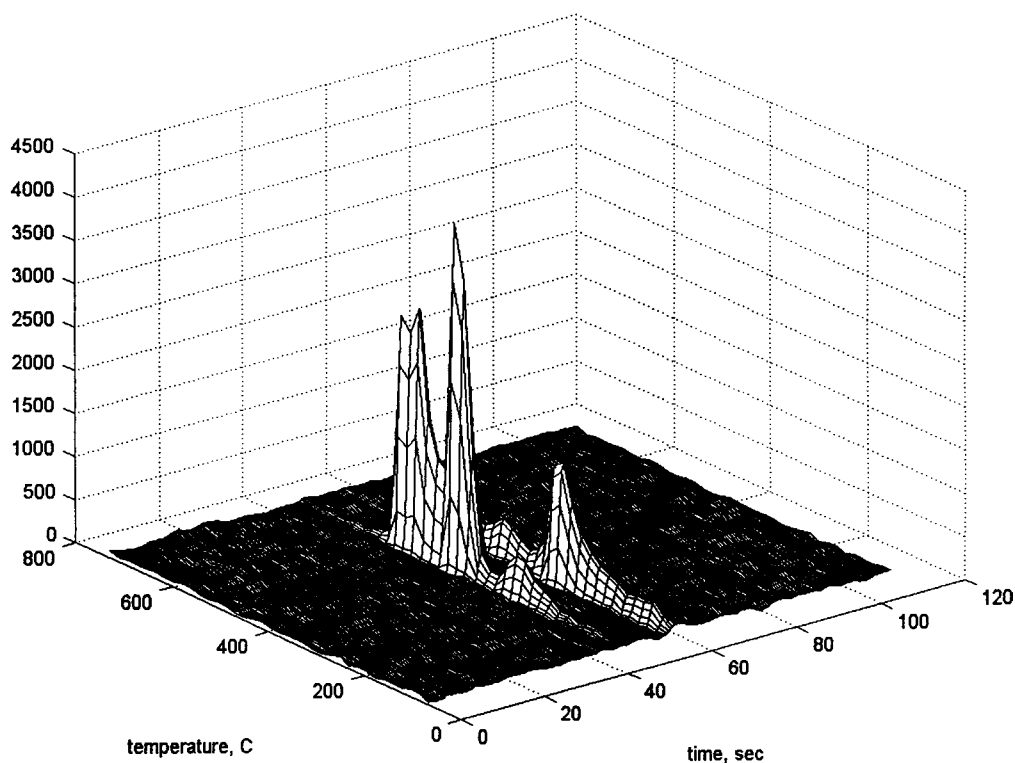


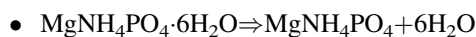
Fig. 2. Mesh plot of magnesium carbonate hydroxide degradation products: peak at retention time 45 s corresponds to CO_2 , at 60 s corresponds to H_2O .

3. Results and discussion

3.1. Magnesium ammonium phosphate hexahydrate

During thermal analysis of ammonium salts, ammonia is evolved along with water as part of the total weight loss at the same temperature. If each evolution process is to be distinguished, there are distinct advantages in obtaining separate evolution curves. In this case, ThGC offers a simpler solution to the detection of simultaneous evolving gases than, for example, the approach Paulik et al. [8] used for thermo-gas titrimetry (TGT).

A relatively complex process of degradation takes place in case of magnesium ammonium phosphate hexahydrate. For $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, the following scheme of thermal decomposition is presented as follows:



- $\text{MgNH}_4\text{PO}_4 \Rightarrow \text{MgHPO}_4 + \text{NH}_3$
- $2\text{MgHPO}_4 \Rightarrow \text{Mg}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O}$

ThGC offers a good chance to check the proposed scheme. On the evolving curve of ThGC (Fig. 3), one can follow three peaks: (1) temperature region 90–190°C, when water is evolving (73.7% of the total amount); (2) temperature region 240–320°C, when water (23.1% of the total amount) and ammonia are simultaneously evolving; and (3) wide temperature region 450–570°C, when water is evolving (3.2%).

