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## The stabilities of calcium arsenates at $23 \pm 1^\circ\text{C}$

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### Abstract

The stabilities of calcium arsenate compounds were established by analysis of suspensions made with varying molar Ca/As ratios. Solution chemistry analyses determined the concentrations of calcium and arsenic and pH. The phases that were shown to form in order of descending pH were  $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$  (arsenate–apatite),  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\frac{2}{3}\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4}\text{H}_2\text{O}$ ,  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$  — ferrarisite,  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$  — guerinite and  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ . The analytical concentrations of calcium and arsenic and pH were used in estimating solubility products. The estimated values were then refined through the comparison of the analytical data with calculated  $K_{\text{sp}}$  values using the computer program PhreeqC. From the refined solubility products, the free energies of formation of the calcium arsenate hydrates were calculated as follows:  $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$  (−4941 kJ/mol),  $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$  (−5087 kJ/mol),  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\frac{2}{3}\text{H}_2\text{O}$  (−3945 kJ/mol),  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4}\text{H}_2\text{O}$  (−4085 kJ/mol),  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$  — ferrarisite (−7808 kJ/mol),  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$  — guerinite (−7803 kJ/mol), and  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$  (−1533 kJ/mol). Unlike other solubility studies on arsenate immobilization, this study was the first to consider the complete array of calcium arsenate hydrates that can form and to use the associated ions,  $\text{CaAsO}_4^-$ ,  $\text{CaHAsO}_4^0$  and  $\text{CaH}_2\text{AsO}_4^+$  in determining their solubility products. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Calcium arsenates; Solubility products; Arsenate–apatite

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## 1. Introduction

Arsenic is toxic and potentially dangerous to humans, animals and plants. It occurs naturally in such minerals as mispickel or arsenopyrite ( $\text{FeAsS}$ ), realgar ( $\text{AsS}$ ) and orpiment ( $\text{As}_2\text{S}_3$ ) [1]. Weathering processes release arsenic from these minerals into ground waters and soils. Under aerobic conditions, arsenic is oxidized and reacts with cations such as Al, Ca, Fe and Mn, which are commonly found in soil, to form relatively insoluble arsenates ( $\text{As}^{5+}$ ) and arsenites ( $\text{As}^{3+}$ ) [1,2]. Soluble arsenic is also adsorbed onto nano-size particles of hydrous ferric oxides and other soil and clay components [1,3,4]. Micro-organisms such as fungi, yeast and bacteria can transform soluble arsenic into organoarsenicals such as monomethylarsinic (MMAA) acid and dimethylarsinic acid (DMAA) [5]. All of these naturally occurring reactions control the mobility of arsenic and the bioaccumulation of arsenic in the environment.

However, the introduction of extraneous quantities of arsenic into the environment from the combustion of coal to produce power, the smelting of ores, mining and the manufacture of glass and ceramic products upsets this natural balance. This includes the use of pesticides, herbicides and fungicides as well as wood preservatives, all of which can contain arsenic [6]. Therefore, technologies have been developed to deal with arsenic levels deemed dangerous to the human population. Adsorption onto fine particulates is one method currently being explored to remove arsenic from industrial waste streams. Both  $\text{As}^{3+}$  and  $\text{As}^{5+}$  were shown to be efficiently removed from aqueous solutions by such high surface area particulates as pyrite fines [7], basic yttrium carbonate [8], colloidal ferric hydroxide (ferrihydrite) [4] and other geological materials [9]. The precipitation of discrete, nearly insoluble arsenic-bearing compounds is another technique commonly used for removing soluble arsenic from contaminated waste-streams. Insoluble precipitates, such as calcium arsenates, ferric arsenates, ferric sulfides [10] and the arsenate apatite, mimetite [ $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ ] [11], were shown to effectively control the solubility of arsenic.

