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Infrared Study of Trapped Carbon Dioxide in Thermally Treated Apatites

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The formation of molecular CO_2 in synthetic apatites (prepared in aqueous systems), dental enamel, dentine, and various apatitic rock phosphates after heating in the range 120–900°C has been investigated by infrared spectroscopy. The CO_2 band at 2340 cm^{-1} was observed in the synthetic samples, enamel, and some of the rock phosphates, but not in dentine or bone. It is suggested that the absence of this band in dentine and bone is caused by the small crystal size of their apatites. The CO_2 band at 667 cm^{-1} was never observed. The polarized infrared spectrum of heated dental enamel showed that the linear CO_2 molecules were either randomly oriented or oriented so that the length of the molecules made an angle of about 56° with the *c* axis. It is suggested that, if the latter is correct, the CO_2 originates from a CO_3^{2-} ion which occupied the sloping face of the phosphate ion site.

Introduction

Apatite structures have been described in detail for stoichiometric compounds, $Ca_5(PO_4)_3X$ where X = F, Cl, OH (*1*). Apatitic powder X-ray diffraction patterns are also found for compounds with considerable substitution and deficiency but the precise structures are not established because it has not been possible to obtain crystals large enough for single crystal X-ray diffraction.

There are, however, two groups of carbonate-containing apatites (CO_3Aps) which are well characterised by other methods:

(I) CO_3Aps in which carbonate ions replace hydroxyl ions have been prepared at 900°C (*2, 3*).

(II) CO_3Aps, in which carbonate ions are thought to replace some phosphate ions and F^- replaces most or all hydroxyl ions, occur naturally as minerals, e.g., francolite (*4, 5*), and have also been prepared at high temperature (*6*). Polarized infrared spectroscopy measurements of single crystals of francolite indicate that (on the assumption of PO_4^{3-} replacement) the oxygen atoms of the carbonate ion approximately occupy the positions of the three oxygen atoms (A, B, and C of Fig. 1) forming the sloping face of the missing PO_4 tetrahedron (*5*).

There is evidence that in dental enamel the majority of carbonate replaces phosphate ions, by analogy with precipitated CO_3Aps (*7*) and that a small amount replaces hydroxyl ions (*5*). The contribution of bicarbonate ions, hydrogen phosphate ions, and adsorbed carbonate ions is uncertain. All of the CO_3Aps prepared in aqueous media and the minerals of tooth and bone are relatively poorly characterised because their infrared absorption bands are broad and often complex.

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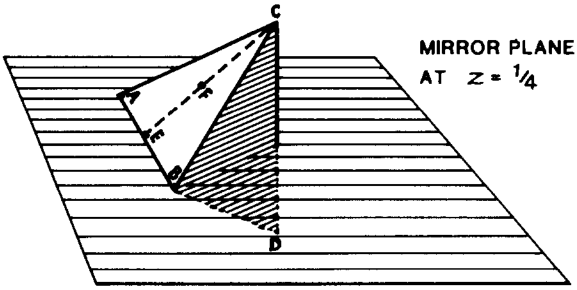

FIG. 1. Postulated formation of CO_2 from CO_3^{2-} in phosphate ion site. A, B, C, and D are the phosphate oxygen atom positions (A and B lie in the mirror plane). It is presumed that the carbonate oxygen atoms occupy positions near A, B, and C with the carbon at the center of ΔABC. On thermal decomposition this carbonate could decompose to a CO_2 molecule lying in the plane of the ΔABC with its oxygen atoms near C and E.

Molecular species may be associated with some apatites, either adsorbed on the surface or possibly incorporated within the lattice or in pores. Various apatites prepared in hydrogen peroxide solution and heated strontium peroxyapatite have been shown to trap molecular oxygen (*8*, *9*) and behave like inclusion compounds (*10*). The trapping of molecules in *c*-axis channels has been inferred from related changes in *a* axis dimension; for oxygen in oxygenated apatites (*10*), and for oxygen, carbon dioxide, and argon in enamel and bone apatite "cold-ashed" in these gases (*11*).

