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The Thermal Decomposition of Mg-Containing Carbonate Apatites

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Carbonate apatites precipitated from an aqueous solution and containing Mg^{2+} and Sr^{2+} ion were studied by thermogravimetric, infrared absorption, and X-ray diffraction methods. In the temperature range of 25–350°C water evolves and at 350–905°C carbonate decomposes. Two effects characterize the Mg-containing system: Weight loss during decomposition is related to carbonate in the apatite and to an additional ion; increased formation of whitlockite. The interrelation between these two phenomena and the presence of carbonate and Mg is discussed. © 1985 Academic Press, Inc.

Introduction

The thermal decomposition of dental enamel and synthetic carbonate apatites have been the subject of several studies. In most of them the decomposition process was studied by thermogravimetry and the products analyzed by ir spectroscopy and X-ray diffraction (*1*, *2*). The main products of the decomposition reactions are water, adsorbed or intracrystalline (*3*), which evolves up to 350°C and CO_2, formed by the decomposition of CO_3^{2-}, in the temperature range of 300–950°C. The carbonate ion occupies mainly the phosphate site of the apatite lattice (B-type) but in certain cases it can be present also at the OH^- site (A-type). Cases in which transition of CO_2 from the B-type to the A-type occurs have been reported (*2*). Evidence of residual molecular CO_2 (400–700°C) in the decomposition system has been shown in a number of synthetic and natural apatites (*4*).

In a previous study data were reported on carbonate apatites containing magnesium and sodium ions (*5*). The present investigation was initiated in order to study the possible effect of Mg on the thermal decomposition reaction of synthetic carbonate apatites. Samples synthesized with carbonate, Mg^{2+}, and Sr^{2+} and a content close to that which is known for dental enamel were analyzed by the thermogravimetric method.

Experimental

1. Synthesis

The carbonate apatite (CA) samples were precipitated from an aqueous solution by adding sodium phosphate solution to a calcium nitrate solution. Carbonate, Mg^{2+}, and Sr^{2+} were added as $NaHCO_3$, $Mg(NO_3)_2$, and $Sr(NO_3)_2$ solutions. This method of synthesis has been described elsewhere (*5*).

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The samples were analyzed for Ca, Na, Mg, and Sr by atomic absorption spectrometry (*5, 6*). Carbonate was estimated from the ir spectra using the ratio of the carbonate band at 1415 cm^{-1} (E_{1415}) to the phosphate band at about 575 cm^{-1} (E_{575}). This ratio was compared with a standard curve of known carbonate apatites previously analyzed by chromatography (*7, 8*). The accuracy of the method is ±5%.

2. *Instrumentation*

The ir spectra of the apatites were determined by a Perkin–Elmer Model 457 using KBr pellets.

The thermal decomposition of the samples was studied by thermogravimetry (TG), using a Standon-Redcroft TG apparatus. The TG analyses were performed in the temperature range of 25–900°C, at a heating rate of 10°C/min under nitrogen gas flow.

The powdered samples were analyzed by X-ray diffraction (XRD) using a Philips diffractometer. Monochromatized Cu$K\alpha$ radiation was used. The samples were scanned in the 2θ range of 20–60°, Ge was used as an internal standard.

Results

Thermogravimetric analyses were carried out on carbonated hydroxyapatites (CA) containing magnesium. Samples containing the carbonate concentration of 1.27–7.4% and different Mg concentrations of 0.0–0.39% as well as samples prepared with Sr were selected for TG analysis. A sample of tooth enamel was also TG-analyzed. Table I lists the carbonate, Mg, or Sr content of the samples.