In an effort to further the understanding of those reactions involving arsenates and arsenites in ground waters and soils, it is often desirable to model experimental observations using theoretical principles. For example, modeling the dissolution behavior of amorphous ferrihydrite in the presence of arsenate ion revealed that surface complexation accounted for arsenic immobilization rather than the precipitation of crystalline  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$  (scorodite) [3]. As another example, the anhydrous tricalcium arsenate,  $\text{Ca}_3(\text{AsO}_4)_2$ , has often been cited as the sole crystalline precipitate responsible for controlling arsenic solubility when lime is used to remove soluble arsenic from aqueous waste-streams [12–15]. In actuality, there exists a range of calcium arsenates, most of which are hydrated, that can form from aqueous solutions [16,17]. A recent study by Nishimura and Robins [18] re-evaluated the solubility and stability regions of the various calcium arsenates, but did not take into account any associated calcium arsenate complexes in their calculations, even though such complexes have been well-established in the calcium phosphate system [19]. It is the objective of the present study to determine the solubility products ( $pK_{\text{sp}}$ ) and free energies of formation ( $\Delta G_f^0$ ) of the various calcium arsenates that were observed to precipitate at pH values between 6.5 and 12.5 taking into account the presence of calcium arsenate ion-pairs.

## 2. Experimental methods

### 2.1. Collection of experimental data

A total of 64 suspensions were made by combining  $\text{Ca}(\text{OH})_2$  and 80.5 wt.% *ortho*-arsenic acid,  $\text{H}_3\text{AsO}_4$  (Riedel–deHaën) with de-ionized water. The suspensions were prepared with a liquid to solid weight ratio of approximately 10 and molar Ca/As ratios which varied from 0.80 to 4.0. The ingredients were combined in 125 ml HDPE Nalgene bottles, along with zirconia milling media for more efficient mixing of the liquid and solid reactants. The bottles were then tightly sealed and their necks wrapped in electrical tape as an added precaution against intrusion of atmospheric  $\text{CO}_2$ . They were stored at room temperature ( $23 \pm 1^\circ\text{C}$ ), and were periodically agitated over a course of 4 years.

The  $\text{Ca}(\text{OH})_2$  was made by calcining  $\text{CaCO}_3$  at  $1000^\circ\text{C}$  for 2 h. The resulting CaO was then hydrated in boiling water and the product filtered in open air followed by drying in a vacuum oven overnight. X-ray diffraction confirmed the absence of  $\text{CaCO}_3$ . Two sources of  $\text{CaCO}_3$  were used. The first five sample sets used  $\text{CaCO}_3$  obtained from Fisher Scientific which contained approximately 0.5 wt.% magnesium. The sixth and seventh sets used ultra pure  $\text{CaCO}_3$  provided courtesy of Osram–Sylvania. Table 1 lists the compositions of the two  $\text{CaCO}_3$  sources used.

During the 4-year period of study, aliquots were periodically characterized to monitor the extents of reaction by extracting two 5 ml samples from each suspension. The pH of the first sample was measured in open air. A second sample was extracted and then centrifuged all within a nitrogen-filled tent (portable glove box). Still under nitrogen, the liquid fraction was filtered through a  $0.22 \mu\text{m}$  syringe filter into a scintillation vial which was tightly sealed with electrical tape. These solutions were later analyzed by DC plasma emission spectroscopy to determine the concentrations of calcium and arsenic. The solid fraction was air-dried and characterized by X-ray diffraction.

### 2.2. Simulation of experimental data

Associated with each suspension is an assemblage of solid phases, a solution phase containing dissolved calcium and arsenic, and a pH value. Assuming equilibrium has been reached, the values of these parameters can be calculated using established theoretical principles. In this study, the simulations were performed using PhreeqC, a program based on the ion-association aqueous model [20]. The input is free-format and

Table 1  
Elemental analysis on the two sources of calcium carbonate used in this study

Impurity	Fisher (wt.%)	Osram–Sylvania (wt.%)
$\text{Al}_2\text{O}_3$	0.03	0.002
BaO	< 0.005	0.005
MgO	0.49	0.02
MnO	< 0.005	< 0.001
$\text{SiO}_2$	0.09	0.002
SrO	0.03	0.06

Table 2

Equilibrium constants for the various aqueous species used by the computer program, PhreeqC. The log  $K$  values of the associated calcium arsenate ions were refined to optimize agreement between the simulated data match and the experimental data