The role of water molecules associated with apatites prepared in aqueous media is still controversial. Speculation that water might be involved in the structure of carbonate-free apatites has been based on lattice dimensions (*12*, *13*), thermal analyses (*14*, *15*), and infrared spectroscopy (*16*). The role of water in dental enamel and synthetic CO_3Aps has been reviewed (*13*, *17*).

The trapping of molecular CO_2 has been reported not only in "cold-ashed" biological apatites (*11*), but also in various CO_3Aps following heat treatment (*5*, *17*–*19*). The thermal decomposition of CO_3Aps in the temperature range 100–900°C is complex; studies of enamel have been reviewed by Holcomb and Young (*17*). Principal findings have included a substantial loss of carbonate sustained without apparent separation of a second crystalline phase, changes in the relative intensities of carbonate infrared absorption bands indicating increased substitution in hydroxyl ion sites and reduced substitution in other (probably phosphate) sites, increase in structural OH^- content, and loss of water.

The identification of molecular CO_2 associated with various CO_3Aps (following heating) has been based on the observation of an infrared band at 2340 cm^{-1}. Elliott (*5*) showed that the predicted isotopic shift to 2277 cm^{-1} occurred for a ^{13}C-enriched synthetic CO_3Ap. Labarthe (*19*) proposed that the 2340 cm^{-1} band seen for a synthetic CO_3Ap (after heating in CO_2) was due to CO_2 held in the *c*-axis channels. The retention of molecular CO_2 in heated enamel, first observed by Elliott (*5*), has been further studied by Holcomb and Young (*17*), who suggested that it acts as an intermediary in the relocation of carbonate ions from phosphate ion sites into hydroxyl ion sites. The trapping of CO_2 in several heated mineral CO_3Aps has been reported by Winand (*18*). He observed that the infrared band at 2360 cm^{-1}, which he assigned to CO_2 formed from carbonate within the lattice, occurred simultaneously with a band at 740 cm^{-1} which he attributed to pyrophosphate formed from the condensation of hydrogen phosphate ions, and he considered that these events were associated.

The purpose of this study was to investigate the site and conditions of CO_2 retention in the thermal decomposition of a variety of CO_3Aps. The work on powders has been briefly reported earlier (*20*) and likewise the polarized infrared work (*5*). The formation of cyanate and cyanamide species in some of the samples prepared for this present study has been described previously (*21*).

Materials

Synthetic Samples

Sample P (precipitated), after Zapanta-LeGeros (*22*). 125 ml of 0.02 *M* calcium acetate solution was added dropwise (approximately 3 ml/min) to a boiling solution of 895 mg triammonium phosphate and 17.6 g ammonium carbonate in 375 ml water with additional ammonia solution (0.880 sp grav). The pH fell from 12.5 to about 9.0. The product was filtered from the hot solution, washed with hot water and dried at room temperature over silica gel for a few days.

Sample T (transformed), after Romo (*23*). A solution of 55.9 g triammonium phosphate in 4 l water containing 37.0 g calcite (5–15 μm edge length) was boiled under reflux for 24 hr. The pH fell from 10.0 to 8.6. The product was filtered from the hot solution, washed with hot water and dried at 130°C for 24 hr. The CO_2 content was 4.5 wt% (*24*).

Sample T′ (^{13}C-enriched). CO_2 evolved from 90% ^{13}C-enriched barium carbonate was bubbled through an aqueous suspension of calcium oxide with nitrogen carrier gas to produce calcite (5–10 μm particle size). The preparative method for *T′* was similar to that for *T*, but the reflux time was 3½ hr and the product dried at room temperature.

TABLE I

FORMATION OF RETAINED CO_2 IN SAMPLES HEATED IN THE RANGE 400–800°C[a]

Sample	Origin
Enamel	Human
Marine phosphorite	Florida
Insular apatite deposit	Nauru
Insular apatite deposit	Christmas Island
Dentine	Human
Bone	Rat
Mineralized cartilage (whole and anorganic)	Shark vertebra
Igneous apatite rock	Kola
Marine phosphorite	Gafsa
Marine phosphorite	Morocco
Marine phosphorite	Togoland

[a] The first four samples gave an infrared band at 2340 cm^{-1} which indicated trapped CO_2, but this band was not detected for the other samples.