Figure 1 shows a representative TG curve of one of the Mg-containing CA. The curve does not show sharp weight loss changes, yet a break can be observed around 350°C, which divides the curve into

TABLE I

THE CARBONATE, Mg, AND Sr CONTENT OF THE SAMPLES (% wt/wt)

Sample	Carbonate determined by ir	Carbonate calculated from weight loss in TG	Magnesium	Strontium
150	2.9	3.7	0.01	n.a.[a]
179	4.8	4.9	0.01	n.a.[a]
169	5.7	6.8	0.01	n.a.[a]
165	7.2	7.4	0.17	n.a.[a]
147	3.1	3.1	0.18	n.a.[a]
149	2.6	3.7	0.20	n.a.[a]
172	2.8	3.8	0.31	n.a.[a]
163	1.3	3.7	0.35	n.a.[a]
164	3.9	5.8	0.35	n.a.[a]
155	2.6	5.5	0.39	n.a.[a]
175	3.9	6.3	0.39	n.a.[a]
108C	3.2	4.9	n.a.[a]	0.02
181B	3.8	4.8	n.a.[a]	0.02
104	6.2	4.4	n.a.[a]	0.10
105	6.9	4.4	n.a.[a]	0.12
109B	3.1	3.1	n.a.[a]	0.12
110B	3.3	3.7	n.a.[a]	0.12
Dental enamel	4.8	6.4		

[a] Indicates not analyzed and not added during synthesis.

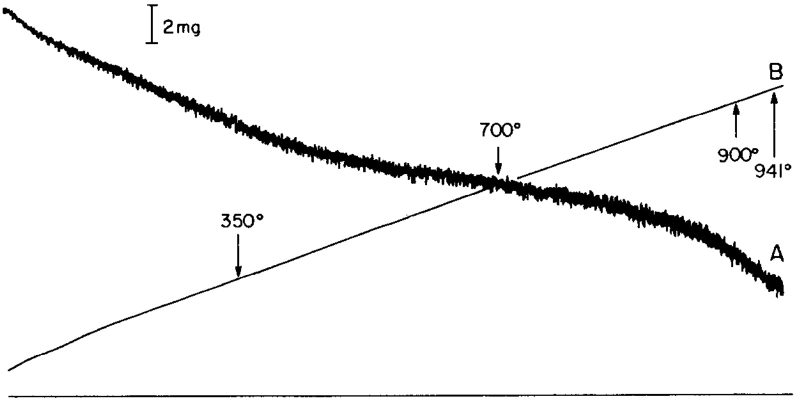

FIG. 1. Thermogravimetric curve of Mg-containing carbonate apatite sample. (A) Weight loss. (B) Temperature.

two. The decomposition up to 350°C is usually associated with water loss, while decomposition occurring above 350°C is associated with carbonate. The weight loss obtained above 350°C was therefore used to calculate the carbonate content of the samples (Table I). When the carbonate content, as calculated from the ir results, was compared to that found by TG, it became clear that in the case of the Mg-containing samples the TG values were always higher. Samples 163 and 155, which had originally relatively low carbonate and high Mg content, resulted in weight losses above 350°C, which were 185 and 112% higher, respectively, compared with those calculated from their ir data. Weight loss somewhat higher than that deduced from ir was also obtained in the case of dental enamel sample and in some of the CA without Mg, but never in the Sr-containing samples. (Samples containing ≤0.02% Sr did not have Sr added during synthesis (*6*).)

Following TG, the samples were tested

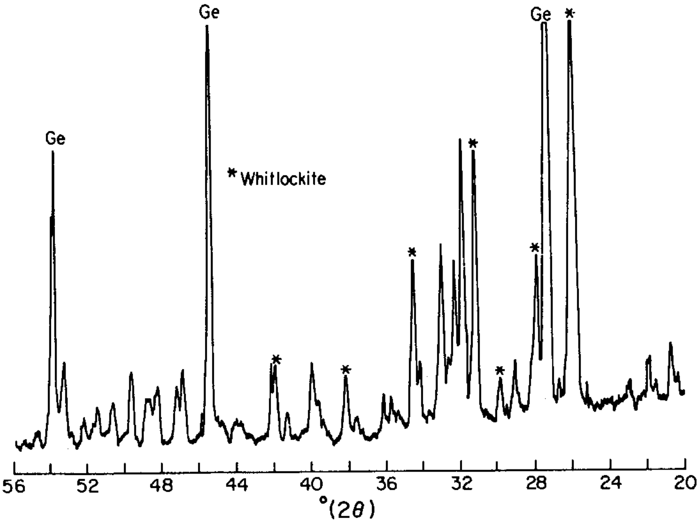

FIG. 2. X-Ray diffraction pattern of sample 163 after thermal decomposition (Ge-internal standard).

