Transformation of chernikovite into meta–uranocircite II, $Ba(UO_2)_2(PO_4)_2.6H_2O$ and study of its solubility

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Abstract

Chernikovite, $(H_3O)_2(UO_2)_2(PO_4)_2$, was synthesized and subsequently transformed into meta-uranocircite II, $Ba(UO_2)_2(PO_4)_2.6H_2O$, by ion-exchange experiments. The crystals are lemon-yellow and strongly fluorescent. From solubility data a mean pK_s value at 25 °C was determined as 51.79 ± 0.21. For a cell volume of 16.31.7 $Å^3$ and $Z = 4$ the density was calculated as 3.970 g/cm^3 whereas the measured density is 3.964 g/cm^3. The X-ray powder pattern shows the following strongest lines: 3.609(60)(114), 3.470(60)($\bar{1}23$), 2.9272(90)(132), 2.9006(90)($\bar{3}12$), 2.6065(80)($\bar{1}16$), 2.4581(75)($\bar{2}33$), 2.2015(100)(143 ; $\bar{1}43$), 2.1869(100) (241 ; 226 ; $\bar{2}41$).

KEYWORDS: meta-uranocircite II, uranylphosphate group, thermal behaviour, solubility product.

Introduction

Different barium-uranylphosphate minerals are known with general formula $Ba(UO_2)_2(PO_4)_2.nH_2O$. These minerals differ only by their water content. The hydrates with n = 12, 10, 8 and 6 are known as uranocircite I, uranocircite II, meta-uranocircite I and meta-uranocircite II respectively (Walenta, 1963). The syntheses of the barium-uranylphosphate species, starting from pure chemicals, were realised by Beintema (1938), resulting in a mixture of different hydrates of barium-uranylphosphate. Fairchild (1929) and Nuffield and Milne (1953) obtained meta-uranocircite I by ion exchange in artificial autunites. The aim of this paper is to prepare a sufficient quantity of pure meta-uranocircite II (barium-uranylphosphate hexahydrate) for the accurate determination of the solubility product in aqueous medium at 25 °C.

Earlier ion-exchagne experiments with synthetic chernikovite, $(H_3O)_2(UO_2)_2(PO_4)_2.6H_2O$, resulted in the formation of bassetite, $Fe(UO_2)_2(PO_4)_2.8H_2O$ (Vochten *et al.*, 1984) and lehnerite, $Mn(UO_2)_2(PO_4)_2.H_2O$ (Vochten, 1990).

In this study the necesary quantity of meta-unranocircite II was obtained in a similar way. Since there is some confusion in the literature concerning the dehydration of meta-uranocircite II, we have extended our studies to the thermal behaviour of synthetic meta-uranocircite II.

Synthesis

Well-formed crystals of chernikovite were obtained by crystallisation of a solution of schoepite, $UO_2(OH)_2.2H_2O$ in diluted phosphoric acid (Vochten, 1990). These crystals were easily transformed into meta-uranocircite II by cation exchange experiments with Ba^{2+} ions. Therefore 0.2 g chernikovite was suspended in 100 ml 0·02M $BaCl_2$ solution and the suspension was kept at 60 °C.

Since deprotonation occurs during the exchange reaction, the $BaCl_2$ solution was replaced every 24 h, until a constant pH of 4.6 was obtained. The exchange reaction was completed after approximately two weeks. The degree of progress of the exchange reaction can be easily controlled by the variation of the pH of the suspension. The exchange reaction is to be written as:

$$(H_3O)_2(UO_2)_2(PO_4)_2.6H_2O + Ba^{2+} \rightarrow Ba(UO_2)_2(PO_4)_2.6H_2O + 2H_3O^+ \quad (1)$$

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Chemical analysis

Meta-uranocircite II, obtained as previously described, is dissolved in 6M HCl and the BaO, UO_3 and P_2O_5 contents were determined. BaO was determined by atomic absorption spectrophotometry (AAS), UO_3 by spectrophotometry using arsenazo III as reagent (Singer and Matuchia, 1962) and P_2O_5 by spectrophotometry using vanadomolybdate reagent (Michelsen, 1957). The water content was determined by thermogravimetry on a separate sample.

The oxide- and crystal-chemical formulae were calculated by the residual oxygen method. The results are given in Table 1.

Thermal behaviour

The uranocircite hydrates were studied by Nuffield and Milne (1953), Walenta (1963) and Čejka *et al.* (1985). According to Walenta (1963) meta-uranocircite I can easily be converted in meta-uranocircite II in a reversible way. He described the dehydration process of meta-uranocircite II by two dehydration steps, where Čejka *et al.* (1985) observed three separate steps. According to the latter, meta-uranicircite II must be considered as a very stable hydrate in the series of uranyl phosphates.

In our study the thermal behaviour of synthetic meta-uranocircite II wa accurately investigated by differential scanning calorimetry (Du Pont DSC-910) in combination with thermogravimetric analysis (Du Pont TGA-956), resulting in four well defined dehydratation steps. Both TGA and DSC curves were recorded with an applied heating rate of 5 °C/min and a constant N_2 flow of 30 ml/min. The curves are represented in Fig. 1. From the TGA curve, we may conclude that the synthetic barium uranyl phosphate originally contains 7 moles of water. It could be suggested that the synthetic material can be seen as an intermediate phase between meta-uranocircite I and meta-uranocircite II. However as can be seen from the thermograms, one mole of water is released as low as 37 °C. This may be an indication that the first mole of water is of zeolitic nature.