Reaction	log $K$	Adjusted log $K$	Ref.
$\text{AsO}_4^{3-} + \text{H}^+ = \text{HAsO}_4^{2-}$ (25°C)	11.602	–	[22]
$\text{HAsO}_4^{2-} + \text{H}^+ = \text{H}_2\text{AsO}_4^-$ (25°C)	6.761	–	[22]
$\text{H}_2\text{AsO}_4^- + \text{H}^+ = \text{H}_3\text{AsO}_4$ (25°C)	2.249	–	[22]
$\text{Ca}^{2+} + \text{AsO}_4^{3-} = \text{CaAsO}_4^-$ (40°C)	4.30	4.36 (23 ± 1°C)	[23]
$\text{Ca}^{2+} + \text{HAsO}_4^{2-} = \text{CaHAsO}_4^0$ (40°C)	2.75	2.66 (23 ± 1°C)	[23]
$\text{Ca}^{2+} + \text{H}_2\text{AsO}_4^- = \text{CaH}_2\text{AsO}_4^+$ (40°C)	1.39	1.30 (23 ± 1°C)	[23]
$\text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+$ (25°C)	1.325	–	[24]
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ (25°C)	–14.00	–	–

uses order-independent keyword data blocks that facilitate the building of models that can simulate a wide variety of aqueous-based scenarios. The thermodynamic data for the aqueous species most critical to the calculations are listed in Table 2. Only the calcium arsenate solids and ionic complexes are defined in the input where their solubility products can be manipulated. The remaining aqueous species and solids used by the model are defined in the data base. The model instructs the program to react  $\text{Ca}(\text{OH})_2$  with  $\text{H}_3\text{AsO}_4$  at various relative proportions. Upon reaching saturation conditions, the input file then instructs the program to precipitate the appropriate solid phases. However, much of the thermodynamic data associated with the calcium arsenate solids are not available in the literature. Therefore, they were first derived from the analytical data produced in this study.

### 3. Results

In elucidating the phase equilibria of the ternary system  $\text{CaO}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$  at  $23 \pm 1^\circ\text{C}$ , certain criteria had to be met for the data to be used. The first criterion was that the solid phase assemblage remain unchanged for long periods of time. In addition, the solid phases must be of substantial crystallinity and give well-defined diffraction peaks. The second criterion was that the elemental analyses of their saturated solutions must give reproducible results over a period of time. Table 3 lists the calcium arsenates precipitated from suspensions that have met the above criteria. Included in Table 3 are the molar quantities of dissolved calcium and arsenic as well as the equilibrium pH from those same suspensions. Following is a brief description of each calcium arsenate that precipitated and the calculations showing how their solubility products were determined from the data in Table 3. A more detailed discussion of the synthesis conditions and of the data associated with each calcium arsenate synthesized is presented in another paper [21].

#### 3.1. $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$

This hydrate forms at a relatively high pH and was consistently observed to form phase-pure at Ca/As ratios between 2.0 and 2.5, but, only when using  $\text{Ca}(\text{OH})_2$  made

Table 3

Selected raw data taken from various suspensions that have achieved equilibrium, and the results (in bold) of simulating the raw data using the computer program, PhreeqC