TABLE II

POWDER X-RAY DIFFRACTION DATA OF SAMPLES AFTER TG

Sample	Lattice constants before TG (Å)		Lattice constants after TG (Å)	
	a	*c*	*a*	*c*
150	9.438	6.887	9.417	6.887
169	9.386	6.873	9.417	6.894
179	9.406	6.884	9.412	6.876
165	9.404	6.884	9.417	6.894
147	9.428	6.917	9.411	6.867
149	9.433	6.889	9.411	6.872
172	9.401	6.873	9.422	6.897
163	9.422	6.873	9.411	6.886
164	9.407	6.889	9.396	6.867
155	9.401	6.862		
175	9.370	6.862	9.411	6.870
Dental enamel			9.427	6.883

Note. The estimated standard deviation of the lattice constants is ±0.003 Å.

by XRD. The diffraction patterns had well-defined sharp peaks characteristic of the apatite structure. In all the samples containing Mg, additional peaks of another phase appeared. The strongest reflections of this had *d* values 2.85–2.87 and 2.59–2.60 Å and have been identified as Mg-whitlockite (*9*). Prior to the TG analysis the XRD patterns of the compounds had well-defined but less sharp reflections and were single-phase patterns with reflections of the apatite phase only. Figure 2 shows the XRD pattern of sample 163 after TG. Fairly strong peaks of the whitlockite can be seen on this pattern (peak at 26° (2θ) is overlapped by an apatite peak and thus its intensity is high). The lattice constants calculated from the reflections are listed in Table II.

The thermal decomposition of four CA samples (~90 mg) was followed by heating them for 2 hr at 350, 500, 700, and 900°C. At the end of each of these stages the carbonate content of the samples was checked by ir. Table III lists the results of these measurements, showing a similar pattern of the decomposition process as obtained by TG; No carbonate decomposition until 350°C, slow decomposition of the carbonate in the range 350–700°C and a more rapid decomposition above 700°C. At 900°C about 90% of the CO_2 has been observed to be evolved.

The ir spectra of sample 151 before and after heating to 900°C is shown in Fig. 3. The spectra contain the characteristic bands of the phosphate group in the ranges 575–635 and the 960–1125 cm^{-1}, with a finer structure in the heated sample. Two broad bands at 1610–1650 and at 3420–3510 cm^{-1} due to adsorbed water appear on the spectrum of the unheated sample. At 875 and at 1420 and 1455 cm^{-1} the bands assigned for B-type carbonate appear. After heating, the bands at 1420 and 1455 cm^{-1} are still present but greatly reduced in intensity. The sample heated to 900°C resulted in a band at 3538 cm^{-1} characteristic of the OH^- group of HA. No bands of A-type carbonate (1545 cm^{-1}) have been observed. A very sharp band at 1385 cm^{-1} appears in the room-temperature spectrum, disappearing gradually after heating to 900°C.

Discussion

The decomposition of the carbonated ap-

TABLE III

CARBONATE CONTENT OF CA SAMPLES DETERMINED BY ir AFTER HEATING AT DIFFERENT TEMPERATURES (%wt/wt)

Sample	Temperature (°C)				
	20	350	500	700	900
151	1.9	1.8	1.5	1.2	0.2
170	2.8	2.8	2.4	2.1	0.4
178	4.7	5.0	4.6	4.2	0.9
154	1.8	1.8	1.6	0.9	0.1

