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# Infrared Study of the Formation, Loss, and Location of Cyanate and Cyanamide in Thermally Treated Apatites

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Infrared spectroscopic studies show that cyanate and cyanamide ions are formed when carbonate-containing apatites are heated with nitrogenous materials such as protein or ammonia gas. The amount formed increases with temperature starting at about 300°C, then falls off, becoming zero about 900°C. Polarized infrared spectra of heated dental enamel sections show that the cyanate ion lies in the direction of the apatite $c$ axis.

## Introduction

Cyanate, $NCO^-$ and cyanamide, $NCN^{2-}$ ions are linear and isoelectronic with $CO_2$. For the free cyanate ion, infrared activity is predicted for $\nu_1$ (symmetric stretch) near 1200 $cm^{-1}$, $\nu_3$ (asymmetric stretch) near 2200 $cm^{-1}$, and $\nu_2$ (bending) in the range 600–640 $cm^{-1}$ with transition moments parallel and perpendicular to the long axis of the ion for the stretching and bending modes, respectively (*1*). For matrix-isolated cyanate ions, the observed intensities of $\nu_1$ and $\nu_2$ are very much weaker than $\nu_3$ (*2*). The frequencies of the cyanamide are in the same region as those of the cyanate ion, but for the free ion, only $\nu_2$ and $\nu_3$ are infrared active because of its higher symmetry (*1*).

An almost stoichiometric cyanamide apatite, $Ca_{10}(PO_4)_6CN_2$, has been prepared by heating an intimate mixture of calcium cyanamide and hydroxyapatite at 900°C in a vacuum (*3*). This had lattice constants $a = 9.47_0$ and $c = 6.87_7$ Å, and it hydrolyzed on heating in air, first to give an apatite with carbonate ions in the $c$-axis channels with the release of ammonia, and then to hydroxyapatite with the release of carbon dioxide. Small amounts of nitrite and cyanate were also formed during the decomposition. An impure form of cyanamide apatite was also prepared by heating an apatite with carbonate ions in the $c$-axis channels in ammonia at 600–900°C. There does not appear to be any report of a cyanate apatite, $Ca_{10}(PO_4)_6(NCO)_2$.

Cyanate and cyanamide $\nu_3$ infrared absorption bands, at 2200 and 2012 $cm^{-1}$, respectively, have been detected in heated apatitic biological tissues and in some heated carbonate-containing apatites ($CO_3$Aps) prepared in ammoniacal aqueous solutions (*4, 5*). These assignments were supported by $^{13}C$ and $^{15}N$ isotopic shifts. This communication reports a study of the effects of time, temperature, and atmosphere on the formation and loss of these

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cyanate and cyanamide species, and polarized infrared measurements which give the orientation of the cyanate ion.

## Materials

Most of the materials have been described previously in a study of the formation of trapped carbon dioxide in thermally treated apatites (*6*). A precipitated carbonate-containing apatite ($CO_3Ap$) designated synthetic P was prepared by the reaction between calcium acetate, ammonium phosphate, and carbonate solutions, and a transformed $CO_3Ap$ (synthetic T) by the reaction between an ammonium phosphate solution and calcite. Both preparations took place at high pH and typically contained 0.12 wt% nitrogen. A $CO_3Ap$ designated synthetic X and prepared by precipitation in an aqueous solution of sodium salts by Zapanta-LeGeros (*7*) was used. Human dental enamel and dentine, rat bone, whole and anorganic shark vertebrae, and two air-dried whole human teeth, apparently caries-free, were also investigated.

## Methods

Details of infrared spectroscopy, X-ray diffraction, and the method of heating samples in air have been described previously (*6*). The whole teeth were heated for 2 hr at 1000°C, one under high vacuum ($1.3 \times 10^{-4}$ Pa) and the other in air. Calcium cyanamide was prepared by the reaction of calcium carbonate and ammonia (*8*). The calcium carbonate was first dried at 230°C in a flow of nitrogen. A slow flow of ammonia at about atmospheric pressure was maintained while the sample was heated to 700°C over 2½ hr, held at 700°C for 75 min, then allowed to cool to room temperature. Samples of synthetics X and T and enamel were similarly heated in ammonia.

