

genes any more. Viruses and carcinogens could cause mutation or could block or disturb repression in another way. It might be possible that different blocks in different spaces are added, so that the sum of many defects, which in themselves are unimportant for tumour formation, could cause disordered cell growth.

From this point of view the formation of melanomas in *Poeciliidae* represents a model for the formation of cancer<sup>41</sup>.

**Zusammenfassung.** Bei bestimmten Zahnkarpfen-Bastarden treten stets erbbedingte Melanome auf. Diese entstehen dadurch, dass bestimmte Gene, die für die Differenzierung von Farbzellen verantwortlich

sind, enthemmt und gleichzeitig zu einer gesteigerten Aktivität angeregt werden. Die Enthemmung beruht auf einem Verlust bestimmter Repressionsgene und die Aktivitätssteigerung auf einer Einführung polyfaktorieller Systeme von Induktionsgenen. Es bestehen schwerwiegende Indizien dafür, dass die Induktorsubstanzen mit Aminosäuren identisch sind.

<sup>41</sup> I should like to thank Dr. C. KOSWIG (Hamburg) and Dr. M. DZWILLO (Hamburg) for their valuable criticism, J. VIELKIND (Giessen) for translation, and W. BACKER (Giessen) for reading through the manuscript. The experiments of the author have been supported by a grant from Deutsche Forschungsgemeinschaft and Stiftung Volkswagenwerk.

## SPECIALIA

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### IR-Spectra of Fluorapatite and Fluorchlorapatite

Apatites are crystalline solids typified by hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , a basic calcium phosphate. Many substituents are possible in the apatite lattice giving rise to a whole series of related compounds.

It is now possible<sup>1</sup> to prepare an apatite with fluoride in the place of the hydroxyl ion, in which case the compound is known as fluorapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ . The mixed apatites have also been prepared by heating together calculated quantities of  $\beta\text{-Ca}_3(\text{PO}_4)_2$ ,  $\text{CaCl}_2$  and  $\text{CaF}_2$  at 800°C or by treating a pure synthetic chlorapatite with different amounts of  $\text{CaF}_2$ .

When fluoride is fully substituted for all the hydroxyl ions in hydroxyapatite, the unit cell of the resulting fluorapatite has a smaller a-axis but the same c-axis as the unsubstituted hydroxyapatite. It is possible that this lattice parameter difference is due to the change centred in the calcium triangle. The OH ions of hydroxyapatite lie with their internuclear axis coincident with the sixfold screw axis and at a distance of 0.3 Å from the nearest trigonal calcium plane. On the other hand, the F ions of fluorapatite lie at the intersection of the plane with the sixfold screw axis, and the Cl ions of chlorapatite lie on the sixfold screw axis but midway between adjacent planes<sup>2</sup>. These positions are illustrated in Figure 1.

The first apatite structure completely worked out was that of the mineral calcium fluorapatite<sup>3,4</sup>. It is of hexagonal structure, having space group  $\text{P6}_3/\text{m}$ . The unit cell dimensions, for hydroxyapatite<sup>5</sup> and fluorapatite<sup>4</sup> are given in Table I.

The IR-spectra of hydroxyapatite, fluorapatite, and fluorchlorapatites are shown in Figures 2–6. The IR-spectrum of hydroxyapatite is included for reference purposes. The hydroxyapatite and other specimens were

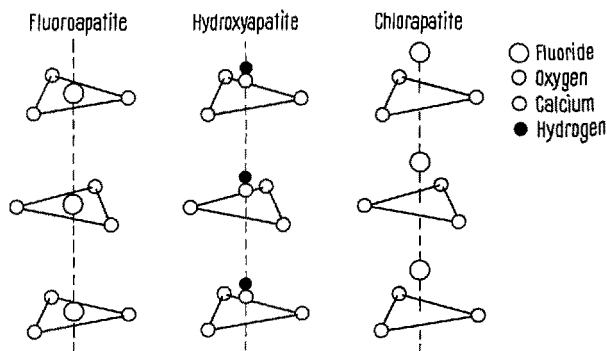


Fig. 1. Diagram showing the fluoride, hydroxyl, and chloride positions in the apatite structure<sup>2</sup>.

