Determination of solubility products of phosphate and vanadate apatites of lead and their solid solutions in 0.165 M sodium chloride solution

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The solubility products of phosphate and vanadate apatites of lead and seven of their solid solutions, spread over the entire compositional range, were determined in 0.165 M sodium chloride solution at 37°C. These solubility products decreased with an increase in vanadium content. A theoretical interpretation was advanced based on changes in lattice and hydration energies resulting from isomorphous ionic substitutions. The aim of the studies was the understanding of the toxic effects of lead and vanadium on the human skeletal system.

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Opérant à 37°C et dans des solutions à 0,165 M de chlorure de sodium, on a déterminé les produits de solubilité du phosphate et du vanadate d'apatites de plomb et de sept de leurs solutions solides qui couvrent le spectre entier de compositions. Ces produits de solubilité diminuent avec une augmentation du contenu en vanadium. On propose une interprétation théorique qui est basée sur des changements dans le réseau et sur les énergies d'hydration qui résultent de substitutions ioniques isomorphes. Le but de ces études était de comprendre les effets toxiques du plomb et du vanadium sur le squelette humain.

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Introduction

Calcium phosphate apatite (CaPA), $Ca_{10}(PO_4)_6(OH)_2$, the principal inorganic constituent of human bones and teeth (1), undergoes several isomorphous cationic and anionic substitutions involving toxic ions. This constitutes the basis of the incorporation of toxic ions into the human skeletal system. It was established that the toxicity is controlled by the extent of incorporation of toxic ions during the principal bone processes calcification and resorption. Significant among such cationic substitutions has been the replacement of Ca^{2+} by Pb^{2+} forming lead phosphate apatite (PbPA), $Pb_{10}(PO_4)_6(OH)_2$, accounting for the incidence of plumbism, an occupational disease prevalent among workers of potteries and paints. While limited information on $Ca^{2+} \rightleftharpoons Pb^{2+}$ substitution in CaPA was available (2–4), substitution of PO_4^{3-} by VO_4^{3-} leading to the formation of lead vanadate apatite (PbVA), $Pb_{10}(VO_4)_6(OH)_2$, in the context of toxic effects of vanadium (5, 6) on human skeletal system, has not been studied. To investigate the combined effect of Pb^{2+} and VO_4^{3-} on calcification and resorption and to explore the possibility of their reversal, it was decided to study the solubility equilibria of PbPA, PbVA, and seven of their solid solutions spread over the entire compositional range, since these bone processes are controlled by the deposition and dissolution of CaPA at the interface of bone and body fluid. In addition, these studies were intended to clarify a few ambiguities associated with the available results on the solubilities of apatites.

Experimental

PbPA, PbVA, and a series of seven of their solid solutions were prepared through appropriate modifications of a wet method[3] and characterized to be of a high order of purity through X-ray, infrared, electromicroscopic, and thermal analyses, in addition to conventional chemical analyses.[3] The solubility product of each sample was determined at the biologically significant temperature of 37°C by analysis of its saturated solution, the pH of the dissolving medium being maintained constant using suitable buffer combinations. Each system was set up by adding 0.1 g of apatite to potassium hydrogen phthalate – hydrochloric acid buffer of required pH prepared in 100 mL of 0.165 M sodium chloride, the latter being needed to maintain the ionic strength of the medium effectively constant (7). Further, 0.165 M NaCl was considered as a standard reference solution (8), in which the activity coefficients of the dissolved ionic species could be taken as unity to avoid inaccuracies in their calculations, especially of polyvalent ions, and to enable products of ionic concentration in saturated solution of substances to be taken as their solubility products. Equilibration was carried out through shaking for about 12 h in air-tight polyethylene containers at a regulated speed using a mechanical shaker. The assembly was kept in a thermally insulated cabin maintained at 37 ± 0.5°C. The period of equilibration for attainment of saturation was found to be about 4 h based on a study of dissolution kinetics (9). To be doubly sure about the attainment of saturation, the equilibration period was extended to 12 h, at the end of which the pH of the system was measured. The colloidal component of the solute was separated from the solution by filtration through a 1G4 sintered glass crucible under suction at the temperature of equilibration, the suitability of the sintered glass crucibles for the purpose being verified by comparison with results obtained using colloidal filters (Millipore Filter Corporation, Bedford, U.S.A.) of pore size 10 mμm (10). From the saturated solutions thus obtained, lead was determined complexometrically (9) while phosphate and vanadate were estimated spectrophotometrically (11, 12), a separate aliquot being taken each time. Based on a series of such determinations the error limits were found to be ±1%.