## Results

### *Cyanate and Cyanamide Infrared Bands for Air-Heated Samples*

Synthetics P and T showed a similar pattern of cyanate and cyanamide production with temperature for a given time of heating (4 hr), although relatively more cyanate was formed in synthetic P (Fig. 1). Synthetic X exhibited neither band. For synthetic T, the cyanate band was always at 2200 $cm^{-1}$ and had a smooth profile. However, for synthetic P the frequency of this band varied progressively with temperature of treatment (Fig. 2) and shoulders (~2179

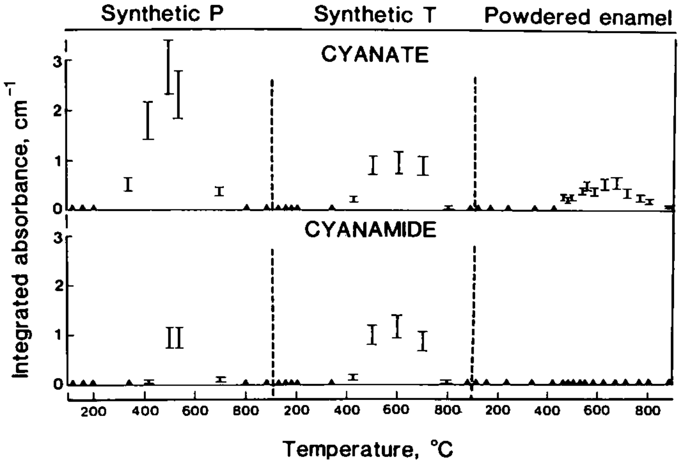

FIG. 1. Integrated absorbances of cyanate and cyanamide bands for synthetics P and T and enamel heated for 4 hr at various temperature (▲ indicates that the band was not detected).

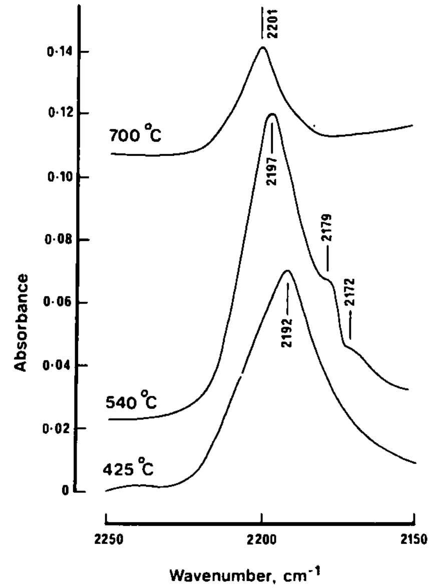

FIG. 2. Profile of the cyanate band of synthetic P after being heated at 425, 540, and 700°C for 4 hr.

and ~2172 $cm^{-1}$) were observed for samples heated at 500 (not shown) and 540°C. Differences were also seen in the development of the cyanate and cyanamide bands with time at fixed temperature. For example, for synthetic T at 340°C, the cyanate band was observed before a cyanamide band was detectable (Fig. 3), while at 630°C, the absorbance of the cyanate band was almost unchanged but the cyanamide band decreased with time (Fig. 4).

For enamel, the cyanamide band was not detected but the cyanate band showed variation in absorbance with temperature similar to that for synthetics P and T (Fig. 1). The polarized infrared spectrum (Fig. 5) shows that the 2200-$cm^{-1}$ band has almost complete parallel dichroism. The actual dichroic ratio reported previously (*6*) is 8.85.

Anorganic shark vertebra exhibited neither band. The limiting conditions of cyanate and cyanamide production for dentine, bone and "whole" shark vertebra were not established but a good yield was obtained after a relatively short time of heating at high temperature (e.g., 1 hr, 800°C). For dentine and bone the frequencies were constant within the limits of measurement (±2 $cm^{-1}$) but the cyanamide band for the whole shark vertebra shifted from 2020 $cm^{-1}$ for material heated at 520°C, to 2015 $cm^{-1}$ for that heated at 700 or 800°C.