Solid phase assemblage	Ca/As	Sample set (days reacted)	Ca [mmol/l]	As [mmol/l]	pH
Ca <sub>4</sub> (OH) <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	2.20	III (411 days)	7.73	5.34E-03	12.14
"	2.20	III (823 days)	7.98	1.60E-03	12.23
<b>PhreeqC simulation</b>	<b>2.22</b>	–	<b>7.98</b>	<b>1.39E-03</b>	<b>12.11</b>
Ca <sub>5</sub> (AsO <sub>4</sub> ) <sub>3</sub> OH (Arsenic–Hydroxyapatite)	1.67	VI (414 days)	0.64	0.14	9.87
"	1.67	VI (562 days)	0.44	0.26	9.54
"	1.67	VI (674 days)	0.48	0.26	9.77
<b>PhreeqC simulation</b>	<b>1.66</b>	–	<b>0.42</b>	<b>0.37</b>	<b>9.78</b>
Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·3 <sup>2</sup> / <sub>3</sub> H <sub>2</sub> O	1.67	I (74 days)	0.80	0.04	11.18
<b>PhreeqC simulation</b>	<b>1.52</b>	–	<b>0.87</b>	<b>0.04</b>	<b>11.18</b>
Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·4 <sup>1</sup> / <sub>4</sub> H <sub>2</sub> O	1.50	III (411 days)	8.73	7.87	7.52
"	1.50	III (823 days)	7.98	6.54	7.55
<b>PhreeqC simulation</b>	<b>1.41</b>	–	<b>7.85</b>	<b>8.10</b>	<b>7.53</b>
Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·4 <sup>1</sup> / <sub>7</sub> H <sub>2</sub> O	1.50	III (137 days)	10.23	10.94	7.36
"	1.50	VI (408 days)	9.98	9.48	7.32
<b>PhreeqC simulation</b>	<b>1.38</b>	–	<b>10.11</b>	<b>10.55</b>	<b>7.36</b>
CaHAsO <sub>4</sub> ·H <sub>2</sub> O	1.00	VII (120 days)	23.70	27.36	6.22
<b>PhreeqC simulation</b>	<b>0.88</b>	–	<b>20.02</b>	<b>26.67</b>	<b>6.22</b>
"	1.00	III (137 days)	29.44	73.41	5.76
<b>PhreeqC simulation</b>	<b>0.76</b>	–	<b>27.80</b>	<b>43.28</b>	<b>5.76</b>
Ca <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O + Ca <sub>4</sub> (OH) <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	1.85	II (237 days)	–	–	11.00
"	1.85	II (672 days)	1.25	0.031	10.93
"	1.85	II (1084 days)	1.40	0.027	11.05
<b>PhreeqC simulation</b> (Guerrinite)	1.82	–	<b>1.40</b>	<b>0.029</b>	<b>11.40</b>
Ca <sub>5</sub> H <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub> ·9H <sub>2</sub> O + CaHAsO <sub>4</sub> ·H <sub>2</sub> O	1.20	III (137 days)	14.72	18.02	6.91
"	1.20	III (411 days)	14.48	17.48	7.04
"	1.20	III (823 days)	14.97	17.35	6.98
<b>PhreeqC simulation</b>	<b>0.98</b>	–	<b>15.94</b>	<b>17.26</b>	<b>7.01</b>

from the less pure calcium source. This hydrate also formed invariantly with Ca(OH)<sub>2</sub> and Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·3<sup>2</sup>/<sub>3</sub>H<sub>2</sub>O. In calculating its solubility product, the pH values listed in Table 3 were first averaged giving a value of 12.18. The program PhreeqC was then used to determine the predominant aqueous species that would account for all the calcium and arsenic in a dilute solution having a pH of 12.18. With the total amount of dissolved calcium and arsenic in equilibrium with Ca<sub>4</sub>(OH)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O known, the following mole balances can be written:

$$[\text{Ca}]_{\text{T}} = [\text{Ca}^{2+}] + [\text{CaOH}^+] = 7.86 \text{ mmol/l} \quad (1)$$

$$[\text{As}]_{\text{T}} = [\text{CaAsO}_4^-] = 3.47 \times 10^{-3} \text{ mmol/l} \quad (2)$$

where the square brackets denote concentration in mol/l and the numerical values associated with these equations are averages of those listed in Table 3. These mole balances can be rewritten in terms of their activities, and assuming the density of water is 1.0, Eqs. (1) and (2) become:

$$[\text{Ca}]_{\text{T}} = (\text{Ca}^{2+}) \left[ \frac{1}{\gamma \text{Ca}^{2+}} + \frac{K_{\text{c}} K_{\text{w}}}{(\text{H}^{+}) \gamma \text{CaOH}^{+}} \right] \quad (3)$$

$$[\text{As}]_{\text{T}} = \frac{(\text{Ca}^{2+})(\text{AsO}_4^{3-}) K_{\text{ca}}}{\gamma \text{CaAsO}_4^{-}} \quad (4)$$