From these data, one can conclude that the release of five water molecules and the decomposition of the intermediate $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ became well separated and a part of crystal water remained and simultaneously evolved with ammonia. This evolution is taking place in the 240–320°C range. By peak height, the amount of water evolving in that region is approximately $1\frac{1}{2}$ molecules and corresponds to the following main reactions:

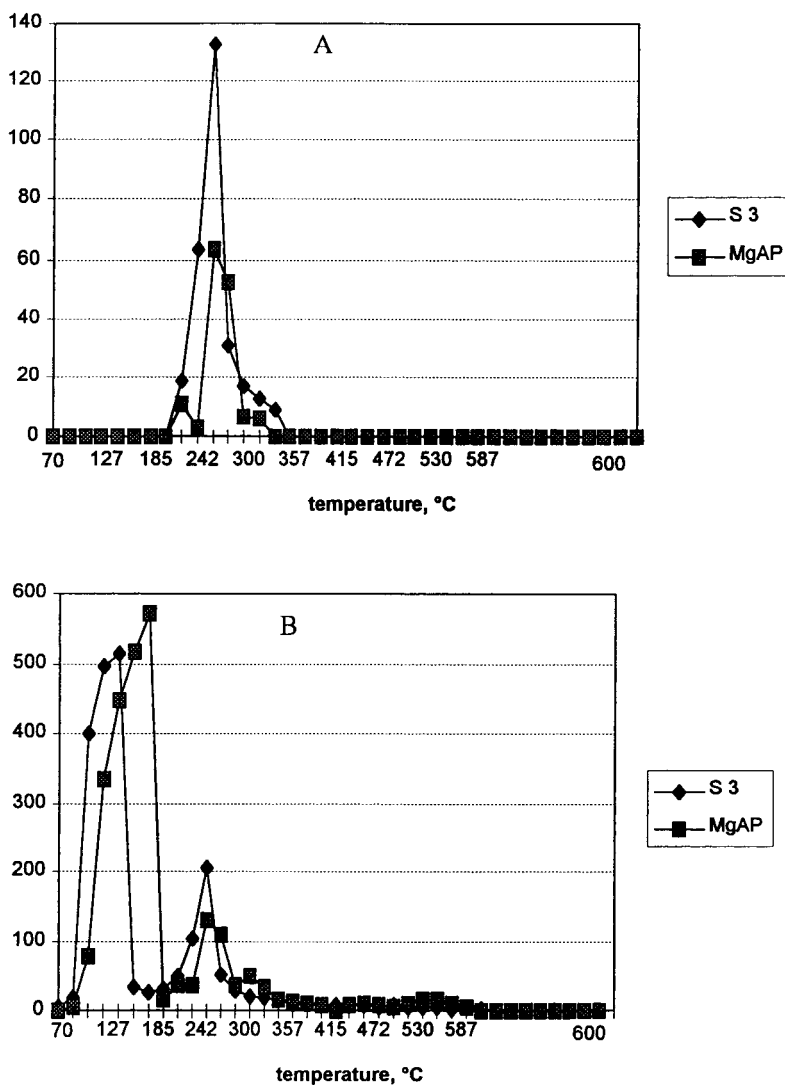
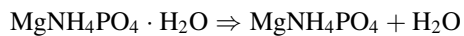
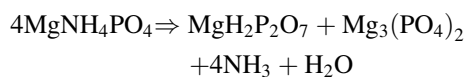
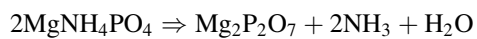


Fig. 3. Thermal decomposition of magnesium ammonium phosphate (MgAP) and carbonate apatite sample 3 (S3): (A) evolution of NH₃; (B) evolution of H₂O.