Table I. Unit cell dimensions of hydroxyapatite<sup>5</sup> and fluorapatite<sup>4</sup>

Apatite	a Å	c Å
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	$9.432 \pm 0.005 \text{ Å}$	$6.881 \pm 0.005 \text{ Å}$
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	$9.37 \pm 0.01 \text{ Å}$	$6.88 \pm 0.01 \text{ Å}$

<sup>1</sup> R. WALLAEYS and G. CHAUDRON, C. r. Acad. Sci., Paris 231, 355 (1950).

<sup>2</sup> J. M. STUTMAN, J. D. TERMINE, and A. S. POSNER, Trans. N.Y. Acad. Sci. 27, 669 (1965).

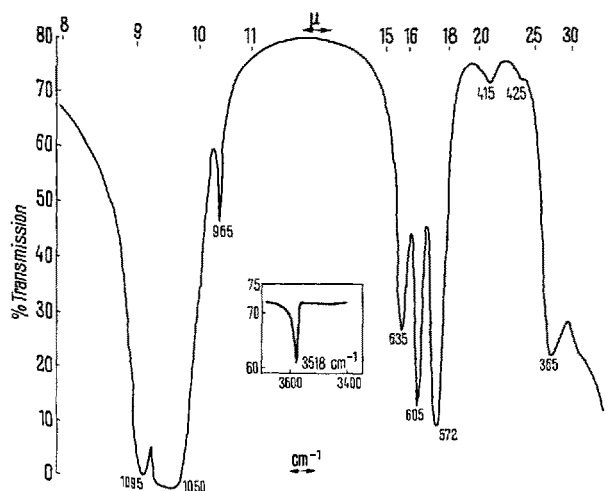
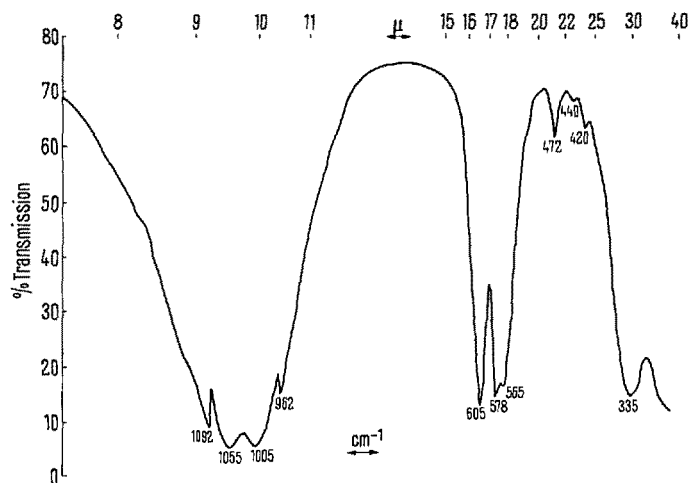
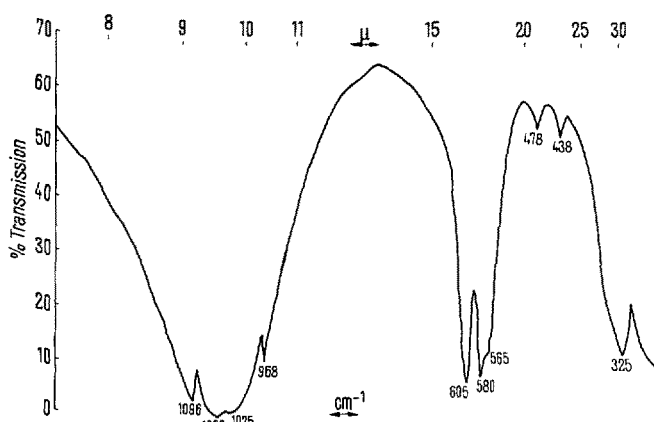
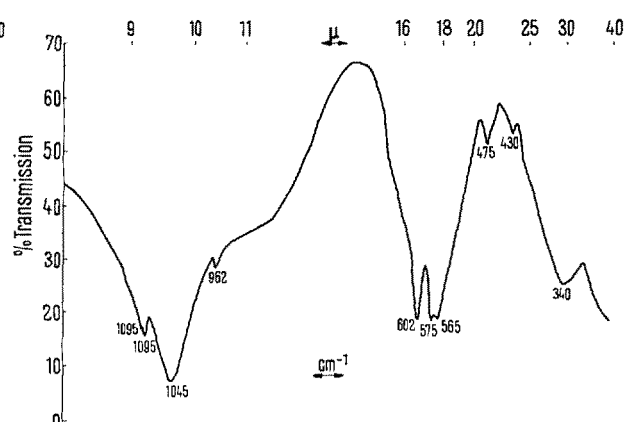
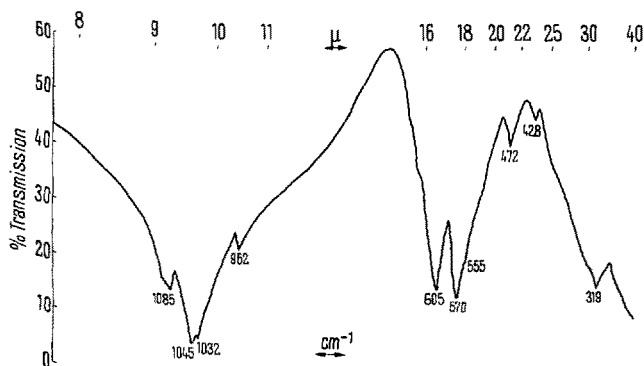
<sup>3</sup> M. MEHREL, Z. Kristallogr. Miner. 75, 323 (1930).

