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Research progress on solubility of $Ca_5(P_xAs_{1-x}O_4)_3(OH)$ and $Ca_5(P_xAs_{1-x}O_4)_3F$

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Abstract. Solubility studies of apatite in water and acidic media have been focused on the solubility products. Aim at highlighting on current developments, the solubility products of calcium arsenate-phosphate hydroxyapatite/fluorapatite [$Ca_5(P_xAs_{1-x}O_4)_3(OH)/Ca_5(P_xAs_{1-x}O_4)_3F$, $1 \geq x \geq 0$] in literature is sorted out. Literature values of the solubility products vary greatly. These discrepant solubility products can be due to differences between the minerals, the way the experiments in the studies have been conducted, the failure to achieve equilibrium.

Introduction

Apatite group minerals, with the general formula of $M_5(XO_4)_3Y$, where M is mostly a divalent cation (Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, etc.), XO_4 is a trivalent or tetravalent anion (PO_4^{3-}, AsO_4^{3-}, VO_4^{3-}, SiO_4^{4-}, etc.) and Y is a monovalent anion (OH^-, F^-, Cl^-, etc.). The main components of the apatite group are hydroxyapatite [$Ca_5(PO_4)_3OH$], fluorapatite [$Ca_5(PO_4)_3F$], chlorapatite [$Ca_5(PO_4)_3Cl$] and carbonated apatite. Because of the properties of PO_4^{3-} and AsO_4^{3-} are very similar, so they often form various types of arsenate-phosphate solid solutions.

Apatites have been widely investigated because of their various applications in several domains such as agronomy (fertilizer), medicine (bone and teeth prosthesis), gemology and technology (phosphors and laser materials) [1]. The importance of apatite in a great variety of fields therefore calls for an understanding of their fundamental chemical properties, especially the dissolution mechanism and solubility at a variety of conditions. Dissolution studies of apatite in water and acidic media have been focused on the solubility products [2].

Literature values of the solubility products vary greatly. These discrepant solubility products can be due to differences between the minerals in the different studies, but also due to differences in the way the experiments in the studies have been conducted [3]. Inconsistency in data presented in literature could be due to the failure to achieve equilibrium. Apatite is known to be often non-stoichiometric, specifically Ca deficient. Many of the discrepancies in the reported values of $\log_{10}K_{sp}$ have been assigned to the effect of the stoichiometry [4]. Whether apatite is dissolved stoichiometrically or non-stoichiometrically might also depend on its initial chemical composition. The non-stoichiometry of hydroxyapatite appears to have a great influence to the formation of compounds with different solubility products [5]. This review aims at highlighting on current developments in the solubility products of calcium arsenate-phosphate hydroxyapatite/fluorapatite [$Ca_5(P_xAs_{1-x}O_4)_3(OH)/Ca_5(P_xAs_{1-x}O_4)_3F$, $1 \geq x \geq 0$] in literature.

Solubility of $Ca_5(P_xAs_{1-x}O_4)_3OH$

Solubility of $Ca_5(PO_4)_3OH$(x=1). Solubility of calcium phosphate hydroxyapatite [$Ca_5(PO_4)_3OH$] plays a important role for its bioreabsorbable ability. Ducheyne and Qiu [6], who clearly stated that one of the key parameters for the bioactivity mechanism of hydroxyapatite is the solubility. Literature values of the solubility products for $Ca_5(PO_4)_3OH$ vary between10^{-59} and $10^{-53.28}$.

The thermodynamic solubility product for $Ca_5(PO_4)_3OH$ was $K_{sp}=10^{-58.3}$ reported by McDowell et al. [7] and $10^{-53.9}$ reported by Narasaraju and Rai [8].

Values for the $\log_{10}K_{sp}$ for $Ca_5(PO_4)_3OH$ with Ca:P=1.67 have been reported to be approximately -59 by Brown et al. [9] whereas a value of -42.5 was reported for $Ca_5(PO_4)_3OH$ with Ca:P=1.5 by Driessens and Verbeeck [10].

LeGeros [11] researched on biologically relevant calcium phosphates, thereinto, the K_{sp} values were calculated for $Ca_5(PO_4)_3OH$ of 2.27×10^{-58}.

