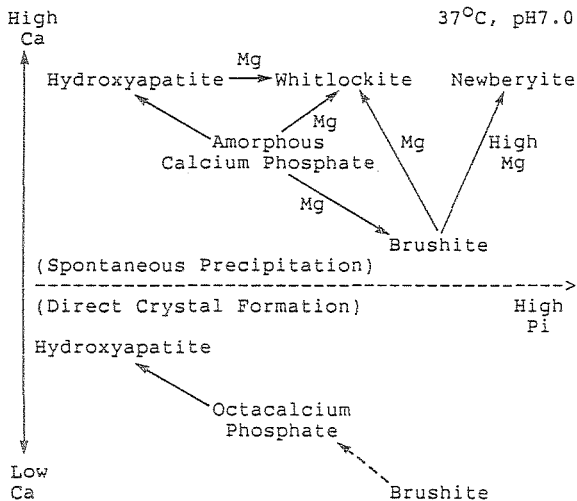


05.1-29 FORMATION AND TRANSFORMATION OF BIOLOGICAL CALCIUM PHOSPHATES: EFFECTS OF CALCIUM, MAGNESIUM AND PHOSPHATE. P.-T. Cheng and J. J. Grabher, Department of Pathology, Mount Sinai Hospital, University of Toronto, Toronto, Canada.

Common biological calcium phosphates as found in bone, teeth, kidney and dental calculi, include hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA], whitlockite [$[(\text{Ca},\text{Mg})_3(\text{PO}_4)_2]$, W], octacalcium phosphate [$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, OCP] and brushite [$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, B]. Recently Cheng has shown that at pH 7 and 37°C these compounds form in various aqueous solutions containing CaCl_2 , Na_2HPO_4 and NaCl ($I = 0.15\text{M}$). Solution Ca/P ratio has an effect on the crystal phase formed: HA is favored by high, OCP by intermediate and B by low Ca/P. W forms only in the presence of 3mM MgCl_2 . (Calcif. Tissue Int. 35:596-601, 1983; 37:91-94, 1985). Here we better define the effect of solution Mg/Ca ratio on the formation and transformation of biological calcium phosphates. Calcium phosphate solutions containing $[\text{Ca}] = 1$ or 3 mM , $[\text{PO}_4] = 0.1 - 90\text{ mM}$, $[\text{MgCl}_2] = 0-9\text{ mM}$ ($\text{Mg}/\text{Ca} = 0-3$), $I = 0.15\text{M}$ (NaCl), were kept at 37°C for 21 d. The pH was maintained at 7.0 ± 0.1 by addition of HCl/NaOH . Most solutions had good buffering property and were incubated without stirring except during occasional pH adjustments. All solids formed were identified by x-ray powder diffraction. Our results showed that direct crystal formation (heterogeneous nucleation) occurred in all solutions containing 1mM Ca and in solutions with $[\text{Ca}] = 3\text{mM}$ and $[\text{PO}_4] < 10\text{mM}$. OCP was favored by $\text{Mg}/\text{Ca} \leq 1$ and B by $\text{Mg}/\text{Ca} > 1$; OCP frequently transformed to HA with time. In contrast, spontaneous precipitation (homogeneous nucleation) occurred in solutions with $[\text{Ca}] = 3\text{mM}$ and $[\text{PO}_4] \geq 10\text{mM}$, forming an unstable amorphous calcium phosphate (ACP). When $\text{Mg}/\text{Ca} = 0$, ACP transformed only to HA. When $\text{Mg}/\text{Ca} \leq 1$, ACP transformed first to either B or HA which then transformed to W. When $\text{Mg}/\text{Ca} > 1$, ACP transformed first to B which, depending on Mg/Ca and $[\text{PO}_4]$, would transform to W, or remain unchanged, or transform to newberyite [$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$]. A graphical summary is provided in the figure below.



05.1-30 DISPLACIVE TRANSITIONS IN WILLHENDERSONITE, A ZEOLITE WITH A FLEXIBLE CHABAZITE-TYPE FRAMEWORK. By N.H.W. Sieber, R.X. Fischer and E. Tillmanns, Mineralogisches Institut, Am Hubland, D-8700 Würzburg, Federal Republic of Germany.

The natural zeolite willhendersonite, $\text{KCaAl}_3\text{Si}_5\text{O}_{12} \cdot 5\text{H}_2\text{O}$, (Peacor et al., Amer. Min. 1984, 69, 186-189; Tillmanns et al., N. Jb. Miner. Mh., 1984, 547-558) crystallizes in space group $\text{P}\bar{1}$ with $a=9.206(2)\text{ \AA}$, $b=9.216(2)\text{ \AA}$, $c=9.500(4)\text{ \AA}$, $\alpha=92.34(3)^\circ$, $\beta=92.70(3)^\circ$ and $\gamma=90.12(3)^\circ$. The crystal structure is topologically similar to rhombohedral chabazite. Unlike in chabazite, however, strict silicon-aluminum ordering is observed in willhendersonite. The elliptical distortion of the double six rings of SiO_4 and AlO_4 -tetrahedra (Fig.1) illustrates the flexibility of the framework.

Most crystals of willhendersonite are twinned. The optical examination at room temperature confirmed the mode of twinning described by Peacor et al., 1984. The investigation of twinned specimens of willhendersonite on a heating stage of a microscope clearly indicated a phase transition at temperatures above 150°C . At temperatures of about 180°C the specimen shows a uniform extinction, indicating the transition from a twin to a single crystal. After 10 to 15 minutes at room temperature, the single crystal transforms back to a twinned specimen, but now polysynthetically twinned in optically not resolvable domains. The phase transition is reversible and gives again a single crystal upon heating. This is obviously not a hydration/dehydration effect as shown by experiments under vacuum in sealed glass tubes with the same results. Single crystal X-ray data collected at various temperatures show that the crystal structure changes upon heating from triclinic to higher symmetry. The lattice constants of the high temperature modification indicate a rhombohedral space group. With respect to the silicon/aluminum ordering, which obeys Loewenstein's rule, it cannot exhibit $\text{R}\bar{3}\text{m}$ symmetry which is usually assumed for chabazite. This is shown in Fig. 2 which represents the $\text{R}\bar{3}\text{m}$ structure, where the mirror plane would imply T-O-T bonds with the same type cations.

Figure 1

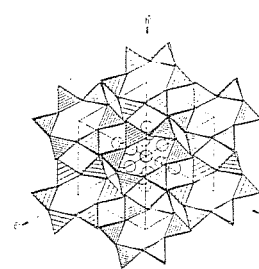


Figure 2