<sup>4</sup> S. NARAY-SZABO, Z. Kristallogr. Miner. 75, 387 (1930).

<sup>5</sup> M. I. KAY, R. A. YOUNG, and A. S. POSNER, Nature 204, 1050 (1964).

synthetic materials which were found to be stoichiometric by chemical analysis. The samples were ground to a fine powder in a small agate mortar. The alkali halide disc technique was used to study the IR-absorption spectra. The spectra were recorded with a Beckman IR-Spectrophotometer IR 12. The frequencies and assignments for the absorption spectra are given in Table II.

The hydroxyl ions give rise to a single very narrow absorption band whose frequency ( $3578\text{ cm}^{-1}$ ) is near to the value ( $3700\text{ cm}^{-1}$ ) expected from the free OH stretching mode. Hydroxyapatite has also one peak at  $635\text{ cm}^{-1}$ , presumably due to the  $\text{PO}_4^{3-}$  ions, which is not present in other apatites. The absence of the  $3578\text{ cm}^{-1}$  band in fluorapatite and fluorchlorapatites is consistent with the

Fig. 2.  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ .Fig. 5.  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{2-x}\text{Cl}_x$  ( $x = \pm 0.06$ ).Fig. 3.  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ .Fig. 6.  $\text{Ca}_{10.4}(\text{PO}_4)_6\text{F}_{1.449}\text{Cl}_{0.579}$ .Fig. 4.  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{0.554}\text{Cl}_{1.446}$ .

high F or F-Cl content of the samples and shows that most of the positions on the sixfold axis are occupied by F or F-Cl rather than hydroxyl ions.

From the structure of fluorapatite<sup>4</sup>, it is obvious that the only symmetry element possessed by the site occupied by the phosphate ions is a plane of symmetry perpendicular to the c-axis. The phosphorus and 2 of the oxygen atoms lie in this plane, whilst the remaining oxygen atoms are symmetrically placed above and below it. The site symmetry is  $C_s$ , consequently all the modes are IR-active and all the degeneracies are lost. The tetrahedral phosphate ion,  $\text{PO}_4^{3-}$ , gives 4 fundamental frequencies around  $1082$ ,  $980$ ,  $515$ , and  $363\text{ cm}^{-1}$ . The lowering of the symmetry of the phosphate ion from  $T_d$  to  $C_s$  causes  $\nu_1$  at  $980\text{ cm}^{-1}$  to become IR-active. The normal mode  $\nu_2$  at

Table II. Frequencies and assignments for hydroxyapatite, fluorapatite and fluorchlorapatites