From the result of a batch dissolution for 6 weeks, the $\log_{10}K_{sp}$ -58±1 for synthetic $Ca_5(PO_4)_3OH$ was obtained by Valsami-Jones et al. [12]. Valsami-Jones et al. report the solubility constant for crystalline synthetic $Ca_5(PO_4)_3OH$ as given in Equation (1).

$$Ca_5(PO_4)_3OH = 5Ca^{2+} + 3PO_4^{3-} + OH^-, \quad (1)$$

By the formalism of Eq (1):

$$\log_{10}K_{sp} = 5 \log_{10}(Ca^{2+}) + 3 \log_{10}(PO_4^{3-}) + \log_{10}(OH^-) = -58 \pm1. \quad (2)$$

But Zhang et al. [13] alternately express the solubility of synthetic $Ca_5(PO_4)_3OH$ in terms of a dissolution reaction, consuming protons, as given in equation (3).

$$Ca_5(PO_4)_3OH + 7H^+ = 5Ca^{2+} + 3H_2PO_4^- + H_2O, \quad (3)$$

By the formalism of Eq (3):

$$\log_{10}K_{sp} = 5 \log_{10}(Ca^{2+}) + 3 \log_{10}(H_2PO_4^-) - 7 \log_{10}(H^+) = 15.8\pm1.7. \quad (4)$$

In Fulmer's study [14], the solubility and rate of dissolution of three apatite sources (Bone Source, Norian cranial repair system, and a sintered hydroxyapatite) are evaluated in a thermodynamically closed system. The measured solubility under physiological conditions (tris buffer solution, pH 7.4, 37°C) of $Ca_5(PO_4)_3OH$ is 1.4 ppm. Solubility product constants at 37°C was calculated to be $2.92\times10^{-42}$for $Ca_5(PO_4)_3OH$. But in this experiment, the dissolution time is only 120 hours, namely five days, do not have completely consider the reaction achieve equilibrium and the solution saturated or not, so that the concentration and the solubility is not consistent with the facts, and the data are also not reliable.

Eight dissolution models of calcium apatite [both $Ca_5(PO_4)_3F$ and $Ca_5(PO_4)_3OH$] were drawn from the previously published material and analyzed by Dorozhkia [15]. The models were shown to deal with different aspects of apatite dissolution and none of them was able to describe the dissolution process in general. Eight models were assumed to complement each other and provide the correct description of the specific aspects of apatite dissolution. In one of his articles [16], K_{sp} $10^{-58.4}$ for $Ca_5(PO_4)_3OH$ is reported by Dorozhkin.

In Zhu's study [17], dissolution of the synthetic $Ca_5(PO_4)_3OH$ in pure water was studied at 25 °C and 45 °C in a series of batch experiments. During the $Ca_5(PO_4)_3OH$ dissolution (0~4320 h), the aqueous calcium and phosphate concentrations reached the maxima after 120 h and then decreased slowly with time. Program PHREEQC was employed to calculate the solubility K_{sp} and free energy. The mean K_{sp} values were calculated for $Ca_5(PO_4)_3OH$ of $10^{-53.28}$ at 25°C and $10^{-55.73}$ at 45°C, on the basis of the obtained $\log_{10}K_{sp}$ values at 25°C, the Gibbs free energies of formation ΔG_f^o [$Ca_5(PO_4)_3OH$] was calculated -6282.82 kJ/mol. The K_{sp} values $10^{-53.28}$ for $Ca_5(PO_4)_3OH$ was approximately 3.72 log units lower than 10^{-57} reported by Stummand Morgan [18] in his book and 5.72 log units lower than 10^{-59} reported early by Santillan Medrano [19].

Solubility of $Ca_5(AsO_4)_3OH$ (x=0). There are few experimental data on the thermodynamic properties of calcium arsenate hydroxyapatite [$Ca_5(AsO_4)_3OH$] in literature. The solubility of $Ca_5(AsO_4)_3OH$ is significantly greater than that of $Ca_5(PO_4)_3OH$ [17,20,21,22,23,24] which suggested that phosphate substitution in the arsenate compound could significantly reduce their solubilities [8,24,25].

