Equilibrium phase diagrams have been determined for the system CaO-P$_2$O$_5$-H$_2$O using hydrothermal synthesis techniques in the temperature range 300–600°C and 2 Kb H$_2$O pressure. Well-crystallized hydroxyapatite has been produced and characterized. Small variations in unit cell parameters dependent on temperature of synthesis and bulk composition of the starting materials have been determined. Precise chemical conditions were required to obtain apatite as the only solid phase in equilibrium with solution. Equilibrium phase diagram results are compared with previous synthetic investigations.

Key words: Hydroxyapatite — Mineral — Phase — Chemistry — Synthesis.

Introduction

The dominant mineral species of vertebrate hard tissues, teeth and bone, is known to be hydroxyapatite. Although hydroxyapatite is a ubiquitous, naturally occurring calcium phosphate mineral, the material that is precipitated in low temperature environments, such as the physiological conditions of hard tissues, is not well defined nor understood. The extremely fine grain size of the precipitate virtually precludes accurate identification of the phase(s) present and hinders the attempts to understand mineral reactions. It is not surprising therefore that investigators turn to synthetic situations, where the chemical and physical conditions can be controlled, to learn about the mineral system.
For reasons not generally understood, hydroxyapatite of "ideal" composition is not easily synthesized. Synthetics, usually precipitated from solution and then heated to increase "crystallinity", often exhibit variable chemical composition. Sometimes the synthetics are a mixture containing more than one mineral species. Often an apatite phase is produced which gives variable unit cell parameters depending on temperature of heating or starting composition. Elements other than Ca, P, O and H required for "ideal" (stoichiometric) hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, are usually present in the starting solutions and it is known that the apatite crystal lattice can incorporate many of them (Cockbain, 1968; Deer, W.A., et al., 1963). The properties of the hydroxyapatite phase (HA) have not been determined directly on pure $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ because well crystallized material of this composition was unavailable. It seemed essential to obtain pure material, in good crystals, in order to properly evaluate the phase and to understand its stability and reactions in the biological system.

Using a method known to give relatively large crystals of hydroxyapatite (Hayek, 1958; Posner and Perloff, 1958) investigations were undertaken in the system $\text{CaO-P}_2\text{O}_5-\text{H}_2\text{O}$. The hydrothermal synthesis method used in these investigations has many advantages. The solid products are well crystallized and, by systematic examination of a range of compositions, the relationships between apatite, solution, and other calcium phosphate phases, can be determined.

Posner and Perloff (1958) used hydrothermal synthesis techniques to obtain well crystallized HA but did not make a systematic study of reactions. Hayek (1958) obtained well-crystallized HA at $400^\circ$ over a pH range of 5 to 11 but starting materials usually contained Na, which was also found in the products. Neither of these authors considered the problems of attainment of equilibrium for their products and this is important in understanding the calcium phosphate system. High temperature studies, 700–900$^\circ$ at 1000 bars $\text{H}_2\text{O}$ pressure have been carried out over a wide composition range, including F, but are only generally applicable (Biggar, 1966), and most of this report is outside the composition range appropriate for calcified tissues. The few experiments in the composition range cannot be extrapolated to physiologic conditions because under the physical conditions of the experiment the products of reaction are in the liquid portion of the system.

In the report that follows hydrothermal studies have been carried out at 2000 bars $\text{H}_2\text{O}$ pressure over the range 300–600$^\circ$. These physical conditions were chosen primarily to accelerate reactions to achieve equilibrium in a reasonable length of time. A systematic range of compositions in the chemical system $\text{CaO-P}_2\text{O}_5-\text{H}_2\text{O}$ have been explored, in particular those areas where HA occurred as a stable phase. Experimental details and a technical discussion of the four phase diagrams drawn in the temperature interval studied have been presented elsewhere (Skinner, 1973). Hydroxyapatite crystals have been well characterized, and small variations in unit cell parameters dependent on temperature of synthesis and bulk composition of the starting materials have been accurately determined. The results emphasize the variability of HA even when produced in a simple chemical system. Secondly, precise chemical conditions were required to obtain apatite as the only solid phase in equilibrium with solution. The detailed relationships between HA and other phases in the basic chemical system...