Biological Samples

These were ground to powders in an agate ball mill run intermittently to minimize heating. Human enamel and dentine were prepared from the crowns of apparently caries-free, recently extracted permanent teeth. Rat bone was prepared from the shafts of the long bones of 2 Wistar-derived AS strain rats. Samples were prepared from the mineralized cartilage of blue shark vertebrae. One came from two whole air-dried vertebrae, and another from a single vertebra which had been deorganified by the action of 10–14% wt/vol available chlorine sodium hypochlorite solution for 2 years, washed and dried. The mineral of the vertebra contained about 1.0 wt% F, exhibited an apatitic X-ray diffraction pattern and had an infrared spectrum which indicated carbonate in only one location (Clement, personal communication).

Mineralogical CO_3Aps

The origins of these powdered minerals are given in Table I. The CO_2 content of these minerals were all in the range 2–5 wt% except for the Kola mineral which was 0.3% (*5*).

Methods

The powdered samples were heated at constant temperature in the range 120–900°C in a closed muffle furnace usually for 4 hr, but some for periods of 1 hr to 3 weeks. Other samples of powdered enamel were heated at 325 or 425°C for 4 hr in atmospheres of nitrogen, oxygen, or carbon dioxide. Synthetic samples were heated to 450°C at about 8°C/min and cooled under high vacuum.

Infrared spectra (4000–500 cm^{-1}) of powdered samples in KBr discs (3 mg/300 mg KBr) were recorded at ambient and liquid nitrogen temperature with a Grubb–Parsons GS2A Grating Spectrometer calibrated against indene and polystyrene (accuracy ± 2 cm^{-1} at 2400 cm^{-1}). The instrument was continuously flushed with dry air of low CO_2 content produced by passing air through a Laporte Zeolite Molecular Sieve 13X. The out-of-balance reponse of the servo system in the region of atmospheric CO_2 band at 2349 cm^{-1} was nevertheless reduced by about 40% compared with the response just outside this region. In the absence of a sample, no CO_2 absorption band from the atmosphere could be observed. All the powder spectra were run under the same instrumental conditions.

The polarized infrared spectra were made on a rock-salt prism spectrometer fitted with a ×10 reflecting microscope (*25*, *26*) and a selenium polarizer (*27*). The angle between the transition moment and the optic axis can be calculated from the formula (*28*)

$$\text{dichroic ratio} = \frac{\text{absorbance for electric vector parallel to the optic axis}}{\text{absorbance for electric vector perpendicular to the optic axis}}$$

$$= 2\cot^2\alpha$$

where α is the angle between the transition moment and the optic axis.

X-ray powder diffraction patterns were recorded by use of a toroid camera (*29*) fitted to a Hilger and Watts Y33 X-ray generator with a copper target.

Results

Synthetic CO_3Aps and Enamel

General Observations

No phase other than apatite was detected by X-ray powder diffraction in any of these unheated materials or in samples heated for 4 hr at temperatures up to 580°C. β-tricalcium phosphate was detected in samples heated for 4 hr at temperatures greater than 700°C. Calcium oxide was not detected in any sample after heating.

Neglecting contributions from inhomogeneous strain, X-ray powder diffraction line widths indicated that the crystal size of synthetic CO_3Aps ranked $T > P > T'$ and the mean crystal size was of the order 400–800 Å.

Both unheated P and T' samples appeared under the polarizing microscope to be a single phase with particle size about 3 μm. In unheated sample T (particle size 5–15 μm), a few small birefringent particles, probably unreacted calcite, were seen.

Infrared Spectra

(*a*) *Samples before thermal treatment.* All the synthetic samples and enamel had

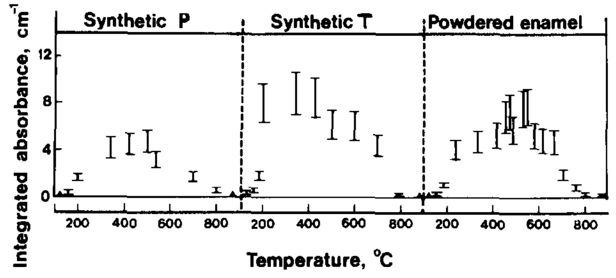

FIG. 2. Integrated absorbances (cm^{-1}) of the carbon dioxide band at 2340 cm^{-1} in synthetic apatites *P* and *T* and dental enamel heated 4 hr in air at various temperatures. The length of the bars indicate the estimated errors, ▲ indicates that the spectrum was recorded but the band was not observed.