The thermodynamic solubility products for $Ca_5(AsO_4)_3OH$ were $10^{-45.20}$ at 35°C, $10^{-45.28}$ at 40°C, $10^{-45.34}$ at 45°C and $10^{-45.46}$ at 50°C in Mahapatra's study [20]. And he thinks the solubility product exhibit a similar temperature dependence.

The effect of pH and Ca/As ratio on the lime precipitation of arsenic-containing wastewater was studied in detail by both precipitation and dissolution by Zhu [26]. In his study $Ca_3(AsO_4)_2 \cdot 3H_2O$, $Ca_3(AsO_4)_2 \cdot 2.25H_2O$, $Ca_5(AsO_4)_3OH$ and $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ were identified in the experiment over a wide range of pH and for Ca/As molar ratios between 1.0 and 4.0. And based on the analytical results, the solubility products for $Ca_5(AsO_4)_3OH$ were calculated as K_{sp} of $10^{-40.12}$ and the Gibbs free energies was calculated -5096.47 kJ/mol. This K_{sp} value is 2.08 log units lower than $10^{-38.04}$ reported by Bothe and Brown [27].

At Xu's research results [28]， the solubility and stability of $Ca_5(AsO_4)_3OH$ were related to pH and temperature, the solubility of $Ca_5(AsO_4)_3OH$ was high in acidic environment and reduced with increasing temperature. PHREEQC program was applied to calculate the solubility product and formation free energy of $Ca_5(AsO_4)_3OH$ which were determined to be$10^{-40.86}$ and -5063.53 kJ/mol. This is approximately the same as the research results from Zhu.

Solubility of $Ca_5(P_xAs_{1-x}O_4)_3(OH)$ solid solution (1>x>0). So far, only Xu [29] have studied on dissolution process, solubility, stability of Arsenate-Phosphate solid solution in the water environment from the angle of solid-solution (SS-AS: Solid solution-Aqueous solution) interaction. The other research results from Xu indicated that the solubility and stability of $Ca_5(P_xAs_{1-x}O_4)_3OH$ solid solution in aqueous solution were strongly dependent on the solution pH. Based on the analytical result at 25°C and initial pH=2, the solubility product (K_{sp}) and the free energy of formation (ΔG_f^o) for the $Ca_5(P_xAs_{1-x}O_4)_3OH$ solid solution were calculated, which decreased with the increasing mole fraction of P and As in the solid solution.

Solubility of $Ca_5(P_xAs_{1-x}O_4)_3F$

Solubility of $Ca_5(PO_4)_3F$ (x=1). In nature, calcium phosphate fluoroapatite [$Ca_5(PO_4)_3F$] is the most abundant apatite phase. The incorporation of trace elements into $Ca_5(PO_4)_3OH$ and $Ca_5(PO_4)_3OH$-like minerals has a considerable influence the mechanical and physiochemical properties of the crystals and significantly affects their reactivity and solubility [30]. Fluorine tends to reduce the crystal size and increases stability of the apatite structure. At lower degrees of fluoridation the apparent solubility declines markedly. It was suggested that $Ca_5(PO_4)_3F$ has a better thermal and chemical stability than $Ca_5(PO_4)_3OH$ [31].

Farr and Elmore [32] calculated a value of pK_{sp} for $Ca_5(PO_4)_3F$ as 60.43 at 25°C. However, their data obtained at pH 1.76 were for mixed $Ca_5(PO_4)_3OH$ and CaF_2. Therefore, the errors introduced by the large excess of solid need to be taken into account.

The thermodynamic solubility product for $Ca_5(PO_4)_3F$ was K_{sp}=$10^{-60.6}$ in Driessensr's book [33]. But in Stummand Morgan's book [18], the K_{sp} values is 10^{-59} for $Ca_5(PO_4)_3F$.