or



The existence of the third step at higher temperatures (450–570 °C) shows the evolution of some part of remaining constitutional water. It means that the hydrous intermediate(s) are formed in the second step

And these intermediates decompose at higher temperatures and give evolution of water:



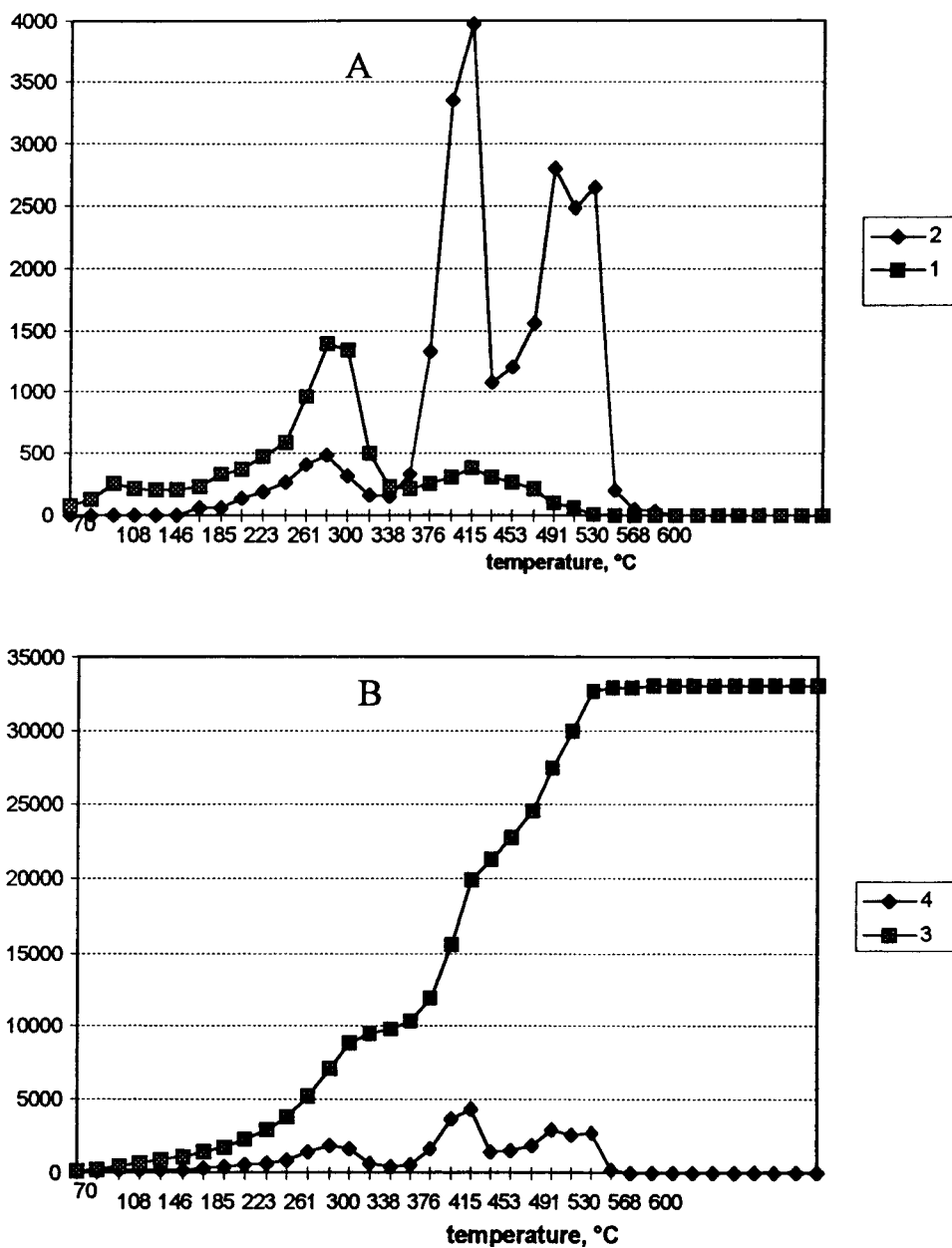


Fig. 4. Thermal decomposition of magnesium carbonate hydroxide: (A) 1, H₂O; 2, CO₂; (B) 3, total evolving curve; 4 – total differential evolving curve.

or



From the evolved gas analysis alone, it is impossible to identify the reactions and one must use other analytical methods to confirm the final products.