similar carbonate absorption bands which showed evidence of some carbonate replacing hydroxyl ions as indicated by a small band or shoulder at 1540 and 878 cm^{-1}. The intensities of the carbonate bands between samples were similar which indicated similar carbonate contents. The presence or absence of the 1540 cm^{-1} band in dentine and bone is uncertain because of absorption from protein. The mineral samples all had carbonate absorption bands typical of francolite without a band at 1540 cm^{-1}.

(*b*) *Samples heated in air for 4 hours at various temperatures.* Progressive changes observed for increased temperature of heating in air resembled those reported by Holcomb and Young (*17*) for enamel except that OH . . . Cl and OH . . . F bands were not seen for synthetic CO_3Aps. Only the ν_3 antisymmetric stretch band (2340 cm^{-1}) for CO_2 was observed for any sample studied. Although the spectral region 690–645 cm^{-1} was scanned manually with 30 sec at each 0.20 μm, the CO_2 ν_2 bending mode was not detected even for a sample exhibiting strong absorption at 2340 cm^{-1}. The changes in integrated absorbance of the 2340 cm^{-1} band for samples *P*, *T*, and enamel are shown in Fig. 2. A single peak was always observed except for samples of enamel heated at 670–765°C which exhibited an additional shoulder at ~2356 cm^{-1} (Fig. 3).

In spectra of samples at liquid nitrogen temperature, the CO_2 band showed an increase in intensity and diminution in half width. There was a high frequency shift of ~5 and ~9 cm^{-1} for *T* and enamel samples, respectively. In the spectrum of an enamel sample, the shoulder at ~2356 cm^{-1} was shifted to ~2363 cm^{-1} but was not resolved. All changes were reversed on warming to room temperature.

(*c*) *Samples heated in air for various times.* The intensity of the CO_2 band was similar for enamel and sample *T* heated 1 hr, 4 hr or 3 weeks at 340°C. The carbonate bands for samples heated for 3 weeks resembled those of samples heated 4 hr at about 425°C. For sample *T* heated at 630°C, there were considerable changes in the CO_2 and carbonate bands with time of heating (Figs. 4 and 5). Initially, CO_2 was formed very rapidly (the maximum CO_2 was

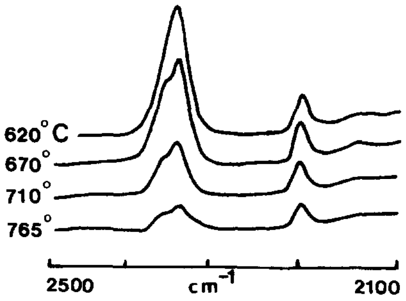

FIG. 3. Variation in the carbon dioxide band profile for enamel heated 4 hr in air at different temperatures (°C).

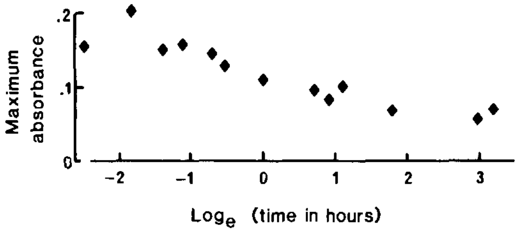

FIG. 4. Changes in the peak absorbance of the carbon dioxide band at 2340 cm^{-1} with time for synthetic apatite *T* heated in air at 630°C.

formed within 10 min) and there was a net loss with prolonged heating (to 25 hr) at this temperature.

(*d*) *Samples heated in carbon dioxide, nitrogen, or oxygen.* The intensity of the CO_2 band for sample *T* or enamel heated for 4 hr at 325 or 425°C was similar to that of the corresponding sample heated in air.

(*e*) *Samples heated under vacuum.* After heating to 450°C, *T* and *T'* samples exhibited bands at 2341 cm^{-1} ($^{12}CO_2$) and 2277 cm^{-1} ($^{13}CO_2$), respectively.

