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Original paper

Synthesis and solubility of brompyromorphite $Pb_5(PO_4)_3Br$

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Abstract. The bromide analogue of pyromorphite $Pb_5(PO_4)_3Br$ was synthesized and characterized by X-ray diffraction, infrared spectroscopy and scanning electron microscopy. The solubility of the brompyromorphite was measured at 25°C and pH values of 2.0, 2.6 and 3.2. For the 3 pH measurements, the average solubility product, log K_{SP}, for the reaction $Pb_5(PO_4)_3Br \Leftrightarrow 5Pb^{2+} + 3PO_4^{3-} + Br^-$ at 25°C is -77.38 ± 0.70. The free energy of formation, $\Delta G°_{f,298}$, calculated from this measured solubility product is -3724.7 ± 4.3 kJ mol^{-1}. These results confirm that brompyromorphite is more soluble than pyromorphite.

Key-words: lead, phosphate, apatite, dissolution, brompyromorphite, solubility product

1. Introduction

Because of numerous possible substitutions, over 40 different minerals belong to the apatite supergroup (Pan, Fleet 2002; Pasero et al. 2010). This fact has inspired many studies of synthetic solid solutions based on the apatite structure. The apatite group of minerals includes the lead-phosphates pyromorphite $Pb_5(PO_4)_3Cl$, hydroxylpyromorphite $Pb_5(PO_4)_3OH$, fluorpyromorphite $Pb_5(PO_4)_3F$, brompyromorphite $Pb_5(PO_4)_3Br$, and various arsenate and vanadate analogs (Pan, Fleet 2002; Pasero et al. 2010). Pyromorphite is one of the most stable lead compounds in earth-surface environments and its precipitation is one of the effective methods used to remove lead ions from contaminated soils and solutions (Cotter-Howells 1996; Shevade et al. 2001; Krik et al. 2002). Other pyromorphite variants such as brompyromorphite (BrPY) are less well known (Nriagu 1973). Its properties are of interest, particularly as $Pb_5(PO_4)_3Br$ can control the concentration of lead and phosphates through Pb and PO_4 sorption on surfactant-modified (amine hexadecyltrimethylammonium bromide) smectite (Figuła, Bajda 2010). The aims of this study are the characterization of the synthetic bromide analogue of pyromorphite and the determination of its solubility product based on the results of dissolution experiments.

2. Material and methods

2.1. Synthesis of brompyromorphite $Pb_5(PO_4)_3Br$

To synthesize 10 g of brompyromorphite, 11.8 g of $Pb(NO_3)_2$, 3.7 g of K_2HPO_4 and 0.85 g of KBr were individually dissolved in 300 mL of redistilled water at 25ºC. With the use of a peristaltic pump, these three solutions were gradually and simultaneously mixed into a 3 L beaker filled with 1.5 L of continuously-stirred redistilled water. A white precipitate appeared immediately upon mixing. After the Pb, PO_4 and Br solutions were exhausted, the suspension was left to age for 28 days. It was then decanted, filtered and then washed first with redistilled water and later with acetone. The precipitate was dried at 110ºC for 12 h.

2.2. Precipitate and solution characterization

The precipitate was analyzed using an X-ray powder diffractometer (Philips PW 3020 X'Pert-APD Diffractometer system with graphite monochromator, Philips, Netherlands) using CuKα radiation, step scan mode with a step size of 0.02 º2Θ and a rate of 1 s per step. Fourier-transform infrared (FTIR) spectra were recorded on a Bio-Rad FTS-60 spectrometer (BIO-RAD, USA) from 4000 to 400 cm^{-1}. Scanning electron microscopy (SEM) was performed using a FEI QUANTA 200 FEG microscope (FEI, USA) with Energy Dispersive Spectrometer (EDS) on carbon-coated samples. From the supernatant solutions, total Pb concentration was determined by atomic absorption spectroscopy (AAS; Philips PU-9100x, Philips, United Kingdom). PO_4 concentrations were determined colourimetrically by the molybdenum blue method (Lenoble et al. 2003) using a Hitachi 1600 spectrophotometer (Hitachi, Japan) at 870 nm wavelength.