Parentheses indicate molar activity and  $\gamma$  is the activity coefficient. The equilibrium constants  $K_{\text{c}}$ ,  $K_{\text{w}}$  and  $K_{\text{ca}}$  (40°C) correspond to the aqueous species  $\text{CaOH}^{+}$ ,  $\text{OH}^{-}$  and  $\text{CaAsO}_4^{-}$ , respectively, and are listed in Table 2. The average pH was used for the activity of hydrogen, ( $\text{H}^{+}$ ). However, before Eqs. (3) and (4) can be solved, the activity coefficients were calculated using the Davies equation:

$$\log \gamma_i = -Az_i^2 \left[ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right] \quad (5)$$

where a value of 0.50 was used for  $A$ , the Debye–Hückel constant at 25°C,  $z_i$  is the valence charge of species  $i$ , and  $I$  is the ionic strength. The ionic strength was calculated using the equation:

$$I = 0.5 \sum c_i z_i^2 \quad (6)$$

where  $c_i$  is the concentration of species  $i$  in moles per liter. Eq. (6) leads for the current case to the following expression:

$$I = 0.50 \{ 4[\text{Ca}^{2+}] + [\text{CaOH}^{+}] + [\text{CaAsO}_4^{-}] + [\text{OH}^{-}] \} \quad (7)$$

Electroneutrality of the solution requires that

$$2[\text{Ca}^{2+}] + [\text{CaOH}^{+}] = [\text{CaAsO}_4^{-}] + [\text{OH}^{-}] \quad (8)$$

Combining Eqs. (7) and (8) gives for the ionic strength the following expression:

$$I = \{ 3[\text{Ca}^{2+}] + [\text{CaOH}^{+}] \} \quad (9)$$

The concentrations of the two aqueous species in Eq. (9) are not explicitly known. However, they may be expressed in terms of the total concentration of calcium,  $[\text{Ca}]_{\text{T}}$ , which is a known quantity. The results of the speciation calculations previously performed by PhreeqC also gave the percentage of each aqueous species at a pH of 12.18. The percentage of the calcium species were determined as follows:

$$[\text{Ca}^{2+}] = 0.83[\text{Ca}]_{\text{T}} \quad (10)$$

$$[\text{CaOH}^{+}] = 0.17[\text{Ca}]_{\text{T}} \quad (11)$$

Substituting Eqs. (10) and (11) into Eq. (9) gives:

$$I = 2.66[\text{Ca}]_{\text{T}} \quad (12)$$

With the ionic strength determined, the activity coefficients can be calculated using Eq. (5); these are used in turn to solve Eqs. (3) and (4) for the activities of  $\text{Ca}^{2+}$  and  $\text{AsO}_4^{3-}$ . The solubility product for  $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$  was then calculated using the following expression:

$$K_{\text{sp}} = (\text{Ca}^{2+})^4 (\text{AsO}_4^{3-})^2 (\text{OH})^2 \quad (13)$$

$$pK_{\text{sp}}(\text{estimate}) = 28.1 \quad (14)$$

### 3.2. $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$

In the first set of suspensions with Ca/As greater than 2.0, the apatite,  $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$ , appeared in conjunction with  $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ , but only in minor amounts. When the higher purity calcium source was used in the sixth set of suspensions, phase-pure apatite was observed to form at Ca/As ratios of 1.67 and 1.90. For the present study, only the 562-day and 674-day data from the suspension with Ca/As = 1.67 were used for calculating the solubility product of the apatite. According to the speciation calculations performed and the averaged results in Table 3, the mole balances that account for the majority of calcium and arsenic in the solution phase in equilibrium with phase-pure  $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$  at an average pH of 9.73 are as follows:

$$[\text{Ca}]_{\text{T}} = [\text{Ca}^{2+}] + [\text{CaHAsO}_4^0] = 0.46 \text{ mmol/l} \quad (15)$$

$$[\text{As}]_{\text{T}} = [\text{HAsO}_4^{2-}] + [\text{CaHAsO}_4^0] = 0.26 \text{ mmol/l} \quad (16)$$

