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THE DEFECT STRUCTURE AND IONIC TRANSPORT PROPERTIES OF CALCIUM APATITE (*)

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Résumé. — L'intérêt des processus de transport des apatites de calcium est dû au fait que la phase microcristalline minérale des os et des dents est l'hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Les résultats obtenus par diffusion, relaxation diélectrique et conductivité montrent : *a*) la nature unidimensionnelle des chemins possibles pour le transport des ions hydroxyles parallèlement à l'axe *c* cristallographique et *b*) l'existence de deux sous-réseaux calcium s'interpénétrant dans la structure avec des énergies différentes d'énergie de formation et de migration des lacunes.

Abstract. — The transport properties of the calcium apatites are of interest since the microcrystalline inorganic phase of bones and teeth is hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. This material plays a structural role in hard tissue but is also involved in the dynamic exchange of its constituents with the blood supply and its *in vivo* environment. In order to provide data for the quantitative evaluation of possible biological processes involving ion exchange and impurity uptake, theoretical and experimental studies of the defect structure and ionic transport processes have been undertaken. The results of diffusion, dielectric relaxation and conductivity measurements will be presented. These indicate that two features are of particular importance in bulk transport processes : *a*) The one dimensional nature of the paths available for the motion of hydroxyl ions parallel to the crystalline *c*-axis, and *b*) The existence of two interpenetrating calcium sub-lattices within the structure with different energies of vacancy formation and frequency of vacancy jump to adjacent sites.

The application of these data to the *in vivo* problem indicates that the bulk diffusion of calcium and phosphate ions at body temperatures is improbable, emphasizing the importance of the surface properties to the biological role of apatite. It is also indicated that fluoride ions, incorporated into hydroxyapatite substitutionally for the hydroxyl ions, are not capable of blocking the migration of hydroxyl ions along the one dimensional *c*-axis paths. Consequently the resistance to dental caries associated with fluoridation does not arise from the decreased enamel solubility resulting from the blocking of hydroxyl ion migration.

1. Introduction. — Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is the microcrystalline inorganic component of bones and dental enamel. In bone, this material is in dynamic equilibrium with the blood supply and maintains the calcium balance in addition to playing its structural role. In tooth enamel, the material is inert but is subject to chemical attack by organic acids produced in the cariogenic environment of the mouth. Although the general phenomenology of the dissolution and growth processes has been formulated, the detailed mechanisms are not well understood. In order to provide data for the quantitative evaluation of possible biological processes involving dissolution, ion exchange and impurity uptake, theoretical and experimental studies of the defect structure and ionic transport properties have been undertaken. Two features of the apatite structure are of particular interest from this stand point. The first is the existence of two interpenetrating calcium sub-lattices within the structure. The energy of vacancy formation is different

on each sub-lattice and, in addition, the low symmetry of the structure results in possible vacancy jumps away from a specific site having different energies. This last fact results in a contribution to the non-randomness of diffusion on the calcium sub-lattices due to the crystal structure in addition to the contribution arising from the effects of mechanistic correlation. In this lattice, therefore, the self-diffusion coefficient of calcium ions is related to the diffusion coefficient calculated for random tracer jumps through a correlation factor containing both a mechanistic and a structural component. The second feature of interest in the transport properties of the lattice is the one dimensional nature of the paths available for the motion of the hydroxyl ions. These ions are situated on the hexad axes of the crystal structure with the sites separated by a distance of circa 3.4 Å. The intercolumn spacing is circa 9.5 Å and calculations of the energy for an ionic jump between columns indicate that this is on the order of 10 eV compared to about 0.5 eV for jumps along the *c*-axis. Since experimental evidence indicates that transport within the apatite structure is due to the presence of vacancies,

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this pseudo one dimensional nature of the hydroxyl ion column has two interesting consequences. Since the motion of a vacancy back and forth along a one dimensional chain cannot change the relative positions of the ions in the chain, the tracer diffusion coefficient for the chain should be zero. Formally, this arises from the mechanistic correlation factor being zero. It is possible to obtain a net uptake of impurity or tracer ions by such a chain if a flux of vacancies can be produced by means of an electric field. In this case, however, uptake will only occur if all the ions present in the column can exchange places with a vacancy with similar facility. If impurity ions exist within the column and have mobilities that are low compared to those of the host ions, they will be able to block effective long range motion along these columns. In the presence of an alternating field, however, vacancies confined to column segments between these blocking points will be able to move freely between them and consequently contribute to the ac conductivity of the crystal despite the fact that they can make only a transient contribution to the dc conductivity.