Also from Zhu's article [17], the mean K_{sp} values were calculated for $Ca_5(PO_4)_3F$ of $10^{-55.71}$ at 25°C and $10^{-55.89}$ at 45°C, on the basis of the obtained $\log_{10}K_{sp}$ values at 25°C, the Gibbs free energies of formation ΔG_f^o [$Ca_5(PO_4)_3F$] was calculated -6415.87 kJ/mol. The K_{sp} values $10^{-55.71}$ for $Ca_5(PO_4)_3F$ were approximately 3.29 log units lower than Stummand Morgan's (10^{-59}).

Solubility of $Ca_5(AsO_4)_3F$ (x=0). Calcium arsenate fluoroapatite [$Ca_5(AsO_4)_3F$], its dissolution and subsequent release of aqueous species play an important role in the cycling of arsenic and fluoride in the environment.

The thermodynamic and kinetic properties of svabite dissolution have never been investigated by anyone but Zhu [24]. In his study, $Ca_5(AsO_4)_3F$ was prepared by precipitation, and then dissolution of synthetic $Ca_5(AsO_4)_3F$ was studied at 25°C, 35°C and 45°C in a series of batch experiments. The aqueous concentrations from the batch dissolution were used to calculate the solubility product and free energy of formation of svabite. For the dissolution of $Ca_5(AsO_4)_3F$ in ultrapure water, The mean

K_{sp} value was calculated for $Ca_5(AsO_4)_3F$ of $10^{-39.21}$ at 25°C, $10^{-39.23}$at 35°C and $10^{-40.04}$at 45°C. On the basis of the obtained $\log_{10}K_{sp}$ values at 25°C, the Gibbs free energy of formation ΔG_f^o [$Ca_5(AsO_4)_3F$] was calculated to be -5210.46 kJ/mol.

Solubility of $Ca_5(P_xAs_{1-x}O_4)_3F$ solid solution (1>x>0). Xu not only research on the the solubility and stability of $Ca_5(P_xAs_{1-x}O_4)_3(OH)$ solid solution but also $Ca_5(P_xAs_{1-x}O_4)_3F$ solid solution. In her other research results [34], indicated that the solubility and stability of $Ca_5(P_xAs_{1-x}O_4)_3F$ solid solution in aqueous solution were strongly dependent on the solution pH. After 120 d, dissolution of $Ca_5(P_xAs_{1-x}O_4)_3F$ solid solution achieve equilibrium .Based on the analytical result at 25°C and pH 6, the solubility product (K_{sp}) and the free energy of formation (ΔG_f^o) for the $Ca_5(P_xAs_{1-x}O_4)_3F$ solid solution were calculated, which increased with the dncreasing mole fraction of P and As in the solid solution. This is due to lattice constant decrease with the increasing mole fraction of P and As in the solid solution, and lead to compact structure, so the smaller K_{sp}.

Summary

Literature values of the solubility products vary greatly. The dissolution of the material and its equilibrium is a long process, so it is necessary to spend sufficient time to ensure the experiment to achieve equilibrium. And it is almost always valuable to think comprehensively about the experimental conditions.

The author is researching on the solubility and stability of calcium phosphate hydroxyl-fluor apatite [$Ca_5(PO_4)_3F_x(OH)_{1-x}$, 1≥x≥0]. The study include two aspects, precipitation and dissolution. And the experiment will test in different conditions, and the program PHREEQC was used for simulation calculation and thermodynamics analysis. It intend to take 300d to achieve equilibrium.