(*f*) *Polarized infrared measurements.* The measured value of the dichroic ratio for the ν_3 band at 2340 cm^{-1} observed in heated tooth enamel (Fig. 6) was 0.926 from which a value for α of 55.77° was calculated. This is only a minimum value because any lack of perfect orientation of the apatite crystals in the enamel will increase the dichroic ratio and hence reduce the angle calculated from it. The upper limit to the true angle can be calculated from methods developed to study partially oriented polymers (*30*). The assumption is made that the effect of disorder on the 2200 and 2330 cm^{-1} bands is the same. The observed dichroic ratio for the 2200 cm^{-1} band is 8.85, therefore the true ratio lies between this value and infinity. A parameter describing the maximum amount of disorder can be calculated on the assumption that the true ratio is infinity. This parameter can then be used to calculate the minimum of the true dichroic ratio for the 2330 cm^{-1} band. This calculated minimum is 0.900 which gives a maximum value of α of 56.14°. Hence α is between 55.77 and 56.14°.

Other samples. Other biological and mineral samples were studied to see if they retained CO_2 when heated in the range 400–800°C. The results are given in Table I.

Discussion

The location of the CO_2 is not established by the available data but some of the possibilities are disfavored. The small low frequency shift (9 cm^{-1}) of the apatite $CO_2\nu_3$ band from the gas phase frequency (2349 cm^{-1}) indicates that the species is subject to only a weak perturbation. The ν_3 transition moment of CO_2 is parallel to the long axis of the molecule. Therefore, the observed dichroic ratio for the 2340 cm^{-1} band could mean that the axis of the linear CO_2 mole-

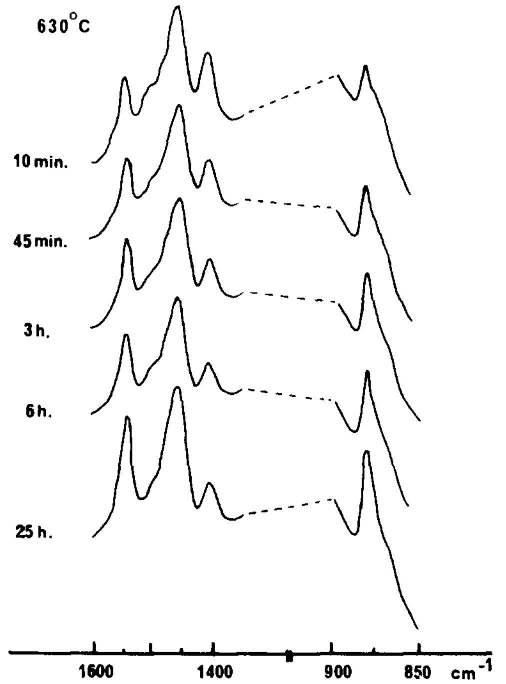

FIG. 5. Carbonate bands for synthetic apatite *T* heated for various times at 630°C in air.

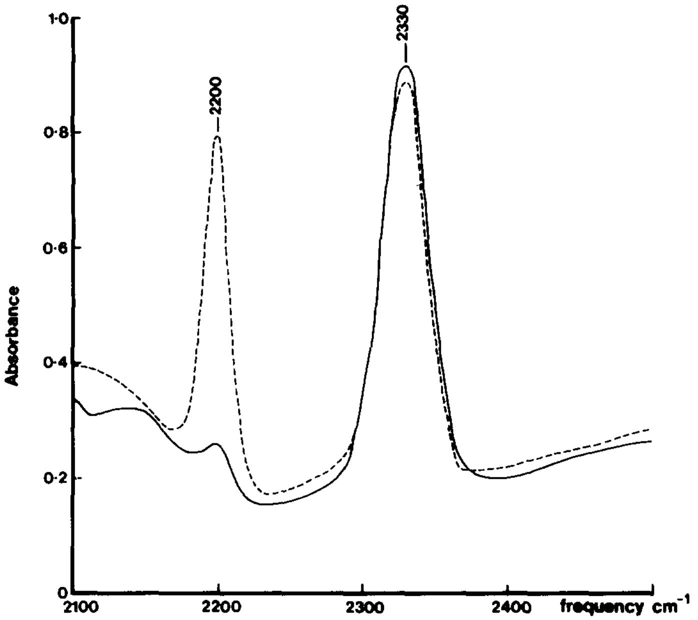

FIG. 6. Polarized infrared spectrum of 250 μm thick longitudinal section cut from a human unerupted third molar heated in CO_2 at 950°C for 30 min. The dashed line is the spectrum with the electric vector parallel to the enamel prisms (approximately the *c* axis of the apatite crystals) and the solid line is the spectrum with the electric vector perpendicular to the enamel prisms. The band at 2200 cm^{-1} is due to cyanate (*21*).