This paper is concerned with the presentation of experimental and theoretical data in support of this picture and with a brief discussion of possible biological consequences.

2. Ionic transport on the calcium sub-lattice. — Biological hydroxyapatite crystals have linear dimensions on the order of a few hundred Angstroms and it is therefore not possible to make experimental diffusion measurements on single crystals from this source. Also, until recently, synthetic hydroxyapatite crystals have been of micron dimensions and consequently single crystal transport measurements have had to be performed on the isomorphous fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. Using single crystals of fluorapatite with polished surfaces having normals parallel and perpendicular to the crystalline c-axis, den Hartog *et al.* [1] measured the self-diffusion coefficient for calcium ions by a standard radioactive tracer technique. Diffusion profiles were obtained by sectioning the crystals, with a liquid scintillation counter being used to measure the activity of the removed material. In this way, the temperature dependence of the calcium self-diffusion coefficient was obtained parallel and perpendicular to the crystalline c-axis. Figure 1 shows the result of these measurements for the direction parallel to the crystalline c-axis. It is seen that the plot has a general curvature and to within experimental error the data can be fit by the sum of two exponentials :

$$D_{\parallel} = 9.3 \times 10^6 \exp \left[-\frac{5.6}{kT} \right] + 3.6 \times 10^{-3} \exp \left[-\frac{2.5}{kT} \right]$$

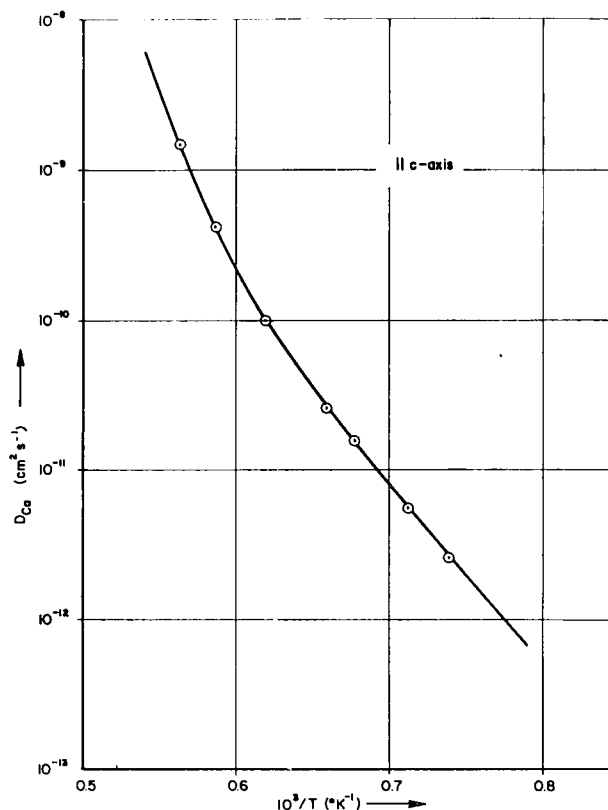


FIG. 1. — Temperature dependence of the calcium diffusion coefficient in fluorapatite.

Also of interest from the biological view point, is the low value of the self-diffusion coefficient.

Curves for the temperature dependence of the self-diffusion coefficient which exhibit a similar « knee » are obtained in simple ionic compounds, such as the alkali halides, when the low temperature behavior is dominated by impurities in the crystal and the high temperature behavior by the thermodynamic generation of vacancies. In this case, the low temperature slope provides information about the temperature dependence of the vacancy jump frequency and the high temperature slope about the vacancy formation energy. It is tempting to use such a simple model with the apatite data but unfortunately, a lack of consistency is obtained when it is applied to the data obtained for both parallel and perpendicular diffusion.