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References

[1] G. Boulon: submitted to Journal of Rev. Phys. Appl (1986).
[2] J. Rakovan, in: Phosphates: Geochemical, Geological and Materials Importance, Growth and surface properties of apatite, edtied by Mineralogical Society of America, Washington (2002).
[3] Å. Bengtsson, Solubility and surface complexation studies of apatites. Doctoral Thesis, Department of Chemistry, Umeå University, Sweden (2007).
[4] R.P. Shellis, R.M. Wilson: submitted to Journal of Colloid Interface Sci (2004).
[5] Å Bengtsson, A. Shchukarev, P. Persson and S. Sjöberg: submitted to Journal of Geochimica et Cosmochimica Acta (2009).
[6] P. Ducheyne, Q. Qiu: submitted to Journal of Biomaterials (1999).
[7] H. McDowell, T.M. Gregory and W.E. Brown: submitted to Journal of Research of the International Bureau of Standards (1977).
[8] T.S.B. Narasaraju, U.S. Rai: submitted to Journal of Chem (1979).
[9] W.E. Brown, T.M. Gregory and L.C. Chow: submitted to Journal of Caries Research (1977).
[10] F.C.M. Driessens, R.M.H. Verbeeck: submitted to Journal of Crystal Growth (1981).
[11] L.R. LeGeros: submitted to Journal of Karger (1991).
[12] E. Valsami-Jones, K.V. Ragnarsdottir, A. Putnis, D. Bosbach, A.J. Kemp and G. Cressey: submitted to Journal of Chemical Geology (1998).
[13] Pengchu Zhang, J.A. Ryan and J. Yang: submitted to Journal of Environ. Sci. Technol (1998).
[14] M.T. Fulmer, I.C. Ison, C.R. Hankermayer: submitted to Journal of Biomaterials (2002).

[15] S.V. Dorozhkia: submitted to Journal of Progress in Crystal Growth and Characterization of Materials (2002).
[16] S.V. Dorozhkin: submitted to Journal of Mater. Sci (2007).
[17] Yinian Zhu, Xuehong Zhang, Yudao Chen, Qinglin Xie, Junkang Lan, Meifang Qian and Na He: submitted to Jour- nal of Chem. Geol (2009).
[18] W.Stumm, J.J. Morgan,. Aquatic chemistry. Chemical Equilibria and Rates in Natural Waters. John Wiley & Sons, Inc., New York (1996).
[19] J. Santillan-Medrano, J.J. Jurinak: submitted to Journal of Soil Sci. Soc. Am. Proc (1975).
[20] P.P. Mahapatra, L.M. Mahapatra and B. Mishra: submitted to Journal of Chem (1986).
[21] S.C.B. Myneni, S.J. Traina, T.J. Logan and G.A. Waychunas: submitted to Journal of Environ. Sci. Technol (1997).
[22] J.V. Bothe, P.W. Brown: submitted to Journal of Environ. Sci. Technol (1999).
[23] Yinian Zhu, Xuehong Zhang, Fei Long, Huili Liu, Meifang Qian and Na He: submitted to Journal of Mater. Lett (2009).
[24] Yinian Zhu, Xuehong Zhang, Honghu Zeng, Huili Liu, Na He and Meifang Qian: submitted to Journal of Environ. Chem. Lett. (2010).
[25] C.M.B. Henderson, A.M.T. Bell, J.M. Charnock, K.S. Knight, R.F. Wendlandt, D.A. Plant and W.J.Harrison: submitted to Journal of Mineral. Mag. (2009).
[26] Yinian Zhu, Hua Zhang ,Yanpeng Liang, Huili Liu and Xuehong Zhang: submitted to Journal of Acta Scientiae Circumstantiae (in Chinese, 2005).
[27] J.V. Bothe, P.W. Brown: submitted to Journal of Hazard. Mater. B (1999).
[28] Liwei Xu, Yinian Zhu, Huili Liu, Tengrui Long: submitted to Journal of Environmental Engineering. (in Chinese, 2010).
[29] Liwei Xu, Study on Solubility and Stability of Arsenate/Phosphate Solid Solution. Doctoral Thesis, Chongqing University, China (in Chinese, 2011).
[30] Y. Pan, M.E. Fleet, in: Phosphates: Geochemical, Geobiological, and Materials Importance, Compositions of the apatite-group minerals: substitution mechanisms and controlling factors (2002).
[31] H. Qu, A.L. Vasiliev and M. Aindow: submitted to Journal of Mater. Sci.Mater.Med (2005).
[32] T.D. Farr, K.L. Elmore: submitted to Journal of Physical Chemistry (1962).
[33] F.C.M. Driessensr, Mineral aspects of dentistry. Karger, Basel (1982).
[34] Liwei Xu, Yinian Zhu, Meina Liang, Na He, Tengrui Long: submitted to Journal of ACTA CHIMICA SINICA. (in Chinese, 2011).