cule makes an angle of about 56° with the *c* axis. Alternatively, the CO_2 molecules could be randomly oriented with the small dichroism of the band arising from some trivial factor, for example, differing scattering losses for the two directions of polarization caused by the oriented arrangement of the 4–7 μm diameter enamel prisms.

The possible sites of the CO_2 molecule will be considered, starting with the interpretation that the molecules are oriented in the structure. The most obvious lattice site for the CO_2 molecules is a vacant PO_4 site which could arise if some of the carbonate ions replacing phosphate ions decomposed *in situ*. Assuming that the oxygen atoms of the carbonate ion occupied the approximate positions A, B, C (Fig. 1) and decomposed into a CO_2 molecule whose oxygen atoms occupied the approximate positions C, E, the axis of the CO_2 molecule would make an angle of about 55° with the *c* axis. This is close to the measured value of 56°. Thus it is possible to make a self-consistent hypothesis about the formation and location of the CO_2 molecule based primarily on the infrared measurements. Although this hypothesis is attractive, it cannot be conclusively proved by these measurements of dichroic ratio.

An alternative lattice site for the CO_2 molecule is within the *c*-axis "channel." Trapping of CO_2 in this location has been proposed for some carbonate-containing apatites (*11*, *19*). Although the carbonate ion is tilted with respect to the *c* axis in the "channel" site (*5*), it would be anticipated that a CO_2 molecule would be colinear with the axis thus presenting least steric interference with other ions and conforming to the site symmetry of the lattice. Such an orientation of CO_2 molecules would result in strong parallel dichroism which was not observed for the 2340 cm^{-1} absorption. Thus it is very unlikely that the CO_2 absorbing at 2340 cm^{-1} in air-heated enamel occupies sites in the *c*-axis channels.

If alternatively the 2340 cm^{-1} band has no true dichroism, the molecules must be randomly oriented, either adsorbed on surfaces or occluded in pores. Several findings suggest that the 2340 cm^{-1} band is not due to CO_2 adsorbed on *external* surfaces. Both the $^{12}CO_2$ and $^{13}CO_2$ bands have been observed for synthetic apatites heated and cooled in a high vacuum. It would be anticipated that a ^{13}C-enriched apatite heated and cooled in air would adsorb a disproportionate amount of $^{12}CO_2$, but the relative intensities of $^{13}CO_2$ and $^{12}CO_2$ have been found to be consistent with the original isotopic enrichment (*5*). The 2340 cm^{-1} band was not reduced in intensity for a synthetic apatite subjected to vacuum (*5*) and little changed for samples boiled in aqueous media (presumably the small reduction in intensity of the CO_2 band after a week in boiling water was due to some dissolution and regrowth of crystals).

Another possibility is that the CO_2 is occluded in the solid, either in pores formed by the loss of several ions adjacent to each other in the lattice, or pores formed between adjacent crystallites. In the latter case, adsorption on an internal surface might occur. The formation of voids within apatite crystallites has been observed under conditions of electron microscopy (*31*) and similar processes might occur during thermal decomposition. The band profile could be explained either by occlusion of CO_2 at a high pressure since rotational fine structure is lost when the pressure of a gas is increased (*32*), or by the loss of free rotation due to adsorption on internal surfaces. Parkyns (*33*) studied CO_2 trapped in micropores of alumina aerogels and suggested that its absorption at 2346 cm^{-1} ($\nu_{\frac{1}{2}} = 20$ cm^{-1}) signified a "quasi-liquid" state. The halfwidth of the CO_2 band in apatites is similar, so that there might be analogies between the state of the CO_2 in apatite and in the alumina aerogels.