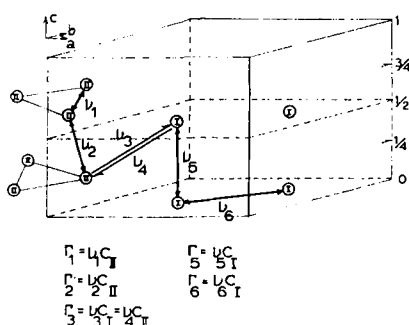
Due to the failure of this simple model, Welch and Royce [2] attempted to develop an expression for the calcium diffusion coefficient based on an atomistic formulation that takes into account the more complex structure of the apatite lattice with its several distinct calcium ion jumps. Because of the non-equivalence of jumps away from a particular lattice site, a contribution to the non-randomness of tracer migration results from the lattice structure. In principle, this source of non-randomness, together with non-randomness arising from the vacancy mechanism of tracer migration, can be incorporated

into the diffusion model through a « correlation factor ». In simple crystal structures, the mechanistic contribution is present and is temperature independent. In the apatite structure, it seems probable that the structural contribution to the correlation factor is dominant and, in particular, has a strong temperature dependence which will be incorporated into the measured diffusion coefficient. Howard and Manning [3] have developed a « T » matrix method for determining correlation factors where the elements of the matrix involve atomic jump probabilities. When applied to the calcium sub-lattice of the apatite structure this method gave rise to a 23×23 square matrix that it has not been possible to invert. It was therefore necessary to evaluate the diffusion coefficient using only the structural contribution to the correlation factor. This was done using a kinetic method in which the time and position dependence of tracer atoms is specified by a set of distribution functions. In the steady state, with a constant concentration gradient, the time dependence of the distribution functions is zero and the net flux of tracers across unit area may be determined in terms of these distribution functions and the jump probability of a tracer between specified sites. By comparing this atomistic expression to the macroscopic form of Fick's first law, the tracer diffusion coefficient may be obtained. For the direction parallel to the crystalline c-axis, this has the form :

$$D_{\parallel} = \left(\frac{c^2}{20} \right) (6 \Gamma_2 + 3 \Gamma_3 + 2 \Gamma_5)$$

where Γ_i is the tracer jump frequency for a specific jump i in the lattice, the nomenclature being in agreement with the allowed jumps indicated in figure 2. Each of the terms Γ_i contains the appropriate calcium vacancy concentration together with a vacancy jump frequency :

$$v_i = v_{0i} \exp \left[- \frac{E_m}{kT} \right]$$



$$D_{aa} = \frac{\sqrt{3}a^2}{10} \left\{ \Gamma_1 \cdot 2\Gamma_3 \left[\frac{6\Gamma_1 + 3\Gamma_2 + 2\Gamma_3}{3\Gamma_1 + 2\Gamma_2 + 4\Gamma_3} \right] \right\}$$

$$D_{cc} = \frac{c^2}{20} \left\{ 6\Gamma_2 + 3\Gamma_3 + 2\Gamma_5 \right\}$$

FIG. 2. — Possible calcium vacancy jumps in the apatite lattice.

In the extrinsic range, where the vacancy concentration is constant, the temperature dependence of D_{\parallel} will still involve the sum of three terms exponentially dependent upon temperature and at higher temperatures the situation will be more complex due to the thermodynamic generation of vacancies introducing another temperature dependence. The model therefore indicates that, even in the simplest case, a plot of $\ln D$ vs. $1/T$ will exhibit substantial curvature and that it will be difficult to separate the contributions due to specific ionic jumps.

From the biological point of view, the low values obtained for the diffusion coefficients indicate that bulk diffusion processes in the mineral phase are probably unimportant at normal body temperatures. This conclusion could be modified if the lattice relaxations associated with the small size of biological material caused a substantial decrease in the energy of vacancy motion. It seems more probable, however, that dislocations and dissolution and regrowth processes dominate the incorporation of impurities into the calcium sub-lattice of biological apatite. Similar measurements indicate that this is also the case for phosphate ions.

