

that such a change would cause a 0.2% shortening at 23° C and only 0.01% at 45° C. Figs. 2 and 3 show that the contraction due to irradiation is much larger, and also that it is the same at both temperatures. A temperature rise cannot therefore be the cause of the contraction. The figures also show that the recovery phases after irradiation are as long as the *cis* to *trans* back reactions of the dye in aqueous solution at these two temperatures. The rate of the dark reaction in a gel of lower dye concentration was the same as in water.

The 20% increased water content after the absorption of the *trans* dye into the membrane is indicative of a rather strong interaction, probably reducing the amount of hydrophobic exposure of the polymer chains in the gel. As the dye undergoes the *trans* to *cis* isomerization the macromolecules in the membrane presumably rearrange conformationally because of a decrease in attachment of the dye in the *cis* form, or a change in its mode of attachment. The gel therefore reverts to a state of lower water content. This is analogous to the contraction of a polymethacrylic acid molecule in solution when the dye is converted from a strongly absorbed *trans* state to a weaker bound *cis* state as Lovrien⁴ suggested. In our experimental arrangement the conversion into the *cis* form causes a macroscopic contraction of a polymer membrane for which light is the driving force. In the dark the dye reverts to its more stable *trans* form and the original situation is restored.

G. VAN DER VEEN
W. PRINS

Department of Chemistry,
Syracuse University,
Syracuse, New York 13210

Received October 12; revised November 20, 1970.

¹ Wald, G., *Science*, **162**, 230 (1968).

² Kaufman, H., Vratsanos, S. M., and Erlanger, B. F., *Science*, **162**, 1487 (1968).

³ Nachmansohn, D., *Science*, **168**, 1064 (1970).

⁴ Lovrien, R., *Proc. US Nat. Acad. Sci.*, **57**, 236 (1967).

⁵ Steinberg, I. Z., Oplatka, A., and Katchalsky, A., *Nature*, **210**, 568 (1966).

⁶ Kuhn, W., *Experientia*, **5**, 318 (1949).

⁷ Katchalsky, A., *Experientia*, **5**, 319 (1949).

⁸ Inscoc, M. N., Gould, F. H., and Brode, W. R., *J. Amer. Chem. Soc.*, **81**, 5634 (1959).

Monoclinic Space Group of Hydroxyapatite

HYDROXYAPATITE is the prototype substance of the inorganic component of bones and teeth and its structure has therefore been studied in some detail using synthetic and mineral samples¹⁻³. In the past it has been reported to have a hexagonal space group $P6_3/m$ but because the samples previously studied were probably not pure, for example, the mineral samples may have contained fluorine, there is reason to believe that the true space group is monoclinic $P2_1/b$. This is by analogy with pure and stoichiometric chlorapatite^{4,5} which has the space group $P2_1/b$ instead of the hexagonal one typical of apatites.

Single crystals of hydroxyapatite were made by heating 0.4 mm diameter spheres of stoichiometric chlorapatite in steam at 1100° C for two weeks in the manner described previously⁶; the chlorapatite was grown by slow cooling of a melt of chlorapatite and calcium chloride as described by Prener⁵. Careful examination of Weissenberg and rotation photographs showed extra very weak reflexions in the (*hk*1), (*hk*2), (*hk*3) . . . sections of reciprocal space which were absent in the (*hk*0) section. These reflexions seemed to indicate that the *a*- and *b*-axes were doubled. The reflexions (001) for *l* = 1, 3, 5 . . . were not detected. These observations uniquely determine the space group as $P2_1/b$ if it is assumed that twins

occur at 120° rotation about the pseudo-hexagonal *c*-axis as has been described for monoclinic chlorapatite⁵. The lattice constants of the monoclinic form of hydroxyapatite are: *a* = 9.42 Å, *b* = 2 × 9.42 Å, *c* = 6.88 Å, and $\gamma = 120^\circ$.

By analogy with the structure of chlorapatite⁷, it is very probable that the monoclinic aspect of hydroxyapatite is associated with the arrangement of the hydroxyl ions. We suggest that all the hydroxyl ions point in the same direction in planes parallel to the *a*- and *c*-axes, but with the direction of orientation alternating between successive parallel planes. The reason why small amounts of fluorine in the mineral samples of hydroxyapatite prevent the development of a monoclinic structure is probably that they replace some of the hydroxyl ions and consequently interfere with the ordering of the remaining ones.

It is not possible to say with certainty what significance the monoclinic space group has for biological and precipitated apatites. It must first be established that the monoclinic space groups exists at body temperatures, that is that hydroxyapatite does not suffer a thermal phase transition to a hexagonal form until significantly above 37° C. Furthermore, it will be necessary to investigate the effects of non-stoichiometry and impurities, such as fluoride, carbonate and magnesium, on the symmetry of the lattice. The monoclinic space group could, however, be an explanation of the tape-like shape of precipitated or biological apatites which is often observed and which contravenes hexagonal symmetry. The chemical reactivity of hydroxyapatite would also depend on its internal symmetry and hence on the impurities, particularly fluoride ions.

This work was supported by the Science Research Council. Assistance in the growing of the chlorapatite single crystals was given by Unilever Limited.

J. C. ELLIOTT

The London Hospital Medical College,
Turner Street,
London E1 2AD

Received September 7, 1970.

¹ Posner, A. S., Perloff, A., and Diorio, A. F., *Acta Cryst.*, **11**, 308 (1958).

² Kay, M. I., Young, R. A., and Posner, A. S., *Nature*, **204**, 1050 (1964).

³ Sudarsanan, K., and Young, R. A., *Acta Cryst.*, **B25**, 1534 (1969).

⁴ Young, R. A., and Elliott, J. C., *Archs. Oral Biol.*, **11**, 699 (1966).

⁵ Prener, J. S., *J. Electrochem. Soc.*, **114**, 77 (1967).

⁶ Elliott, J. C., and Young, R. A., *Nature*, **214**, 904 (1967).

⁷ Mackie, P. E., Elliott, J. C., and Young, R. A., *American Crystallographic Association Program and Abstracts*, Atlanta winter meeting, paper E7 (A.C.A., January 1967).

Editorial and Publishing Offices of NATURE

MACMILLAN JOURNALS LIMITED
4 LITTLE ESSEX STREET, LONDON WC2R 3LF
Telephone Number : 01-836 6633. Telegrams : Phusis London WC2R 3LF

711 NATIONAL PRESS BUILDING
WASHINGTON DC 20004
Telephone Number : 202-737 2355

Subscription Department

MACMILLAN JOURNALS LIMITED
BRUNEL ROAD, BASINGSTOKE, HANTS
Telephone Number : Basingstoke 5431

Advertisements only should be addressed to

T. G. SCOTT & SON, LIMITED
1 CLEMENT'S INN LONDON WC2A 2ED
Telephone : 01-242 6264/01-405 4743
Telegrams : Textualist London WC2A 2ED

Registered as a newspaper at the Post Office

Copyright © Macmillan Journals Limited, March 15, 1971