2.3. Dissolution experiments

Dissolution experiments were conducted at 25ºC with initial pH values of 2.0, 2.6 and 3.2. For each, an 250 mg aliquot of synthetic $Pb_5(PO_4)_3Br$ was added to 250 mL of 0.05 M KNO_3 and the pH adjusted to the desired value using 0.1 M HNO_3. All experiments were conducted in triplicate in unbuffered suspensions. In each case, the pH was allowed to drift freely after the initial value was set. To determine that equilibration had been reached, samples of the reaction solutions were taken after 2 h and after 1, 2, 4, 7, 14, 21, 28, 42, 56, and 93 days. The bottles containing the suspensions were shaken twice a week and always after sampling. For each sample, the solids were allowed to settle before 7 mL of the supernatant was withdrawn, without refilling with the solution afterwards. The samples were analyzed for pH (combined glass electrode), Pb_{tot} (AAS) and $P(V)_{tot}$ (molybdene blue method; Lenoble et al. 2003) while [Br] was calculated from the stoichiometry of the dissolved solids. Calculations of solubility products were performed with the aid of the computer program PHREEQC with modified MINTEQ.v4 thermodynamic database (Allison et al. 1991). The activities of ionic species were calculated from measured concentrations of elements by applying the Davies equation or the extended Debye-Huckel equation.

3. Results and discussion

3.1. X-Ray diffraction (XRD)

The white precipitate produced in the synthesis was identified as the bromide analogue of pyromorphite $Pb_5(PO_4)_3Br$ by comparing peak positions with those of Br-pyromorphite reported in Joint Committee on Powder Diffraction Standards (JCPDS) cards 32-0533 and 06-0365. All peaks produced by the precipitate were identified as brompyromorphite peaks (Fig. 1). Calculated unit cell parameters are: a = 10.074(1) Å and c = 7.373(1) Å. These values agree well with the values of a = 10.145 Å and c = 7.347 Å reported for synthetic lead bromide phosphate (JCPDS card 32-0533) and with the values of a = 10.1 Å and c = 7.38 Å reported for the lead bromide phosphate (JCPDS card 06-0365).

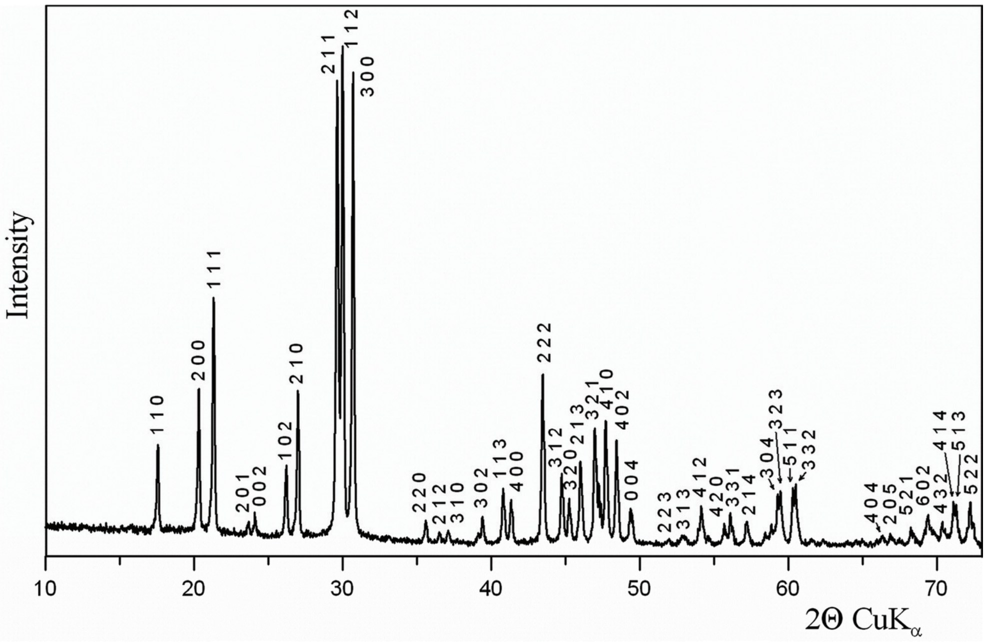

Fig. 1. XRD pattern of synthetic brompyromorphite.

3.2. Mid-IR spectra

Mid-infrared spectra of synthetic brompyromorphite show characteristic bands originating from P–O or O–P–O vibrations present in [PO_4] tetrahedra (Fig. 2). These are the bands due to the symmetric stretching vibration ν_1 (922 cm^{-1}) and the ν_3 asymmetric stretching modes (1038, 988, 966 cm^{-1}) as well as bands originating from the asymmetric vibrations ν_4 (575, 542 cm^{-1}) and ν_2 bending symmetric vibrations (438 cm^{-1}) occurring within these tetrahedra. The number of bands due to $(PO_4)^{3-}$ tetrahedra vibrations indicates a lowering of their symmetry from the T_d point group to the C_{2v} group (Nakamoto et al. 1969).