## *Teeth Heated at 1000°C in Vacuum or in Air*

Neither cyanate nor cyanamide was detected in the air-heated materials, but cyanate ($\nu_3$ at 2200 $cm^{-1}$ very weak) was seen for enamel, and cyanamide ($\nu_3$ at 2012 $cm^{-1}$ medium; $\nu_2$ at 697 $cm^{-1}$ very weak) for dentine from the tooth heated in vacuum. The vacuum-heated materials exhibited weaker hydroxyl absorption but stronger carbonate bands than the air-heated materials.

## *Products of Reactions with Ammonia*

The calcium cyanamide prepared from calcium carbonate exhibited cyanamide bands were generally observed at 2012 and $cm^{-1}$ (not shown), similar to those observed for an impure commercial product, Nitro-

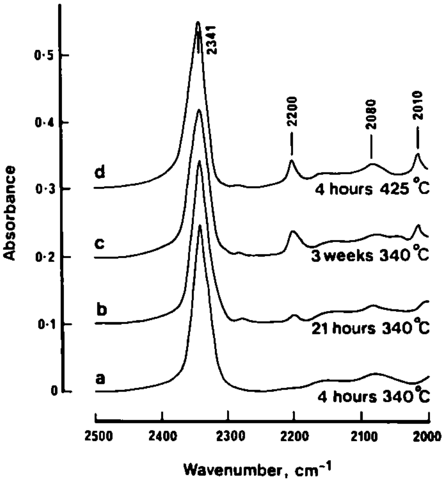

FIG. 3. Changes in cyanate (2200 $cm^{-1}$) and cyanamide (2010 $cm^{-1}$) bands for synthetic T heated for various times at 340°C compared with heating for 4 hr at 425°C. The band at 2341 $cm^{-1}$ is due to $CO_2$ (*6*) and the broad band at 2080 $cm^{-1}$ is of unknown origin.

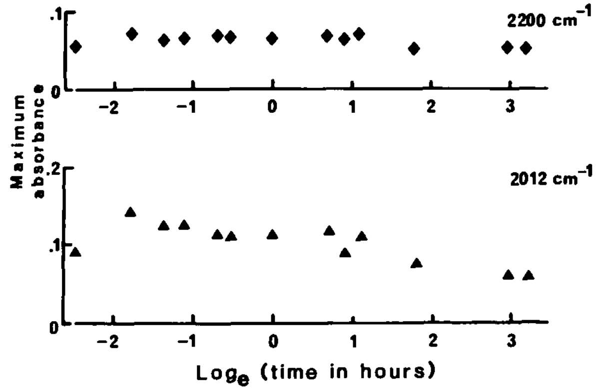

FIG. 4. Changes in the peak absorbance of the cyanate band at 2200 $cm^{-1}$ and cyanamide band at 2012 $cm^{-1}$ with time for synthetic T after heating in air at 630°C.