3.2. Magnesium carbonate hydroxide hydrate

4MgCO₃·Mg(OH)₂·5H₂O belongs to group of hydrated oxides with a complicated crystal structure and they commonly exhibit a multi-stage decomposition [9]. The curve (Fig. 4) of total evolution for ThGC

of magnesium carbonate hydroxide hydrate has three distinct steps, all proceeding consecutively with some overlap:

1. A range 220–335°C, when mainly water and some CO₂ are evolved.
2. A range 350–450°C, where CO₂ and a small part of H₂O is evolved.
3. A range 450–550°C, when only CO₂ is evolved.

As ThGC permits one to follow the evolution of gaseous products independently, it is possible to measure amounts of a given gas at distinct temperature intervals. This way, it is found that five parts of water evolve during the first step, and one part of water during the second step. This corresponds to the water of hydration (five molecules) and hydroxide (one group). Amounts of evolved CO₂ in different stages suggests that there are distinct intermediates undergoing decomposition in each range. The major phase of CO₂ evolution occurs during steps 2 and 3. Apparently, equal parts of carbonate degrades at these steps. These data could be interpreted as the following reactions are occurring in the sample

- $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O} \Rightarrow 4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 + 5\text{H}_2\text{O} \uparrow$ (220–335°C)
- $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \Rightarrow 2\text{MgCO}_3 \cdot 3\text{MgO} + \text{H}_2\text{O} \uparrow + 2\text{CO}_2 \uparrow$ (350–450°C)
- $2\text{MgCO}_3 \cdot 3\text{MgO} \Rightarrow 5\text{MgO} + 2\text{CO}_2 \uparrow$ (450–550°C)

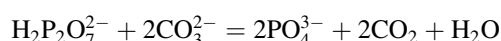
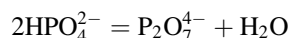
Eventually, it was concluded that the partial processes (degradation of carbonate and hydroxide) were not separated. Thus, some other processes must be responsible for the temporary ceasing and subsequent gradual change of the thermal decomposition and this could be the cessation of re-crystallisation of the new phase [9].

3.3. Carbonate apatites

The thermally induced changes in synthetic carbonate apatites are rather complex, involving overlapping reactions with release of several gaseous species. Their behavior on thermal influence depends much on the pattern of synthesis and conditions of heating. Using ThGC equipment, it was possible to cover the main temperature regions up to 600°C, where evolution of gases takes place. The main products evolved

during the heating of precipitated apatites are water and carbon dioxide, as well as ammonia.

The water evolving during thermal treatment of synthesized apatites is of three different origins: adsorbed water, structurally incorporated water and water evolving as a result of interactions of the apatite constituents [9]:



The adsorbed water is loosened at 100–160°C for all samples (Fig. 5). Evolution of the lattice water from fluorocarbonate apatite without substitutions in the cationic site of the structure (sample 1) occurs in a wide temperature interval, up to 500°C, with maximum in the 300–320°C region. In substituted magnesium carbonate apatite (sample 2), the evolution of lattice water proceeds at lower temperatures because of weakening of the crystal structure, with a maximum at ca. 200°C. The loss of water, resulting from the above-mentioned reactions also proceeds in the temperature range up to 600°C.

