addition. The infrared spectrum of a sample of the reaction mixture, withdrawn before hydrolysis, indicated a strong absorption at 5·85 μ, and was identical, over the range 5·75–6·00 μ, to the spectrum obtained from a synthetic mixture containing benzotriazole, the benzamide of benzotriazole, benzaldehyde and ether, and was different from that obtained from the synthetic mixture in the absence of benzaldehyde. The reduction products, after hydrolysis and the usual work-up, were benzaldehyde and benzotriazole. It has previously been reported that the reduction of the benzamide of benzotriazole with excess lithium aluminium hydride yields benzyl alcohol and benzotriazole[1].

A nitrogen-aluminium bond has been postulated as an intermediate in the cleavage of compounds containing the $-\overset{|}{\underset{\cdot\cdot}{N}}-\overset{|}{\underset{|}{C}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-$ grouping[2]. The failure to form an oxygen-aluminium bond in such compounds may be due to the non-polarizability of this carbon-oxygen bond.

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Yerkes Research Laboratory, Film Department, E. I. du Pont de Nemours and Company, Inc., Buffalo 7, N.Y., June 30, 1954.

Zusammenfassung

Ein einfacher Mechanismus wurde vorgeschlagen und ein experimenteller Beweis gegeben, um die Bildung von Aminen oder Abspaltungsprodukten in der Reduktion von Amiden mit Lithiumaluminiumhydrid zu erklären.

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Infra-red Study of the Carbonate in Bone, Teeth and Francolite[1]

Introduction

One of the major problems in the crystallography of the inorganic portion of teeth and bone, as well as the mineral francolite, is the elucidation of their carbonate content. Many investigators have claimed that the carbonate is found as an amorphous calcium and magnesium carbonate physically mixed with the apatite phase of these substances[1]. There are others who believe that a carbon radical substitutes in some way, in a structural position of the apatite, forming a carbonate-bearing member of the apatite series[2].

The amount of carbon dioxide released by treating these materials with acid is by no means a trace amount. In the four samples studied, we have the following analyses based on samples purified by specific gravity separation and dried at 110°C. (It is well to note that the bone, dentine and enamel were freed of organic material by boiling in a solution of KOH in glycerine according to the method of GABRIEL[3].)

Sample	% CO_2
cow enamel	2·88
cow dentine	3·91
cow bone (femur)	5·15
francolite	2·70

X-ray work

It is evident that if the CO_2 were present as well crystallized $CaCO_3$ and $MgCO_3$, it would be possible to see the lines of these materials by X-ray diffraction. In fact it was demonstrated that it is possible to detect as little as 3% $CaCO_3$ admixed with apatite by X-ray diffraction methods[4]. However, the latter proof depends upon well crystallized calcite and in the case of the materials studied, it is postulated that the carbonates are too finely crystallized to be detected by X-ray

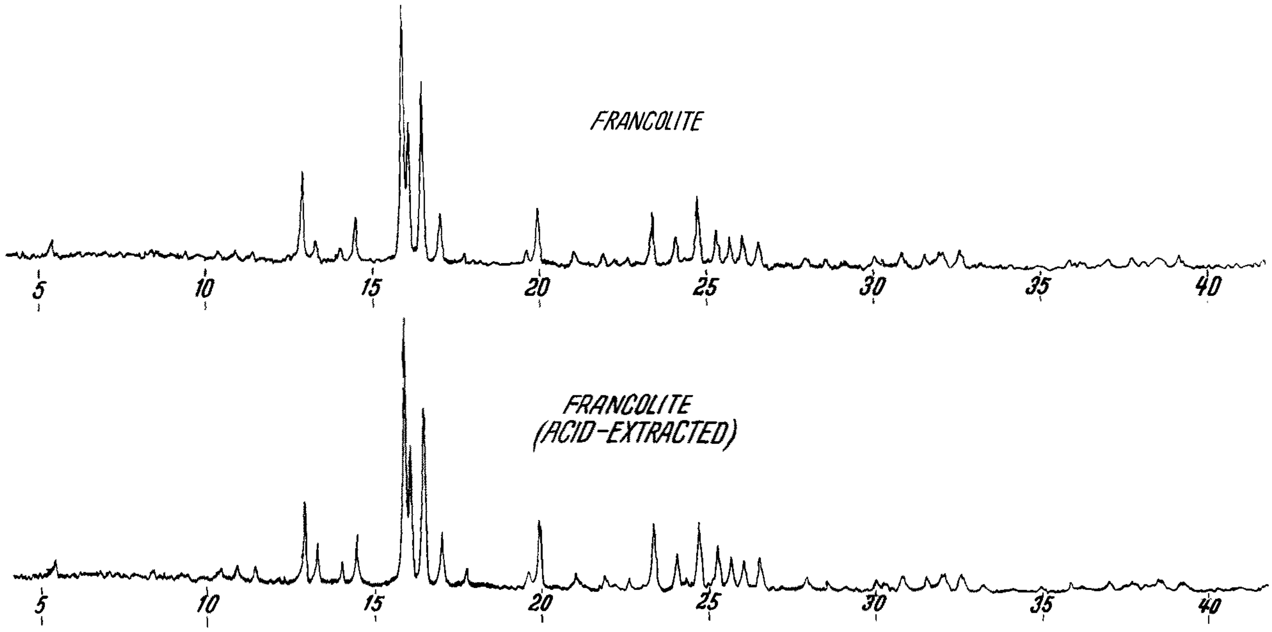

Fig. 1.–X-rays patterns taken with Copper K-alpha radiation. Angles given in degrees theta (Θ).