3. Ionic transport on the hydroxyl ion sub-lattice. —

As pointed out above the hydroxyl ion sub-lattice in hydroxyapatite has a pseudo one dimensional nature. This is also true for the fluoride ion sub-lattice in fluorapatite but, due to differences in the charge distribution on the two ions, their location on the hexad axis with respect to the calcium triangles

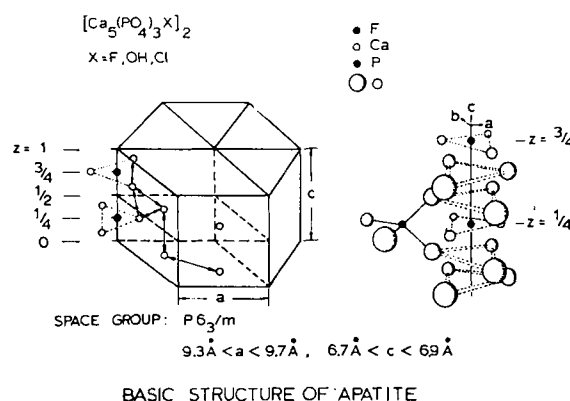


FIG. 3. — The basic structure of apatite with a detail of the c-axis column.

is different. Figure 3 shows the ionic arrangement in the neighbourhood of a c-axis column in fluorapatite and it can be seen that the interchange of a vacancy and a fluoride ion on this sub-lattice requires the negative ion to pass through two triangular arrays of oxygen ions from neighbouring phosphate groups. This has the interesting consequence of making the « barrier » to ionic motion on this sub-lattice elec-

trostatic in nature, and consequently, very sensitive to the charge distribution on the migrating ion.

Preliminary measurements of diffusion on this sub-lattice were reported by den Hartog *et al.* [1] who used an infrared absorption technique to measure the total amount of OD^- ions incorporated into fluorapatite single crystals as a function of the diffusion time and temperature. Contrary to expectations, it was found that OD^- ions diffused into the crystal with similar facility both parallel and perpendicular to the c-axis. The temperature dependence of the OD^- diffusion coefficient over most of the temperature range studied was essentially the same as that measured for calcium diffusion below the « knee » in crystals having the same orientation. Subsequent measurements by den Hartog [4] and in this laboratory have verified these observations and indicated that the OD^- dipoles are incorporated into the crystals with their axis parallel to the crystalline c-axis. The spectroscopic data does however suggest that there may be two different environments for these ions. This uptake of OD^- ions in a diffusion process is contrary to the behavior expected on the basis of the one dimensional nature of the fluoride ion sub-lattice and a vacancy mechanism for diffusion. Den Hartog *et al.* [1] suggested that the OD^- ions might be incorporated in the lattice due to the presence of electric fields produced by a partial decomposition of the apatite structure. Separate experiments performed on crystals having an electric field of a few volts per centimeter applied over part of their surface showed that OD^- uptake could be enhanced by about a factor of two by this method, but for both orientations of the diffusion direction with respect to the crystalline c-axis. At the present time, it seems probable that the observed OD^- ion uptake is due either to a process involving decomposition of the fluorapatite substrate and the epitaxial growth of hydroxyapatite on its surface or to the incorporation of deuterons in the lattice which can migrate interstitially and form OD^- molecules *in situ* by combining with oxygen ions already present in the lattice.

In order to obtain more experimental information about ion migration on the fluoride sub-lattice, dielectric loss measurements [5] were made on synthetic fluorapatite samples known from optical and esr data to contain oxygen impurities substitutionally on this sub-lattice. A large dielectric loss peak was found for samples in which the applied field was parallel to the crystalline c-axis. No such peak was found for samples cut from the same boule but with the electric field normal to the c-axis. Figure 4 shows both a Cole-Cole plot of the dielectric data and the temperature dependence of the dielectric loss at a constant frequency. The former is consistent with the behavior expected for « dipoles », having a distribution of relaxation times, reorienting in the applied field. The dielectric loss peak shown in the latter plot occurs at different temperatures for different