Results and discussion

In Table 1 are included a few representative sets of results on the determination of the solubility products of PbPA, PbVA, and seven of their solid solutions. While the experimentally determined concentrations of lead, phosphorus, and vanadium are given in columns 2 to 4, the concentration of OH^- calculated from the final pH of each system is given in column 5, all the concentrations being taken as synonymous with activities as explained earlier. The gram atom ratios, Pb/P, Pb/V, and Pb/(P + V) calculated from the results of columns 2–4, are reported in column 8 of the table. It is evident that the ionic product K_{ip} of PbPA is equal to the product of the concentrations of the dissolved ions raised to appropriate powers, as given by $[Pb^{2+}]^{10}[PO_4^{3-}]^6[OH^-]^2$. While the concentrations of Pb^{2+} and

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TABLE 1. Solubility products of phosphate and vanadate apatites of lead and their solid solutions in 0.165 *M* sodium chloride

Sol'n.	Measured conc. (g atom/L)			Calculated conc. (g ion/L)			Gram atom ratio		
No. (1)†	$[Pb] \times 10^4$ (2)	$[P_{Tot}] \times 10^4$ (3)	$[V_{Tot}] \times 10^5$ (4)	$[OH^-] \times 10^{11}$* (5)	$[PO_4^{3-}] \times 10^{19}$ (6)	$[VO_4^{3-}] \times 10^{22}$ (7)	$\frac{Pb}{P+V}$ (8)	pK_{ip} (9)	Average pK_{ip} (10)
Solute: lead phosphate apatite, $Pb_{10}(PO_4)_6(OH)_2$									
1.	8.200	5.069	—	0.2818	0.614	—	1.62	169.23	
2.	2.970	1.736	—	1.0233	4.758	—	1.72	167.20	
3.	2.480	1.340	—	1.2882	4.968	—	1.85	167.66	
4.	1.982	1.138	—	1.4791	7.116	—	1.74	167.57	167.91
Solute: solid solution no. 1, $Pb_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$									
5.	10.000	4.876	12.269	0.3548	1.061	1.143	1.64	168.53	
6.	2.970	1.615	0.393	0.9330	3.588	0.619	1.79	170.26	
7.	2.480	1.453	1.099	1.3200	7.024	4.648	1.59	168.64	
8.	1.790	1.162	0.314	1.4800	7.267	1.846	1.50	170.12	169.39
Solute: solid solution no. 2, $Pb_{10}(PO_4)_{4.5}(VO_4)_{1.5}(OH)_2$									
9.	2.970	1.615	0.982	0.6457	1.519	0.531	1.73	175.75	
10.	2.356	1.421	0.785	1.2590	6.217	2.923	1.57	172.31	
11.	1.988	1.162	0.259	1.5500	8.064	1.741	1.67	172.69	173.58
Solute: solid solution no. 3, $Pb_{10}(PO_4)_{3.69}(VO_4)_{2.31}(OH)_2$									
12.	2.970	1.485	2.110	0.6920	1.645	1.394	1.75	177.39	
13.	2.233	1.292	0.785	1.0700	3.936	1.844	1.63	176.57	
14.	1.988	1.074	2.042	1.5500	7.449	13.716	1.56	173.72	175.89
Solute: solid solution no. 4, $Pb_{10}(PO_4)_3(VO_4)_3(OH)_2$									
15.	2.970	1.615	3.485	0.8320	2.746	3.926	1.51	177.33	
16.	2.236	1.179	1.885	1.2000	4.644	6.137	1.64	176.98	
17.	2.087	1.074	2.788	1.7800	10.077	27.623	1.54	173.97	176.09
Solute: solid solution no. 5, $Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$									
18.	9.500	3.713	19.631	0.3020	0.537	1.136	1.67	177.98	
19.	2.970	1.421	4.417	0.7250	1.756	3.343	1.59	179.33	
20.	2.144	0.969	1.220	1.2300	4.039	7.421	1.79	178.23	178.51
Solute: solid solution no. 6, $Pb_{10}(PO_4)_{1.9}(VO_4)_{4.1}(OH)_2$									
21.	2.970	1.292	4.859	0.6760	1.353	2.996	1.67	181.71	
22.	2.285	0.953	2.650	1.0700	2.902	6.224	1.87	180.52	
23.	1.998	0.827	7.852	1.1500	2.927	2.204	2.19	182.90	181.71
Solute: solid solution no. 7, $Pb_{10}(PO_4)_{1.2}(VO_4)_{4.8}(OH)_2$									
24.	1.980	0.517	6.478	0.6610	0.512	3.734	1.70	185.40	
25.	1.394	0.355	3.926	1.3489	1.324	11.914	1.86	183.50	184.45
Solute: lead vanadate apatite, $Pb_{10}(VO_4)_6(OH)_2$									
26.	0.800	—	4.711	1.4454	—	13.497	1.70	188.07	
27.	0.899	—	5.104	1.2882	—	20.237	1.76	186.40	187.24