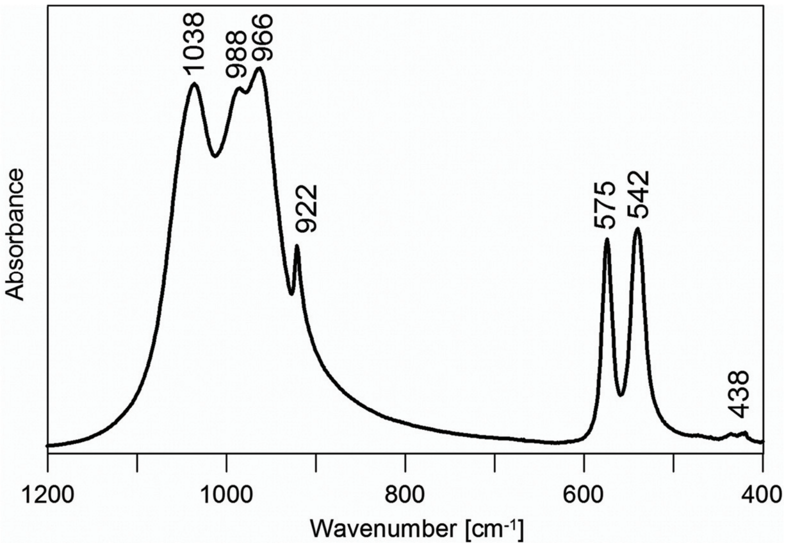

Fig. 2. Mid-IR absorption spectrum of synthetic brompyromorphite.

3.3. Scanning electron microscopy (SEM)

The SEM observations indicate that the precipitate is composed mainly of 1–2 μm grains. Among these grains, idiomorphic crystals in the form of a hexagonal prism and pyramid reach lengths of 5–10 μm (Fig. 3). The surface of the grains is smooth. The crystals are composed of Pb, P, O and Br as determined by EDS. Neither the formation of others phases nor changes in crystal size or morphology were detected after 4 months.

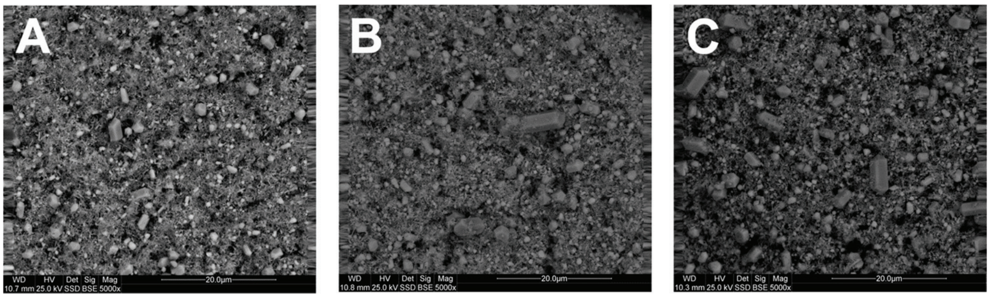

Fig. 3. Scanning electron microscope (SEM) image of synthetic brompyromorphite after 2 hours (A), 21 hours (B) and 28 days (C).

3.4. Dissolution experiments

In the dissolution experiments, most of the reaction occurred within the first week with dissolution rates, as indicated by the increase in lead concentration, declining with time. An example of the evolution of the solution composition over time is shown in Figure 4. The bromide analogue of pyromorphite dissolved stoichiometrically. The molar ratio of ions of Pb and PO_4 in the aqueous solution was approximately 5:3 in accordance with the chemical formula $Pb_5(PO_4)_3Br$. This indicates that the dissolution is congruent.

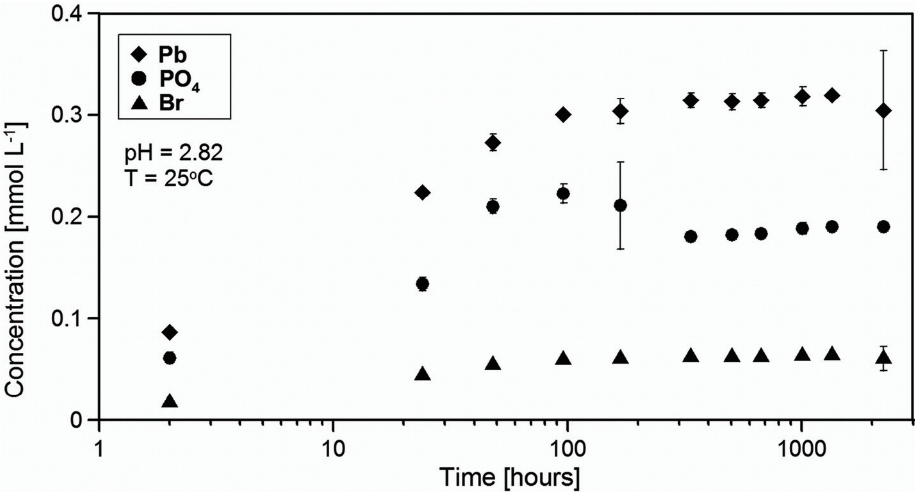

Fig. 4. Concentrations of Pb, PO_4, and Br in the dissolution experiment with initial pH of 2.60 (equilibrium pH 2.82) and temperature 25°C.