The above arguments have to be qualified in the case of powdered enamel heated at 670°C and above in which a high frequency shoulder is observed (Fig. 3). This could indicate some hindered rotation of the molecules or the presence of CO_2 in an additional site (possibly a lattice site). The dichroism of this shoulder is not known, so that possibilities cannot be restricted.

Among the synthetic CO_3Aps, the trapping of carbon dioxide appeared to be favored by increased crystallite size of the apatite prior to thermal treatment. Also the carbon dioxide band was not observed for apatites formed from biological minerals of smaller crystallite size than enamel (Table I). This observation would be consistent with the generation of gas molecules within crystallites and their low mobility by diffusion (*34*). However, the unheated materials differed not only in crystallite size. The retention of carbon dioxide might depend on factors such as carbonate ion content and distribution, or the ultrastructure of the material. Dependence on a physical characteristic such as pore size might explain the differences in CO_2 trapping among the biological apatites having different ultrastructure and the (as yet) unpredictable behavior of mineralogical apatites (Table I). It might also account for the greater variations in the amount of CO_2 trapped by different enamel samples after a given heating regime than was observed for synthetic apatites.

The mechanism of CO_2 production is unknown, but evidence from isotopic substitution and the heating of apatites in different atmospheres shows that the CO_2 arises from decomposition of the compound itself and not from reaction with atmospheric CO_2.

Possible reactions include

$$CO_3^{2-} \rightarrow CO_2 + O^{2-} \quad \text{(I)}$$

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \quad \text{(II)}$$

$$HCO_3^- \rightarrow CO_2 + OH^- \quad \text{(III)}$$

$$CO_3^{2-} + 2HPO_4^{2-} \rightarrow CO_2 + 2PO_4^{3-} + H_2O \quad \text{(IV)}$$

$$CO_3^{2-} + P_2O_7^{4-} \rightarrow CO_2 + 2PO_4^{3-} \quad \text{(V)}$$

If carbonate ions decompose by reaction (I), the oxide ions may undergo further reaction. By analogy with the reaction of oxyapatite in which the O^{2-} are very reactive (*35*), the oxide ions may react with water forming hydroxyl ions. Some O^{2-} ions may also react with hydrogen phosphate or pyrophosphate ions (*36*).

The production of CO_2 at relatively low temperatures (300°C) has been attributed to the decomposition of bicarbonate ions present in apatite before heating (*37, 38*). Bicarbonate might also be formed as a transient species from reaction (II). Both reactions (II) and (III) would contribute to the observed increase in hydroxyl ion content.

Hydrogen phosphate ions may be involved in the formation of CO_2. Pyrophosphate ions are formed by the thermal condensation of hydrogen phosphate ions in nonstoichiometric hydroxyapatite (*39*). However, Greenfield *et al.* (*36*) noted that the production of pyrophosphate was depressed in the presence of carbonate ions and suggested this was through reactions (IV) and (V). Although the presence of hydrogen phosphate ions in our samples was not indicated by infrared spectroscopy, small amounts may escape detection because the characteristic band at 870 cm^{-1} (*14*) would be masked by strong carbonate absorption in this region.

The association between the formation of CO_2 and pyrophosphate, proposed by Winand (*18*) is not substantiated by this study. In the spectra of all samples exhibiting a CO_2 band, Winand noted the appearance of a band at 740 cm^{-1} which he assigned to pyrophosphate. In the present study, a 740 cm^{-1} band was not observed and no significant absorption band was seen for any sample in the region of 725 cm^{-1}, the frequency generally assigned to β-calcium pyrophosphate (*40*).

Whatever the origin or location of the CO_2, its retention may influence the thermal decomposition of CO_3Aps in two ways. First, the extent of decomposition under given conditions may be retarded by the presence of the gaseous product. Second, the CO_2 may react in other ways with the initial apatite decomposition product. It is possible (*17*) that it acts as an intermediate in the observed reorganization of carbonate ion locales with prolonged heating (Fig. 5), and might also be involved in the formation of cyanate and cyanamide species (*24*).

Finally, it is noted that the presence of molecular CO_2 may be a source of error in the carbonate assay of thermally treated apatites since this generally depends on the measurement of CO_2 evolved by reaction with acid.

Acknowledgments

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