In terms of activities, the mole balances become

$$[\text{Ca}]_{\text{T}} = \frac{(\text{Ca}^{2+})}{\gamma_{\text{Ca}^{2+}}} + \frac{(\text{Ca}^{2+})(\text{AsO}_4^{3-})(\text{H}^+) K_{\text{cha}}}{\gamma_0} \quad (17)$$

$$[\text{As}]_{\text{T}} = \frac{(\text{AsO}_4^{3-})(\text{H}^+) K_{\text{ha}}}{\gamma_{\text{HAsO}_4^{2-}}} + \frac{(\text{Ca}^{2+})(\text{AsO}_4^{3-})(\text{H}^+) K_{\text{cha}}}{\gamma_0} \quad (18)$$

where  $K_{\text{cha}}$  (40°C) and  $K_{\text{ha}}$  are the equilibrium constants for  $\text{CaHAsO}_4^0$  and  $\text{HAsO}_4^{2-}$ , respectively. The ionic strength was estimated in the same manner as above and was used to calculate the activity coefficients of the aqueous species  $\text{Ca}^{2+}$  and  $\text{HAsO}_4^{2-}$  again using Eq. (5). The activity coefficient for neutral species can be calculated using the formula:

$$\log \gamma_0 = (0.1) I \quad (19)$$

Now, with two equations and two unknowns, Eqs. (17) and (18) can be solved for the activities ( $\text{Ca}^{2+}$ ) and ( $\text{AsO}_4^{3-}$ ). The solubility product was then determined through the following expression:

$$K_{\text{sp}} = (\text{Ca}^{2+})^5 (\text{AsO}_4^{3-})^3 (\text{OH}) \quad (20)$$

$$pK_{\text{sp}}(\text{estimate}) = 38.3 \quad (21)$$

The tricalcium arsenate hydrate,  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\frac{2}{3} \text{H}_2\text{O}$ , formed at Ca/As ratios between 1.50 and 1.80 and at pH values greater than 9.0. Alternatively, the higher hydrate  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4} \text{H}_2\text{O}$  formed consistently at a Ca/As ratio of 1.50 and at near neutral pH regardless of the source of calcium used [21]. The same observation was made of the most acidic calcium arsenate synthesized in this study, haidingerite,  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ . This hydrate was readily synthesized using either source of calcium and was formed phase-pure at Ca/As ratios of 0.80 and 1.00. In determining the solubility products of  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\frac{2}{3} \text{H}_2\text{O}$  and  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4} \text{H}_2\text{O}$ , the same procedures described above were used. For brevity, only the mole balances and the estimated solubility products for these hydrates are presented.

### 3.3. $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\frac{2}{3} \text{H}_2\text{O}$

At a pH of 11.18,

$$[\text{Ca}]_{\text{T}} = [\text{Ca}^{2+}] + [\text{CaAsO}_4^-] = 0.80 \text{ mmol/l} \quad (22)$$

$$[\text{As}]_{\text{T}} = [\text{HAsO}_4^{2-}] + [\text{AsO}_4^{3-}] + [\text{CaAsO}_4^-] = 3.74 \times 10^{-2} \text{ mmol/l} \quad (23)$$

$$K_{\text{sp}} = (\text{Ca}^{2+})^3 (\text{AsO}_4^{3-})^2 \quad (24)$$

$$pK_{\text{sp}}(\text{estimate}) = 21.02 \quad (25)$$

### 3.4. $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4} \text{H}_2\text{O}$

At an average pH of 7.34,

$$[\text{Ca}]_{\text{T}} = [\text{Ca}^{2+}] + [\text{CaHAsO}_4^0] = 10.10 \text{ mmol/l (averaged)} \quad (26)$$

$$[\text{As}]_{\text{T}} = [\text{HAsO}_4^{2-}] + [\text{CaHAsO}_4^0] = 10.21 \text{ mmol/l (averaged)} \quad (27)$$