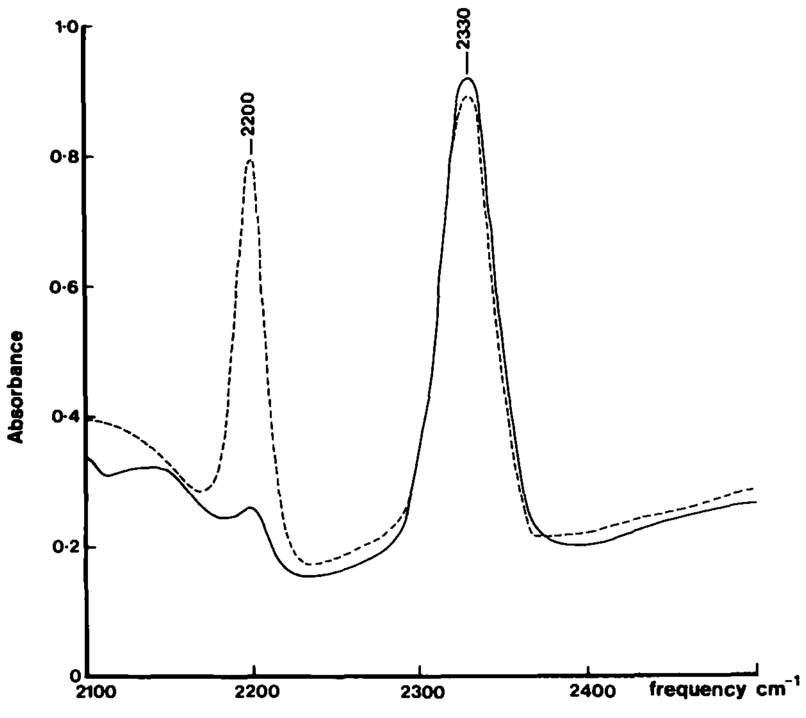

FIG. 5. Polarized infrared spectrum of 250-μm-thick longitudinal section cut from a human unerupted third molar heated in $CO_2$ at 950°C for 30 min (*6*). The dotted line is the spectrum with the electric vector parallel to the enamel prisms (approximately the *c* axis of the apatite crystals) and the full line is the spectrum with the electric vector perpendicular to the enamel prisms. The band at 2330 $cm^{-1}$ is due to $CO_2$.

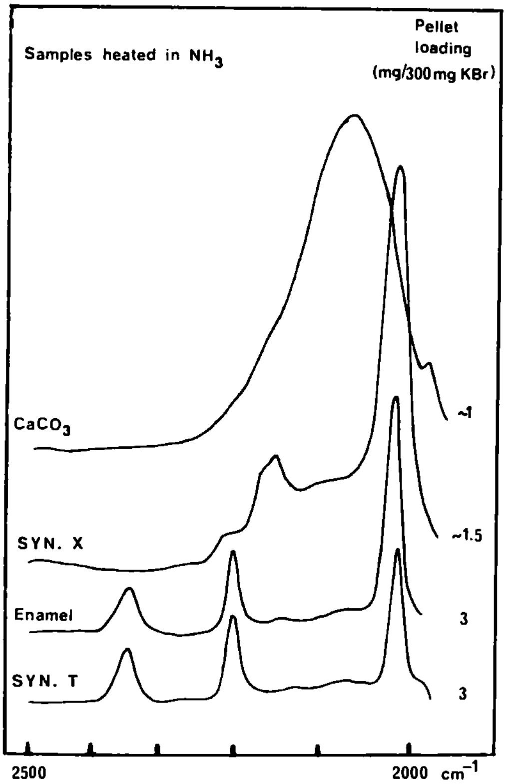

FIG. 6. Spectra of the $\nu_3$ cyanamide band for $CaCO_3$, enamel, and synthetics X and T heated in ammonia.

lim. The low frequency band was slightly split but this may have been an artifact due to atmospheric $CO_2$ absorption.

The spectrum of the synthetic T product resembled that of a sample similarly heated in air except that the cyanate (2200 $cm^{-1}$) and cyanamide (2010 and 697 $cm^{-1}$) bands (Fig. 6) were considerably stronger.

X-Ray diffraction showed that the product from synthetic X contained apatite and calcium cyanamide. The presence of another crystalline phase was indicated by several very weak extra lines between the 310 and 222 apatite lines. Calcium cyanide was excluded because the strongest line at 2.87 Å (*9*) was not detected. In the infrared spectrum the ~200-$cm^{-1}$ broad background centered at ~2100 $cm^{-1}$ (Fig. 6) and the ~667-$cm^{-1}$ band were assigned to calcium cyanamide. The assignment of the fairly strong unresolved bands at ~2155 $cm^{-1}$ is unknown but may be the additional phase noted previously. The cyanamide bands (2013 and 699 $cm^{-1}$) were the strongest for any apatite sample in this study (note that the pellet loading was only 1.5 mg sample/300 mg KBr). In contrast to a sample similarly heated in air, no hydroxyl band for calcium hydroxide (3640 $cm^{-1}$) or apatite (3568 and 630 $cm^{-1}$) was observed but the carbonate bands were much stronger.

The spectrum of enamel heated in ammonia resembled that of enamel similarly heated in air except that cyanamide bands (2013 and 699 $cm^{-1}$) were also observed (Fig. 6).

## Discussion

### *Infrared Spectra of Cyanate and Cyanamide Ions*

The polarized infrared results clearly indicate that the cyanate ion lies parallel to the apatite *c* axis. This strongly suggests that the ion is located on this axis.