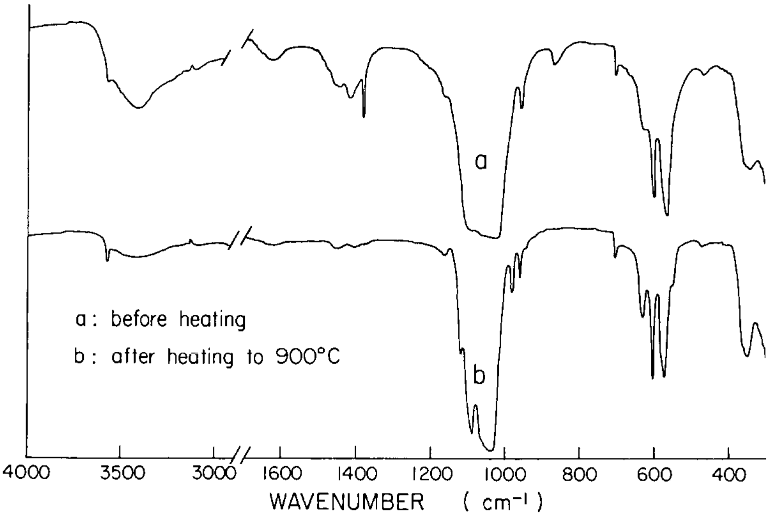

FIG. 3. Infrared absorption spectra of sample 151 before and after heating.

atites as observed in the present study is similar to that reported in the past (*1–3*). The first stage of decomposition was the evolvement of water until 350°C, this stage was followed by the stage of complete decomposition of carbonate above this temperature, until 900°C. This type of decomposition was also clearly demonstrated in a process in which heating of the samples was interrupted at different temperatures (Table III). The ir patterns of the partly or completely decomposed samples have shown bands of phosphate, B-type carbonate and hydroxyl group only. Any indication of A-type carbonate or molecular CO_2 were not obtained in the present decomposition experiments.

The X-ray diffraction patterns of the decomposed samples were characteristic of well-crystallized apatite patterns. Table II demonstrates the lattice constant *a* decreasing after decomposition of samples with carbonate content up to 4%, and increasing in samples with higher carbonate content as determined by ir. Loss of water might be the cause of decrease, and loss of carbonate of an increase in the lattice constant *a* (*2, 10*). The changes in the constant *a* seem to indicate that at low carbonate content water loss affects predominantly the lattice dimensions, consequently *a* decreases, while at higher carbonate content the loss of carbonate is the governing factor causing an increase of *a* in these cases.

The XRD patterns have also revealed that following heating, the apatite phase is accompanied by the formation of the whitlockite phase. This phase was present in a rather large amount in the Mg-containing compound, with lines stronger in some cases than those of the apatite phase. Formation of whitlockite occurred in the case of natural and synthetic apatites (*11, 12*). At moderate temperatures β-$Ca_3(PO_4)_2$ was present as an amorphous phase often stabilized by Mg^{2+} ions (*13*), whereas at the higher temperatures, in the TG runs up to 900°C, the amorphous phase crystallizes and whitlockite was detected by X-ray analysis.

In many of the analysed samples there was a difference in the amount of carbonate as determined by ir and the weight loss found by TG. The fact that these differences were observed mainly in the Mg and none in the cases when Sr was added during synthesis and were accompanied by the formation of the whitlockite phase, indicates an interrelationship between the presence of Mg, the formation of whitlockite and an additional decomposing phase. Sr^{2+} appears to inhibit the formation of these additional phases and counteract the presence of Mg^{2+} in carbonated apatites.

HPO_4^{2-} and CO_3^{2-} ions bound to Ca or Mg as a distinct phase might undergo decomposition in addition to the carbonate ions of the apatite lattice. The HPO_4^{2-} ion is very often found as one of the anions in apatite (*14, 15*). The observed weight losses in TG which cannot be related to carbonate in the apatite might originate from the HPO_4^{2-} ions incorporated in the apatite. Heating causes the decomposition of HPO_4^{2-} and at the same time the crystallization of whitlockite. The whitlockite is stabilized by the Mg ions and therefore this phase appears in increasing amounts whenever the system contains Mg ions.

Two findings observed in the present study seem to be specific to the Mg-containing system: (i) The weight loss during decomposition cannot be related only to carbonate of the apatite lattice, but also to an additional decomposition process, (ii) the increased formation of whitlockite in the Mg-containing samples. The results seem to indicate that the ion decomposing in parallel with carbonate, HPO_4^{2-}, might have a retarding effect on the insertion of carbonate into the apatite lattice, as its presence increased with decrease of carbonate in the CA. This retarding effect is apparently connected to the increased formation, in the presence of Mg, of a whitlockite-type phosphate, a known precursor of apatite.

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