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[1] This work was partially sponsored by the *Air Research and Development Command*, United States Air Force, through its European Office under contract n° AF 61 (514) 647 C.

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methods. The presence of particles in the inorganic portion of bone and teeth which range in size below 100 Å has been demonstrated by low angle X-ray scattering techniques[1]. However this technique does not tell us exactly what crystalline phase is in that size range. Thus X-ray diffraction techniques alone have been unsuccessful in positively elucidating the character of the carbonate containing apatites. This is illustrated in Figure 1 which compares the X-ray patterns of the mineral francolite before and after about one third of the CO_2 has been leached out by lactic acid treatment. The two patterns are identical, showing the absence of the carbonate in the apatite phase, in a sort of negative manner.

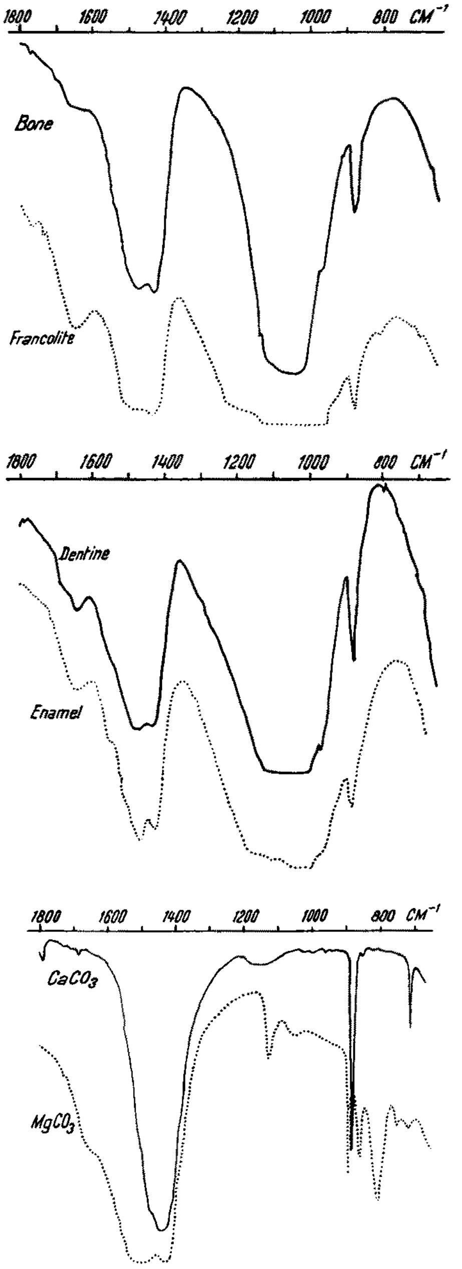

Fig. 2. – A comparison of the infra-red spectrum of dentine, enamel, bone and francolite with the standards calcite and magnesite. The large band appearing at about 1050 cm^{-1} is the orthophosphate band of apatite.

Infra-red studies

It has been shown in the case of calcite that, as its particle size decreases, the intensity and resolution of the characteristic infra-red absorption spectrum increases[1]. This makes the infra-red absorption method ideal for characterizing a possible mixture of amorphous calcite and well crystallized apatite. Due to excessive broadening of the maxima, X-ray diffraction is unable to show crystals which are below about 100 Å in diameter. On the other hand, infra-red spectroscopy can demonstrate the presence of fine crystals.

The samples were prepared for examination by making a dry mixture of chemically pure KBr containing 2·5% of the apatite. After mixing in a hand mortar, the mixture was pressed into a pastille of wafer shape (about 12 mm diameter and 1 mm thick) in a press which was constantly evacuated to avoid air and moisture entrapment and kept at a pressure of 10 tons for 5 min. The pastille was balanced against a standard pastille of pure KBr in a double beam PERKIN-ELMER infra-red spectrometer and the spectrum taken between 1800 cm^{-1} and 650 cm^{-1}. The results are shown in Figure 2.

Conclusions

It seems apparent that there exists in francolite, enamel, bone and dentine a chemical bond between calcium and carbonate and between magnesium and carbonate which is identical to these bonds in calcite and magnesite. This would tend to support the negative X-ray diffraction evidence which shows no change in the apatite phase when the CO_2 is removed.

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Institute of experimental Therapeutics and Laboratory of analytical Chemistry, University of Liège, March 23, 1954.

Résumé

La diffraction des rayons X et la spectrographie infrarouge ont été employées pour rechercher la présence de calcite et de magnésite dans la fraction minérale de l'os et des dents ainsi que dans le minéral qui lui est le plus proche au point de vue chimique, la francolite. Le résultat positif obtenu dans l'infra-rouge indique la présence de liaisons $CaCO_3$ et $MgCO_3$ associées à la matrice fondamentale du type apatite de ces substances.

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Multiple Spots on Paper Chromatograms

It is normally assumed that pure organic compounds give single spots on paper chromatograms and there is no doubt that, in the majority of cases, the assumption is justified. There are, however, various recorded instances of pure compounds giving multiple spots. In some cases the development of several spots is due to the formation of a new molecular species under the conditions of chromatography. Glucuronic acid gives spots corresponding to the original compound and the