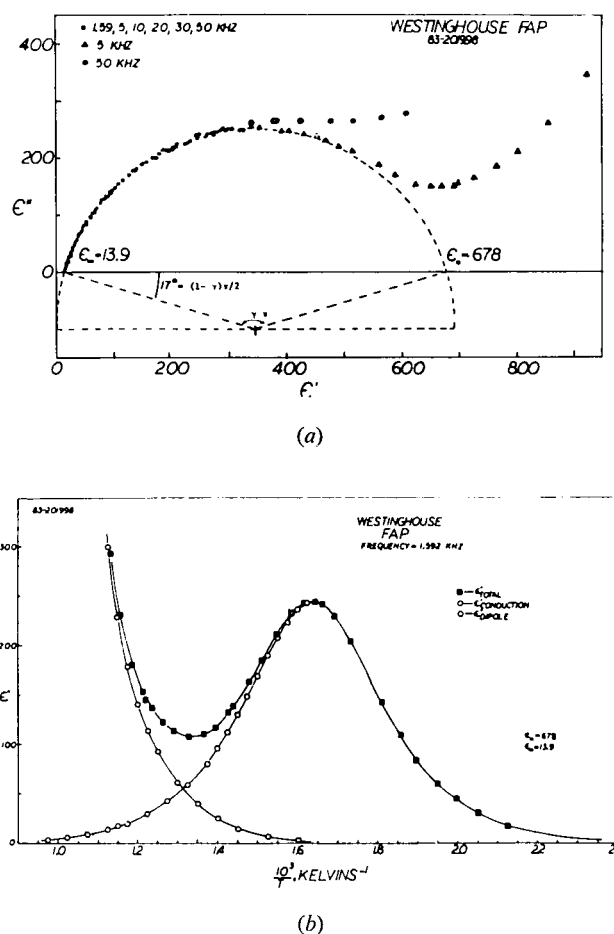


FIG. 4. — a) Cole-Cole plot of dielectric data for fluorapatite b) Temperature dependence of dielectric loss in fluorapatite.

measurement frequencies, this temperature dependence corresponding to a « dipole » reorientation energy of *circa* 0.8 eV. The magnitude of the loss would indicate a large dipole moment for this defect.

In order to explain the above experimental observations, Welch [6] developed a model, consistent with the structure of the fluoride sub-lattice, involving a one dimensional chain of lattice sites with blocking points (oxygen impurities) and containing fluoride vacancies that are free to move in the applied periodic field. It is assumed that the oxygen impurities are unable to exchange places with a vacancy and consequently the vacancies are trapped by the chain segment in which they occur. In an applied field, vacancy migration occurs resulting in a relative displacement of the center of positive and negative charge within the chain and the consequent creation of a dipole with a c-axis orientation. Using an atomistic model of the vacancy migration process Welch developed an expression for the dielectric loss to be expected due to these « dipoles ». This has the form :

$$\epsilon'' = \left(\frac{A}{T} \right) \frac{[V]}{[O]} \frac{\omega\tau/2[O]}{1 + (\omega\tau/2[O])^2}$$

where A is a constant, $[V]$ and $[O]$ are the vacancy and oxygen impurity concentrations on the fluoride sub-lattice, respectively, and τ is the relaxation time for a vacancy jump. For the specimens used in the experiments $[V]/[O]$ is *circa* 10^3 and responsible for the large values of ϵ'' observed. This model gives an excellent fit to the experimental data and the model allows the frequency dependence of the temperature of the dielectric loss maximum to be interpreted in terms of the vacancy jump energy. The data indicate an energy of fluorine ion vacancy migration of *circa* 0.8 eV.

Calculations have also been performed on the energies of ion migration on this one dimensional sub-lattice. Tse *et al.* [7] computed the migration energies for F^- , OH^- and O^{2-} ions along the c-axis columns of both fluorapatite and hydroxyapatite. Using a Born model of the crystal in which polarizable ions interacted electrostatically and through short range repulsive overlap forces, these energies were calculated in an approximation in which all ions, except the jumping ion, were held in their perfect crystal positions. This simplification was necessary due to the complexity of the apatite structure. A factor of considerable importance in these calculations is the charge distribution on the jumping ion. Several charge distributions have been postulated for the hydroxyl ion [8], [9] and a choice between these was made by computing the equilibrium positions of these ions in hydroxyapatite for each charge distribution and comparing these with the experimental data of Kay *et al.* [10]. It was found that the distribution using Pauling effective charges [9] gave the best agreement and this model was used for both the hydroxyl and phosphate charge distributions. Figure 5 shows the results obtained for hydroxyl ion migration in hydroxyapatite. It is seen that the barrier to ion migration is electrostatic in nature, as would be expected from the presence of the negative oxide ion « lenses » along the jump trajectory. The sensitivity to the charge distribution can be seen by treating the OH^- ion either as a point charge or as a dipole

