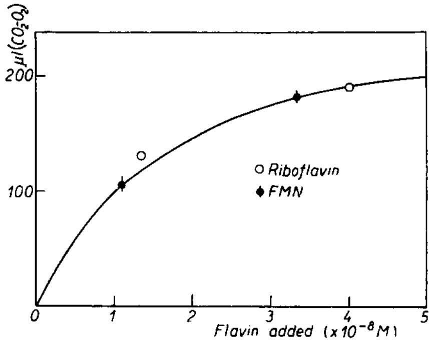

Fig. 2. Activation of the protein component of moss oxalic acid oxidase by various flavin compounds. Warburg experiment, temperature 21° C. Main compartment: 1 ml of apo-enzyme, 1 ml *M*/15 phosphate buffer pH 4.0, 1 ml of aqeuous flavin solution. Side arm: 0.2 ml of *M*/10 oxalate pH. 3.9. No KOH in center well. Measured: excess CO_2-production over O_2-consumption. The blank, without any addition of flavin (not plotted), was very close to zero.

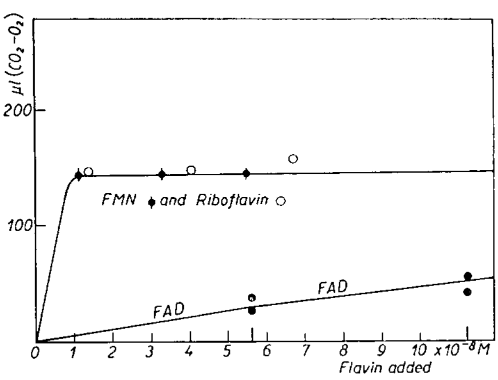

Fig. 3. Comparison of the activating effect of riboflavin and riboflavin phosphate on the apoenzyme of moss oxalic acid oxidase, in *M*/15 malate buffer pH 4.0. Otherwise conditions as in Fig. 2.

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Particle size and chemical composition of the crystallites in bone and synthetic apatites

The form and size of the crystallites in bone has been determined by several methods. From the broadening of the reflections in the high-angle X-ray diffraction patterns it was soon clear that the particles were elongated in the direction of the *c*-axis and their length has been measured to 200–290 A[1,2,3,4]. The width is much less and cannot be settled with any accuracy from line-broadening measurements. However, the diffuse particle scatter in the low-angle X-ray region has revealed that the rod-shaped crystallites have a length of 210–220 A and a width of 65–75 A[5,6]. Electron microscopy of bone on the other hand, has shown that the crystallites are tabular with dimensions of about 350 × 400 × 25–50 A[7]. Tabular crystals, only a few unit cells thick, having a large extension in two dimensions have been observed in some apatite-like precipitates[4,8], but long needle-shaped crystallites, apparently hexagonal prisms, are also found in such synthetic samples[9].

It is a well-known fact that bone as well as precipitates in the CaO-P_2O_5-H_2O-system show a wide variation in chemical composition although their X-ray diffraction patterns are identical. This discrepancy has been interpreted in various ways and several types of calcium phosphates having an apatite structure and molar Ca to P-ratios ranging from 1.3 to 2.0 have been proposed.

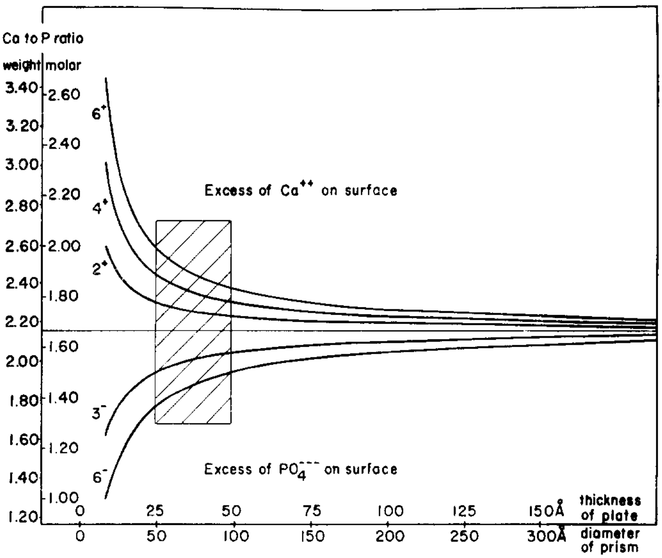

Fig. 1

The extremely small crystallite size of the bone salt and most preparations of synthetic apatites seems, however, to offer a simple explanation to the variation in composition observed. Depending on the circumstances during the precipitation the surfaces of the crystallites can end up in different ways and the composition of the surface will, as long as the crystallites are very small, contribute considerably to their overall composition. The surface of an hydroxyapatite particle may either be electrically neutral or be finished with an excess of positive or negative charges of Ca^{+2} of $PO_4{}^{3}$ and OH^- respectively. These charges can attract hydronium- and hydroxyl-ions or other ions from the solution in order to establish electroneutrality. It is observed[10] that apatite-like precipitates obtained from solutions containing an excess of phosphate are more negatively charged than those precipitated from solutions having an excess of calcium-ions.

Fig. 1 gives the reltaionship between the particle size and the Ca to P-ratio when the particles are assumed either to be regular hexagonal prisms (the diameter of a prism is taken as the distance between two parallel surfaces) but with infinite lengths, or plates with infinite extension in two dimensions. This simplification is justified by the experimental data reported above and these assumptions give the *minimal* surface area. It is further assumed that each free unit cell surface can carry an excess of one, two or three Ca-ions or one or two phosphate groups. The hatched area in the figure covers the particle sizes of the apatite crystallites in bone and most synthetic precipitates as they commonly appear. It is immediately clear that such colloidal particles carrying an excess of positive or negative ions covers the range in chemical composition observed in all precipitates giving an apatite X-ray diffraction pattern. At larger particle sizes, which do not exist in bone, the composition approaches the theoretical value of hydroxyapatite (Ca/P = 1.667). For example, a hexagonal prism having a diameter of 3100 A cannot deviate in its calcium content from that of hydroxyapatite more than 0.32% even if each exposed unit cell surface is assumed to carry an excess of three calcium-ions. From these considerations it is clear that chemical analyses of bone and most synthetic apatites have a very restricted value when interpreting their crystallographic structure and it is not necessary to assume new types of apatites whether "defect" or substituted in order to explain the chemical composition and physical properties of such colloidal calcium phosphates.

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