*Calculated from the measured final pH of the equilibrated system.
†Column numbers referred to text.

OH^- were available directly from the measurements, that of PO_4^{3-} was calculated as shown below from the overall analytical concentration of PO_4^{3-} represented as $C_{(PO_4)}$.

$$[1] \quad C_{(PO_4)} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

$$[2] \quad [PO_4^{3-}] = \frac{C_{(PO_4)} \times K_1K_2K_3}{[H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3}$$

where K_1, K_2, K_3 are dissociation constants for H_3PO_4 (13, 14) given respectively by 7.51×10^{-3}, 6.33×10^{-8}, and 4.73×10^{-13}. A similar set of calculations (15) was done for the K_{ip} of PbVA, while a combination of the two gave K_{ip} values of the solid solutions. In all such calculations the dissociation of H_3VO_4 to $H_2VO_4^-$, HVO_4^{2-}, and VO_4^{3-} was considered. The possibility of existence of polyphosphates and polyvanadates in presence of cations such as Pb^{2+} is remote under conditions prevalent in the present systems. All these subdivided values, excepting those of PO_4^{3-} and VO_4^{3-} given in columns 6 and 7, are not reported for the sake of brevity. For the apatite phase, the calculated values of the pK_{ip} and their averages are given in columns 9 and 10 respectively of the table; the corresponding values of the other possible phases such as $Pb(HPO_4)$, $Pb(H_2PO_4)_2$, and $Pb_2(HPO_4)(OH)_2$ (16) and their vanadate counter parts are not reported, again for the sake of brevity.

Since the powers to which the ionic concentrations are to be raised to get K_{ip} values of apatites are high, the errors in their determinations play a significant role in deciding the fluctuations of the K_{ip} values calculated. While establishing the constancy of K_{ip} values of each one of the samples at 37 ± 0.5°C, care was taken to see that there was an unambiguous constancy after making allowance for the fluctuations caused by errors in the determination of ionic concentrations required. For this purpose sets of positive and negative error limits of determination of Pb^{2+}, PO_4^{3-}, VO_4^{3-}, and pH/OH^- obtained from pilot experiments with known quantities were chosen to calculate the upper and lower limits of K_{ip}/pK_{ip} values of each sample. A similar scrutiny was made before concluding the effect of ionic replacement on pK_{ip} values of PbPA, PbVA, and their solid solutions.