Apatites					Assignment
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ Frequency $\text{cm}^{-1}$	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{0.554}\text{Cl}_{1.446}$	$\text{Ca}_{10.4}(\text{PO}_4)_6\text{F}_{1.449}\text{Cl}_{0.579}$	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_{2-x}\text{Cl}_x$ ( $x = \pm 0.06$ )	
365 m	325 w	319 w	340 w	335 m	$\nu_2 \text{PO}_4$ ?
425 vw	438 w	428 w	430 w	420 vw	$\nu_3 1050 - \nu_4 605 = 445$
475 w	478 w	472 m	475 m	440 vw 472 m	$\nu_3 1050 - \nu_4 605 = 445$ $\nu_3 1050 - \nu_4 572 = 478$
572 s	565 s	555 s	565 s	565 s	$\nu_4 \text{PO}_4$
605 s	580 s	570 s	575 s	578 s	
635 s	605 s	605 s	602 s	605 s	
965 m	968 w	962 w	962 w	962 w	$\nu_1 \text{PO}_4$
1050 s	1025 s	1032 s	1045 s	1005 s	$\nu_3 \text{PO}_4$
1095 s	1050 s	1045 s	1090 s	1055 s	
	1096 s	1085 s	1095 s	1092 s	
3578 m	—	—	—	—	OH

$363 \text{ cm}^{-1}$  should also thus become IR-active. The triple degeneracies of  $\nu_3$  and  $\nu_4$  are both lost. This loss of degeneracy causes the band at about  $1090 \text{ cm}^{-1}$ , which could also arise due to interactions between the 6 phosphate ions in the apatite unit cell. However, the band at about  $962 \text{ cm}^{-1}$ , which is IR-inactive in the undistorted ion, arises from the lowering of the symmetry.

2 bands which appear consistently in the spectra of fluorapatite and fluorchlorapatites absorb in the region  $420\text{--}480 \text{ cm}^{-1}$ . They are assigned as the difference tones, as the numerical values of their frequencies are close in magnitude to the difference between  $\nu_3$  and  $\nu_4$ . STUTMAN et al.<sup>2</sup> also observed 1 band in this region and they excluded it from a  $\nu_4$  designation<sup>6</sup>.

**Zusammenfassung.** Es wird eine Zuordnung der IR-Absorptionsbanden zu den Tetraederschwingungen des  $\text{PO}_4$ -Tetraeders in Apatit gegeben.

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Nashville (Tennessee, USA), May 31, 1966.*

<sup>6</sup> This work was supported by Research Grant No. DE-02102-02 U.S. Public Health Service. I thank Prof. NELSON FUSON for his keen interest and very useful discussions. The samples were kindly supplied by Dr. E. F. APPLE of General Electric Company.

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### Astaxanthin in the Blue Oceanic Barnacle *Lepas fascicularis*<sup>1</sup>

Specimens of the blue, oceanic, stalked barnacle *Lepas fascicularis* are encountered occasionally during spring cruises, or more rarely when swept shoreward by strong prevailing winds. This pelagic, hermaphroditic crustacean adheres, through its stalk, to such objects as floating feathers, bits of tar, cork, wood or other flotsam, and relatively frequently to the small oceanic siphonophore *Velella lata*, whose blue color it closely matches. After the barnacle's own float has grown sufficiently large and air-laden to afford independent support, the animal relinquishes its adherence to a foreign object.

Inspection of the materials consumed by *L. fascicularis* reveals that the animal feeds extensively upon microcrustaceans such as copepods. Earlier studies of the carrying host, *V. lata*, had shown that these animals also feed upon small pelagic crustaceans, floating marine eggs, larvae and microscopic detritus, and that the blue pigment of this colonial coelenterate involves astaxanthin chromoprotein complexes<sup>2</sup>. And indeed BALL reported,

in 1944, that the blue eggs of *L. fascicularis* involved protein conjugated with a xanthophyll carotenoid suspected of being astaxanthin<sup>3</sup>.

In April 1966 a blue *Lepas* was taken from one of a *Velella* population which had been wind-transported toward shore off the Scripps Institution. Since this species of barnacle is of such chromatic interest, but so relatively rare, it was decided to complete such carotenoid analyses as might be feasible, in order to outline some main facts about its body pigmentation (e.g. whether pigmentary or Tyndall-blue) until, in a later spring, additional specimens should make possible a more searching investigation.

<sup>1</sup> These researches are among those supported by Research Grant No. GB-2312 to the senior author from the National Science Foundation. We are indebted also to Dr. W. A. NEWMAN for his help and information concerning the biology of this barnacle.

<sup>2</sup> D. L. FOX and F. T. HAXO, XVth Int. Congr. Zool., Sect. III, No. 2 (1958).

<sup>3</sup> E. G. BALL, J. biol. Chem. 152, 627 (1944).