The loss of CO₂ on heating carbonate apatites, investigated by gas chromatography and FTIR analysis of evolved gases, occurs between 450° and 950°C, with two or three maxima [7,10,11]. On account of ThGC of the fluorocarbonate apatite (sample 1), there is a slight loss of CO₂ on heating up to 600°C, making up to 13% of its total content. On the contrary, evolution of CO₂ from magnesium-substituted carbonate apatite proceeds at lower temperatures – to a greater extent – in amounts of 72%, with a maximum at 580°C. The release of CO₂ gives rise to thermally induced rearrangements in the apatite structure leading to more stable crystalline phase of fluoroapatite.

The evolution of ammonia from magnesium–ammonium carbonate apatite (sample 3) proceeds in ThGC experiments to completion, mainly in the temperature interval 220–300°C, that is as by heating of MgNH₄PO₄ (Fig. 3). The possibility of the existence of MgNH₄PO₄ as a separate phase in sample 3 is not excluded.

Thus, the ThGC can be successfully used for obtaining information on the composition and thermal stability of carbonate apatites. Also, these are the examples where EGA must be applied together with

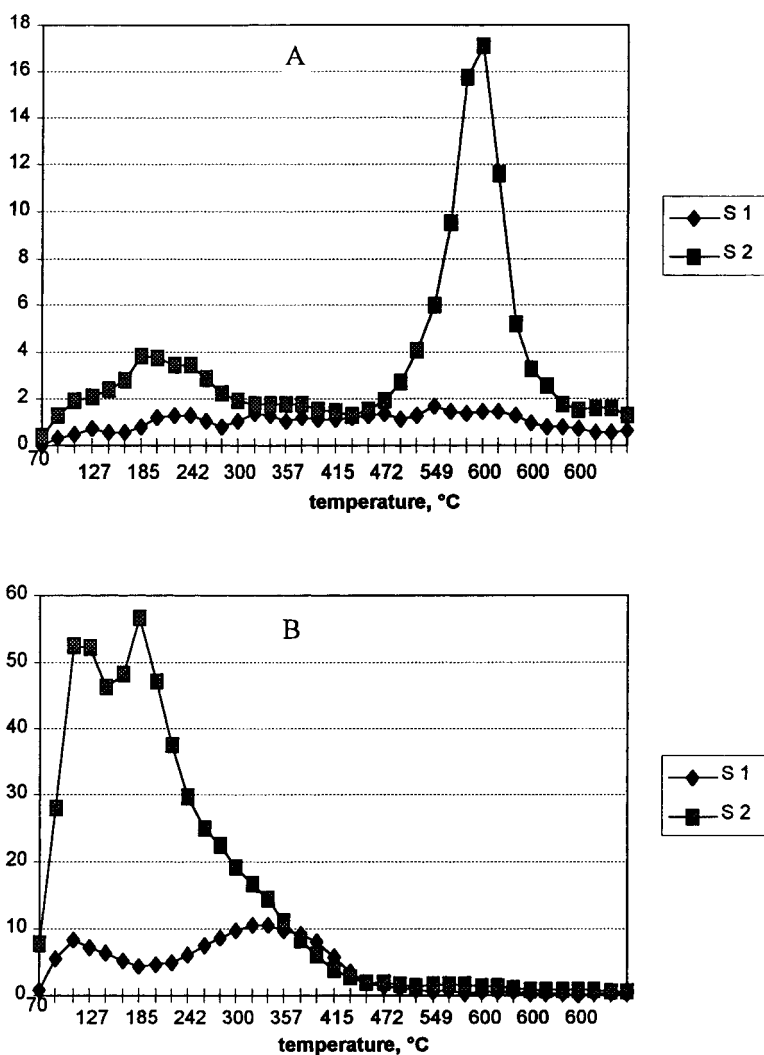


Fig. 5. Evolving of gases from the precipitated apatites – sample 1 (S1) and sample 2 (S2): (A) evolution of CO₂; and (B) evolution of H₂O.

other thermoanalytical methods like DSC, and others, to obtain a full description of the processes.

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