Solubility Behaviour of Synthetic Whitlockite Containing Magnesium in Aqueous Medium

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Samples of whitlockite containing varying amounts of magnesium have been prepared in aqueous medium and characterised by chemical analysis, X-ray and IR spectra. The shift in the major frequencies observed in the IR spectra of the samples with increase in magnesium content is consistent with the change in the cation mass and force field constant. The solubility of the samples in aqueous medium is found to decrease with increase in both the pH of the medium and the magnesium content of the samples at a chosen pH.

Whitlockite is a mineral structurally related to B-tricalcium phosphate, Ca$_3$(PO$_4$)$_2$(B-TCP). Mackay suggested its idealised formula as (Ca,Mg)$_{20}$H$_2$(PO$_4$)$_{14}$, showing that some calcium ions can be substituted by magnesium though the extent of possible substitution is yet unknown. Whitlockite has been reported to be associated with various pathological conditions of caries lesions, dental calculus, calcified aortas and urinary concentrations. The extent of association was found to be directly dependent upon the presence of magnesium in drinking water. It was, therefore, considered relevant to investigate the role of magnesium in the formation of stable whitlockite and the dependence of its solubility on the magnesium content within the biologically important pH range of 5.0 to 7.5 at 37°C.

Samples of whitlockite were prepared as follows: Two solutions (500 ml each) containing stoichiometric amounts of disodium hydrogen phosphate and a mixture of calcium acetate and magnesium acetate respectively were prepared so as to give a theoretical yield of 10 g of the sample according to the stoichiometric equation given below (Eq. 1). Both the solutions were made alkaline by the addition of NaOH solution. The phosphate solution was added dropwise to the mixed solutions of acetates maintained at 37°C in CO$_2$-free atmosphere. The gram atom ratio of calcium to magnesium in the solution taken for preparation was altered as desired for the solid in each preparation. For preparation of the samples, one mole of whitlockite was considered to contain a total of 20 cations of calcium and magnesium taken together.

\[
(20 - n) (\text{CH}_3\text{COO})_2\text{Ca} + n\text{Mg(CH}_3\text{COO})_2 + 14\text{Na}_2\text{HPO}_4 + 12\text{NaOH} = 
\text{Ca}_{20 - n}\text{Mg}_n\text{(PO}_4)_4\text{H}_2 + 40\text{CH}_3\text{COONa} + 12\text{H}_2\text{O} \quad (1)
\]

After completion of precipitation the samples were separated by filtration, washed repeatedly with CO$_2$-free water and 0.01 M NaOH solution till the washed liquid was free from calcium and magnesium. The samples were then washed with ether and dried at 110°C for 4 hr.

The samples were analysed for Ca, Mg and P by the complexometric methods, IR spectra and X-ray diffraction patterns. The analytical data and calculated lattice constants are given in Table I. A gradual decrease in the values of lattice constants was observed with the introduction of smaller Mg$^{2+}$ ion in place of Ca$^{2+}$ ions. The characteristic phosphate peaks at 575, 875, 1010, 1040 and 1120 cm$^{-1}$ in the IR spectra shift towards higher wavelength region indicating substitutional effect of calcium by magnesium in the samples.

The solubility-studies were undertaken by the method of equilibration. About 0.2 g of the powdered sample sieved to 200 mesh (BSS) was equilibrated with 100 ml of the solvent by constant shaking at regulated speed (using a flask shaker at 37°C). The time required for attainment of saturation was determined...
by analysing the phosphorus content at the end of each convenient period of equilibration. Since the system in vivo behaves as a reservoir of buffer combinations maintaining a constant pH of 7.2, acetic acid-sodium acetate and borax-boric acid buffers were selected to investigate the pH-dependence of solubility of whitlockite in the biologically important pH range of 5.0 to 7.5. Various quantities of a given buffer combination gave reproducible results indicating that the buffer ions had no effect.

The results of solubility investigations are shown graphically in Figs 1 and 2.

A decrease in solubility of all the samples with the increase in pH of the medium and increase in the magnesium content at a chosen pH was observed. The observed pH-dependence of the samples can be explained on the basis of proton accepting capacity of phosphate (PO$_4^{3-}$) in acid-base equilibria shown below.

\[
\text{PO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{HPO}_4^{2-}
\]

In acid medium the tribasic phosphate (PO$_4^{3-}$) ion is converted into the dibasic phosphate ion (HPO$_4^{2-}$) while in the basic medium the reverse occurs. The acidic medium favours the forward reaction while the basic medium facilitates the backward process.

The structure of whitlockite containing magnesium in some calcium positions attains greater stability. Introduction of smaller Mg$^{2+}$ in place of Ca$^{2+}$ ions increases the compactness of the structure which explains the observed decrease in solubility of the samples with increase in magnesium content at a given pH.

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References