The brompyromorphite was considered to be in equilibrium with the solution when the compositions of two consecutive samples of the reaction solution were equal within error. At the initial pH values of 2.0 and 3.2, equilibrium was attained in 2 months whereas, for the initial pH of 2.6, equilibrium was reached after 14 days. The drift of pH was small (±0.1

pH units) and speciation calculations on the equilibrium solutions indicate the formation of $H_2PO_4^-$ and HPO_4^{2-} ions from orthophosphate PO_4^{3-} released to the solution from dissolving $Pb_5(PO_4)_3Br$. The initial pH values of 2.0, 2.6 and 3.2 increased slightly to 2.12, 2.82 and 3.46, respectively, as equilibrium was attained.

The ion activity product (IAP) for the dissolution reaction of brompyromorphite

$$Pb_5(PO_4)_3Br \Leftrightarrow 5Pb^{2+} + 3PO_4^{3-} + Br^- \tag{1}$$

can be written as

$$\log IAP = 5\log\{Pb^{2+}\} + 3\log\{PO_4^{3-}\} + \{Br^-\} \tag{2}$$

where brackets denote activities. At equilibrium, the IAP is equal to the solubility product, K_{sp}. On the basis of measured concentrations and pH at equilibrium, the activities of Pb^{2+}, PO_4^{3-} and Br^- were calculated with the aid of computer program PHREEQC. Based on the calculated activities, the log IAP was calculated using Eq. (2). The results of these calculations are presented in Table 1. Since K_{sp} is independent of pH, the average equilibrium log IAP from the three pH experiments, represents the log K_{sp} at 25ºC and equals –77.38 ± 0.70. This value agrees well with the log K_{sp} = –78.1 ± 0.1 reported by Nriagu (1973).

TABLE 1

Calculated equilibrium activities

Sample	Temperature [°C]	pH	$\log\{Pb^{2+}\}$	$\log\{PO_4^{3-}\}$	$\log\{Br^-\}$	log IAP
BrPY–2.0	25	2.12	–3.331	–18.770	–3.611	–76.58 ± 0.84
BrPY–2.6	25	2.82	–3.992	–17.816	–4.289	–77.70 ± 0.38
BrPY–3.2	25	3.46	–4.453	–16.952	–4.743	–77.86 ± 0.14

Based on the solubility product determined for brompyromorphite (BrPY) in the experiments, the Gibbs free energy of formation $\Delta G°_f(BrPY)$ is calculated. The Gibbs free energy $\Delta G°_r$ of dissolution reaction (1) expressed by the equation

$$\Delta G°_r = 5\Delta G°_f(Pb^{2+}) + 3\Delta G°_f(PO_4^{3-}) + \Delta G°_f(Br^-) - \Delta G°_f(BrPY) \tag{3}$$

is, at equilibrium, related to the solubility product K_{sp} as follows:

$$\Delta G°_r = -RT\ln K_{sp} \tag{4}$$

where R is the gas constant (8.314472 J mol^{-1} K^{-1}) and T is the temperature (298.15 K). This gives a value for $\Delta G°_r$ of 441.7 ± 4.3 kJ mol^{-1}. Calculation of the Gibbs free energy of the formation of brompyromorphite is enabled by equation 3 as follows:

$$\Delta G°_f(BrPY) = 5\Delta G°_f(Pb^{2+}) + 3\Delta G°_f(PO_4^{3-}) + \Delta G°_f(Br^-) + RT\ln K_{sp} \tag{5}$$

Based on available values of $\Delta G°_f(Pb^{2+})$ = -24.40, $\Delta G°_f(PO_4^{3-})$ = -1019.00 and $\Delta G°_f(Br^-)$ = -104.01 kJ mol^{-1} from Robie et al. (1978) and the value of K_{sp} = -77.38 ± 0.70

experimentally determined above, the Gibbs free energy of formation of BrPY may be calculated as ΔG°_f(BrPY) = –3724.7 ± 4.3 kJ mol^{-1}. This value corresponds very well with the value of 3731.6 kJ mol^{-1} calculated by Nriagu (1973).

4. Conclusions

Experiments conducted by Nriagu (1973) indicated that in dilute phosphate solutions, Pb halides are rapidly converted to pyromorphites and/or pyromorphite solid solutions. Therefore, pyromorphites and brompyromorphites are believed to be the possible end products of Pb released to the environment. Because bromide is less abundant than chloride, the bromide analogue of pyromorphite will readily transform into pyromorhite. This is possible because pyromorhite is less soluble (log K_{SP} = -79.6; Flis et al. 2011) than the bromide analogue of pyromorphite (log K_{SP} = -77.38; this study).

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