The variation in the cyanate and cyanamide infrared frequences requires further investigation. The significance of the variation in frequency and the appearance of shoulders in the cyanate absorption of synthetic P products is unknown. The variation in cyanamide frequency suggests that the absorption is sensitive to small changes in environment within the apatite lattice. Trombe and Montel (*3*) reported apatite cyanamide bands at 3230, 2010, 1960, and 695 $cm^{-1}$ for a nearly stoichiometric compound. By contrast in this study of $CO_3$Aps with relatively low cyanamide substitution the bands were generally observed at 2012 and 699 $cm^{-1}$, except for the fluoride-containing shark vertebra where the $\nu_3$ frequency shifted progressively from 2020 to 2015 $cm^{-1}$ with increasing temperature of heating. There is no obvious explanation for the differences in frequencies observed for calcium cyanamide; 2059 and 668 $cm^{-1}$ in this work, 3220, 2040, 1935, and 660 $cm^{-1}$ in (*3*); 2170 and 620 $cm^{-1}$ in (*10*); and 2022 $cm^{-1}$ in (*11*).

### *Formation and Loss of Cyanate and Cyanamide Species*

The reactions are probably analogous to those found in the general chemistry of cyanate and cyanamide ions. The apatitic materials studied contained carbonate or trapped carbon dioxide (*6*) as a source of carbon and oxygen, and protein or residual ammonia or ammonium ions as a source of nitrogen.

The detection of cyanate ions in enamel heated in vacuum and in both enamel and synthetic T heated in ammonia indicates that the oxidation of apatite cyanamide ions in air (*3*) is not the only mechanism of apatite cyanate ion formation. It is probable that a reaction analogous to the *in situ* production of cyanate ions in alkali halide matrices by reaction of dopant ammonium ions (or trapped ammonia) and carbonate or bicarbonate ions (or trapped carbon dioxide) (*12*) may also occur. Evidence for this comes from the fact that cyanate ion formation appears to be associated with the reorganization of carbonate ion localized in the apatite lattice. One group of $CO_3$Aps, enamel and synthetics T and P, exhibited an increase in carbonate for hydroxyl ion substitution and cyanate formation at relatively low temperatures in air. By contrast, dentine, bone, and shark vertebra showed both these changes only at higher temperatures in air. Under the latter conditions the production of cyanate by oxidation of cyanamide may also be significant. The association of cyanate ion formation with the relocation of carbonate ions is also supported by the observation of both of these features in enamel heated at 1000°C in vacuum, but neither feature in similarly treated dentine.

The extent of substitution of the univalent cyanate ion in the *c*-axis channels is probably rather limited because its size would not allow the two ions per unit cell required for charge balance. Thus it would seem that on oxidation the formation of nitrate and carbonate would be encouraged as has been found for cyanate in molten alkali halides (*13*). In this study, neither nitrate nor nitrite ions were detected in any of the materials, but this is not surprising in view of the very small amounts of cyanate or cyanamide ever formed. However, nitrite has been detected in the thermal decomposition of nearly stoichiometric cyanamide apatite (*3*).

Reinterpretation can be made of Labarthe's observations (*14*) that the infrared bands at 2200 and 2010 $cm^{-1}$ were exhibited by heated "direct" $CO_3$Aps (prepared by addition of calcium acetate solution to a solution of ammonium phosphate and carbonate) but not by "inverse" $CO_3$Aps (prepared by addition of ammonium phosphate and carbonate solution to calcium acetate solution). The implication is that incorporation of the nitrogenous precursor of the cyanate and cyanamide species is favoured for apatites precipitated in solutions rich in ammonia and ammonium ions. This appears to be analogous to the enhanced incorporation of sodium ions in "direct" $CO_3$Aps prepared by Bonel *et al.* (*15*). Some of the other differences between the properties of "direct" and "inverse" $CO_3$Aps (as prepared and after heating) (*14*) may be related to the influence of nitrogenous components. Doi *et al.* (*16*) have suggested that $NH_4^+$ ions may substitute in the lattice of precipitated $CO_3$Aps.

## Acknowledgment

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