$$K_{\text{sp}} = (\text{Ca}^{2+})^3 (\text{AsO}_4^{3-})^2 \quad (28)$$

$$pK_{\text{sp}}(\text{estimate}) = 21.15 \quad (29)$$

### 3.5. $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$

At a pH of 6.22,

$$[\text{Ca}]_{\text{T}} = [\text{Ca}^{2+}] + [\text{CaHAsO}_4^0] = 23.70 \text{ mmol/l} \quad (30)$$

$$[\text{As}]_{\text{T}} = [\text{H}_2\text{AsO}_4^-] + [\text{HAsO}_4^{2-}] + [\text{CaHAsO}_4^0] = 27.36 \text{ mmol/l} \quad (31)$$

$$K_{\text{sp}} = (\text{Ca}^{2+})(\text{HAsO}_4^{2-}) \quad (32)$$

$$pK_{\text{sp}}(\text{estimate}) = 4.74. \quad (33)$$

Two polymorphs of  $\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$ , ferrarisite and guerinite, were identified but both were difficult to produce phase-pure. Rather, these hydrates were most readily



formed in conjunction with other phases. For example, ferrarisite was consistently observed to form invariantly with  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4} \text{H}_2\text{O}$ , whereas the guerinite polymorph was observed to form invariantly with the more acidic arsenate,  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ . Only the phase assemblage which included guerinite as a constituent phase was associated with reproducible data and was therefore included in Table 3.

#### 4. Computer modeling

It is typically desirable to duplicate experimental results using established theoretical principles. This was accomplished through the use of the computer program PhreeqC which used the solubility products estimated above to generate solution parameters for the phase assemblages listed in Table 3. These parameters include concentrations of dissolved calcium and arsenic as well as the corresponding solution pH. When the calculated values did not match satisfactorily to the ones determined experimentally for that particular phase assemblage, then the  $pK_{\text{sp}}$  value was refined and the simulation run again to produce a new set of solution parameters.

The dissociation constants for the aqueous calcium arsenate ions (Table 2) were also refined which only slightly improved the agreement between the calculated and analytical solution parameters. This was done because those listed are for 40°C. The changes, with the exception of  $\text{CaAsO}_4^-$  (aq), were consistent with the van't Hoff equation which dictates a decrease in the  $\log K$  value with a decrease in temperature.

This procedure of refining the solubility products was repeated until an optimal agreement between experimental and calculated was achieved for each phase assemblage. Due to the lack of reliable solution chemistry data for phase-pure guerinite, its solubility product was determined strictly through its invariant relationship with  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ . The results are presented in Table 3 which compares the solution parameters determined analytically with those calculated by PhreeqC using the refined solubility products.

In the case of the dimorph, ferrarisite, the solution chemistry data were very reproducible, but the X-ray diffraction patterns were difficult to reproduce over long periods of time, and ferrarisite was therefore excluded from Table 3. It was later revealed that ferrarisite is sensitive to its drying conditions, thereby giving ambiguous

Table 4

Experimental data from the suspensions which precipitated ferrarisite. Also listed (in bold) are the results of simulating these compositions using the computer program PhreeqC and a  $pK_{\text{sp}}$  value of 31.49

Solid phase assemblage	Ca/As	Sample	Ca [mmol/l]	As [mmol/l]	pH
Ferrarisite + $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4} \text{H}_2\text{O}$	1.40	I (73 days)	7.48	5.34	7.99
	1.45	II (237 days)	6.24	3.87	8.13
	1.45	II (672 days)	6.69	4.87	7.89
<b>PhreeqC simulation</b>	<b>1.28</b>	–	<b>6.62</b>	<b>6.79</b>	<b>7.65</b>
Ferrarisite (single phase)	1.25	II (555 days)	15.22	17.08	6.88
<b>PhreeqC simulation</b>	<b>1.10</b>	–	<b>15.45</b>	<b>17.85</b>	<b>6.70</b>

Table 5

Summary of the refined solubility products used by PhreeqC to simulate equilibria involving the following calcium arsenate hydrates synthesized during this study. Also included are the values of  $\Delta G_f^0$  as determined by Ref. [18]