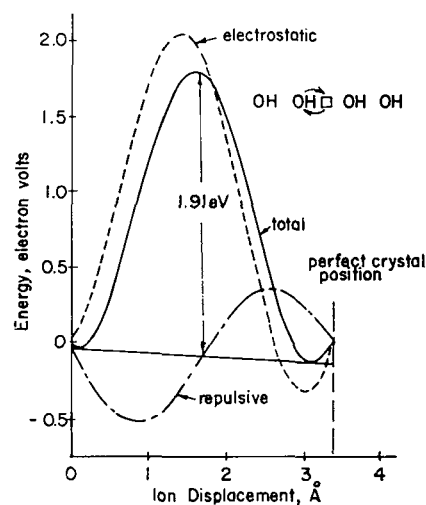


FIG. 5. — Calculated energies of hydroxyl ion migration in hydroxyapatite.

in which each component has its full ionic character. In the former case, the migration energy is reduced to 0.5 eV and in the latter, increased sharply to about 5.0 eV. For hydroxyapatite, it is found that $E_m(F^-) \simeq 0.4$ eV; $E_m(O^{2-}) \simeq 1.5$ eV and $E_m(OH^-) \simeq 2.1$ eV with similar values obtaining for fluorapatite. It thus seems reasonable to treat substitutional oxygen ions as barriers to vacancy motion in fluorapatite as was assumed in the model of the dielectric response. It is also indicated that substitutional fluoride ions are unable to block the migration of hydroxyl ions within the hydroxyapatite structure, a mechanism that had been postulated by Young *et al.* [11] to be responsible for the reduced solubility of fluoridated dental enamel.

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DISCUSSION

A. LODDING. — *a)* Has anybody measured the diffusivity of F and Cl in pure apatite ?

b) Is there any significant difference in the diffusion behavior of fluor — or chlor — apatite on one hand, hydroxy-apatite on the other ?

c) Up to which temperature may one study apatite without chemical decomposition, and what are the orders of magnitude of Ca, P and OH diffusivities at this temperature ?

d) Has one tried comparatory measurements on biological apatites (teeth or bones), and if so are there any meaningfully definable differences from the behavior of pure material ?

B. S. H. ROYCE. — *a)* To the best of my knowledge no such data has yet been published. G. Flim and J. Arends at Groningen University are attempting such measurements.

b) Again, diffusion data is not available. Large pure hydroxyapatite crystals have not yet been studied since synthetic crystals of this material are in very limited supply. Preliminary ionic conductivity data made in our laboratory would indicate that ionic

transport is very similar in fluor- and chlorapatite, but diffusion data is only available on fluorapatite.

c) The data of Prenner *et al.* (*J. Phys. & Chem. Solids* **30** (1969) 1456) would suggest that 1 000 °C was the upper limit for safe operation in a vacuum without decomposition occurring. The data of den Hartog *et al.* (ref. [1] above) shows that at 1 000 °C the diffusivities of Ca parallel to the crystalline c-axis is $\sim 1 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and perpendicular to this axis $\sim 3.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Phosphate diffusivity could not be measured at this temperature but at 1 400 °C it had a value of circa $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ again being approximately three times larger for diffusion perpendicular to the c-axis than parallel to it. At 1 000 °C the OH⁻ diffusivity parallel to the c-axis was measured as $2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. It is not clear however, what the mechanism of OH⁻ uptake is in these experiments.

d) Measurements are currently being made by G. Flim and J. Arends on biological apatites in tooth. More rapid uptake of constituent ions is observed but the matrix rather than the crystalline matter would seem to be responsible. The small size of biological apatites precludes measurements on individual single crystals.