The results could unambiguously confirm that the samples exhibited a stoichiometric dissolution since the gram-atom ratios given in column 8 are in close proximity with the theoretical value of 1.67 and the pK_{ip} values of the apatite phase are constant for each system. The earlier results (16–18) (which were based on the supposition that the solubility of apatites is non-stoichiometric, being controlled either by the secondary phosphates or surface coatings of extraneous phases) are not substantiated by the present findings which confirm the thermodynamically expected stoichiometric dissolution (19–23). An important finding of the present investigations was that the solubilities of the samples exhibited a marked decrease with an increase in vanadium content, the average pK_{ip} values of PbPA and PbVA being 168 and 187, respectively, with the solid solutions having intermediary values. A theoretical interpretation of dependence of solubility of an ionic crystal on cationic and anionic replacement is possible through thermodynamic considerations (24).

For an ionic compound, the free-energy change accompanying dissolution, ΔG_{soln}, is related to K_{sp} as shown below at a given temperature T,

$$[3] \quad \Delta G_{soln} = -RT \ln K_{sp}$$

and can be calculated from experimental values of K_{sp}. Alternatively, it can be evaluated by considering dissolution of an ionic compound to be consisting of, (*i*) breaking down of its crystal architecture and (*ii*) the hydration of the constituent ions so set free resulting in the expression

$$[4] \quad \Delta G_{soln} = \Sigma \Delta G_{hi} - \Delta G_{lattice}$$

where $\Sigma\Delta G_{hi}$ is the sum of the free-energy changes of hydration of the constituting ions of the solute, while $\Delta G_{lattice}$ is the free-energy change of formation of the lattice. It is evident from this expression that a high solubility results when the hydration energy is high and lattice energy low, the converse being the case for low solubility. The terms on the right-hand side of the above equation can be calculated (24) by the following expression for an ionic crystal of general formula M_mN_n.

$$[5] \quad \Delta G_{soln} = \frac{-164 Z_+^2 m}{r_+ + 0.85} - \frac{164 Z_-^2 n}{r_- + 0.1} + \frac{332 A z_-^2}{R_0}\left(1 - \frac{1}{n_B}\right) - 8.03\,(m + n)\ \text{kcal/mol}$$

where Z_+ and Z_-, r_+ and r_- given the charges and ionic radii, respectively of the concerned ions; A, the Madelung constant; n_B, the Born exponent; R_0, the crystallographic radius; and 0.85 and 0.1 are the correction terms in the respective ionic radii. If the cation remains the same, the dependence of ΔG_{soln} on r_- is given by the equation

$$[6] \quad \left(\frac{\partial \Delta G_{soln}}{\partial r_-}\right)_{r_+} = \left(\frac{164 Z_-^2 n}{(r_- + 0.1)^2}\right) - \left(\frac{332 A z_-^2}{R_0^2}\left(1 - \frac{1}{n_B}\right)\right) \times \left(\frac{\partial R_0}{\partial r_-}\right)_{r_+}$$

while the corresponding expression in the case of anion remaining the same is given by

$$[7] \quad \left(\frac{\partial \Delta G_{soln}}{\partial r_+}\right)_{r_-} = \left(\frac{164 Z_+^2 m}{(r_+ + 0.85)^2}\right) - \left(\frac{332 A z_-^2}{R_0^2}\left(1 - \frac{1}{n_B}\right)\right) \times \left(\frac{\partial R_0}{\partial r_+}\right)_{r_-}$$

in either case the term $(1 - 1/n_B)$ being assumed to be constant.

It could be shown that the above equations are adequate to explain qualitatively the dependence of solubility of ionic crystals on ionic replacement. The first and second terms on the right-hand side of eqs. [5] and [6] represent, respectively, changes in hydration and lattice energies consequent upon anionic replacement. It is evident that on increasing the value of r_- a constant r_+, both these terms diminish, although the diminution in the second is less than that in the first, contributing to a decrease in solubility. The lower solubilities of PbVA and the solid solutions over that of PbPA could thus be explained. These conclusions are found to be in agreement with the corresponding results on the halides of Cs. Further, it can be shown from eq. [5] that for systems involving comparable values of r_+ and r_- as is the case with Pb^{2+} and VO_4^{3-} a solubility decrease is expected relative to its counterpart for which the disparity is more.

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