Calcium arsenate hydrate	Estimated $pK_{sp}$	Refined $pK_{sp}$	$\Delta G_f^0$ (kJ/mol)	$\Delta G_f^0$ (kJ/mol) <sup>a</sup>
$\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$	28.13	<b>29.20</b>	−4941	−4920
$\text{Ca}_5(\text{AsO}_4)_3\text{OH}$	38.30	<b>38.04</b>	−5087	−
$\text{Ca}_3(\text{AsO}_4)_2 \cdot 3\frac{2}{3}\text{H}_2\text{O}$	21.02	<b>21.00</b>	−3945	−
$\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4}\text{H}_2\text{O}$	21.15	<b>21.00</b>	−4085	−4007 <sup>b</sup>
$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$ — Ferrarisite	−	<b>31.49</b>	−7808	−
$\text{Ca}_5\text{H}_2(\text{AsO}_4)_4 \cdot 9\text{H}_2\text{O}$ — Guerinite	−	<b>30.69</b>	−7803	−
$\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$	4.74	<b>4.79</b>	−1533	−1526

<sup>a</sup> Values from Ref. [18].

<sup>b</sup> Value calculated for  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ , from Ref. [18].

diffraction patterns that could not be matched to any known phase. As a result of the diminished confidence in the data, the analytical and calculated solution parameters for ferrarisite are presented separately in Table 4. In determining the solubility product of ferrarisite, the solubility product of guerinite was used as a first estimate then refined to match the analytical data associated with ferrarisite. The result is a slightly larger  $pK_{sp}$  value for ferrarisite indicating it to be slightly less soluble than guerinite.

The results of refining the solubility products are summarized in Table 5 and are listed along with the original estimated values. The corresponding free energies of formation are also listed and agree well with those determined by Nishimura and Robins [18]. The refined values constitute a set of thermodynamic properties that best describe the phase equilibria among the various calcium arsenates that form under ambient conditions.

## 5. Conclusions

Aqueous suspensions initially containing  $\text{Ca}(\text{OH})_2$  and  $\text{H}_3\text{AsO}_4$  in various proportions were allowed to react under ambient conditions. The most alkaline calcium arsenate that precipitated was  $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$  ( $pK_{sp} = 29.20$ ;  $\Delta G_f^0 = -4941$  kJ/mol) which formed consistently as a single phase between the Ca/As of 2.0 and 2.5, and most predictably when the calcium source containing magnesium impurity was used. The apatite phase,  $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$  ( $pK_{sp} = 38.04$ ;  $\Delta G_f^0 = -5087$  kJ/mol), formed most readily when the more pure calcium source was used and at Ca/As ratios of 1.67 and 1.90. Two hydrated forms of the tricalcium arsenate,  $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$ , were observed to precipitate, where  $x = 3\frac{2}{3}$  and  $4\frac{1}{4}$ . The  $3\frac{2}{3}$ -hydrate ( $pK_{sp} = 21.00$ ;  $\Delta G_f^0 = -3945$  kJ/mol) formed at high pH and between the Ca/As ratios of 1.50 and 1.80. The  $4\frac{1}{4}$ -hydrate ( $pK_{sp} = 21.00$ ;  $\Delta G_f^0 = -4085$  kJ/mol) was observed to form at near neutral pH and at a Ca/As ratio of 1.50. It was also observed that the  $4\frac{1}{4}$ -hydrate formed phase-pure when both sources of calcium were used. The most acidic compound formed in this study was haidingerite,  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$  ( $pK_{sp} = 4.79$ ;  $\Delta G_f^0 = -1533$

kJ/mol). It formed from solutions with pH values between 5.5 and 7.0, regardless of the calcium used. Both guerinite and ferrarisite polymorphs were difficult to synthesize phase-pure, but were easily formed invariantly with other phases: ferrarisite ( $pK_{sp} = 31.49$ ;  $\Delta G_f^0 = -7808$  kJ/mol) with  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\frac{1}{4}\text{H}_2\text{O}$  and guerinite ( $pK_{sp} = 30.69$ ;  $\Delta G_f^0 = -7803$  kJ/mol) with the more acidic  $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$ .

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