Based on this assumption, and taking into consideration the TGA and DSC curves, the hydratation process of synthetic meta-uranocircite II may be described by four separate steps which could be summarised as follows:

$$\begin{array}{ccc} & Ba(UO_2)_2(PO_4]_2.6H_2O & \\ 37\text{–}94\,^{\circ}C & \downarrow & -4H_2O \\ & Ba(UO_2)_2(PO_4)_2.2H_2O & \\ 94\text{–}175\,^{\circ}C & \downarrow & -H_2O \\ & Ba(UO_2)_2(PO_4)_2.H_2O & \\ 175\text{–}206\,^{\circ}C & \downarrow & -\frac{1}{2}H_2O \\ & Ba(UO_2)_2(PO_4)_2.\frac{1}{2}H_2O & \\ 206\text{–}300\,^{\circ}C & \downarrow & -\frac{1}{2}H_2O \\ & Ba(UO_2)_2(PO_4)_2 & \end{array}$$

Crystallography

Crystal morphology. Since the crystal habit of chernikovite is not affected by ion exchange processes, the synthesised crystals of meta-uranocircite II should be considered as pseudomorphic after chernikovite. A scanning electron micrograph of chernikovite transformed into meta-uranocircite II is shown in Fig. 2.

The crystals consist of a typical multilayer structure, which is obviously due to the negatively charged $[UO_2PO_4]_n^{n-}$ layers. This layered structure may be responsible for the presence of the above mentioned zeolitic water. The transformation of the chernikovite crystals may be explained by a diffusion controlled process of the exchanging ions between these layer structures.

X-ray crystallography. X-ray diffraction data of synthetic meta-uranocircite II have been obtained

Table 1. Chemical analysis of synthetic meta-uranocircite II

oxide	wh %	Molar quantity . 10^4	Atomic ratio
UO_3	58.08	2030	1.96
BaO	15.22	992	0.96
P_2O_5	15.17	1068	2.06
H_2O	11.73	—	—
	100.20		

Empirical formula : $Ba_{0.96}\ (UO_2)_{1.96}\ (PO_4)_{2.06}.\ 6.3\ H_2O$

Ideal formula : $Ba(UO_2)_2(PO_4)_2\ .\ 6H_2O$

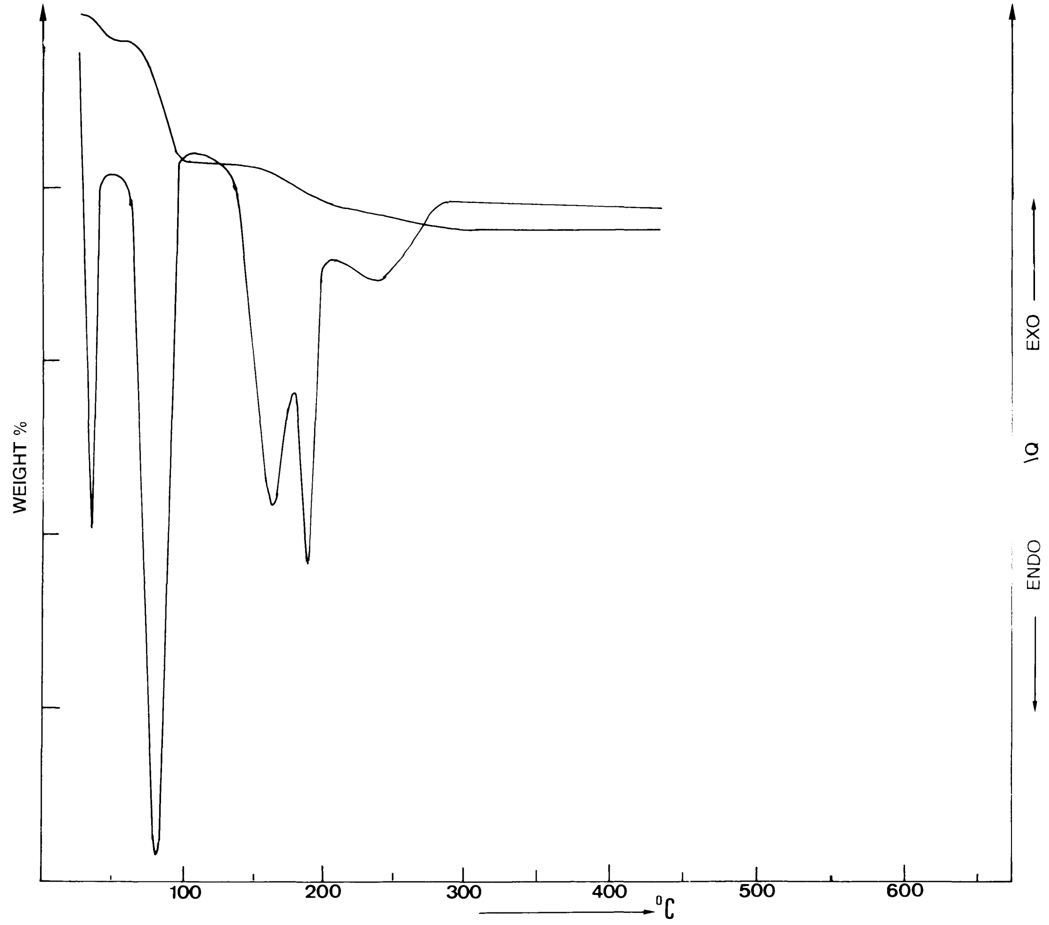

FIG. 1. Thermogrametric- and differential-scanning calorimetric analyses of synthetic meta-uranocircite II. Heating rate 5 °C/min; N_2-flow 30 ml/min.

FIG. 2. Scanning electron micrographs of synthetic meta-uranocircite II crystals derived from chernikovite. Field width is 60 and 120 μm respectively. Field width is 60 μm (A, *left*) and 120 μm (B, deatil of A, *right*).

at 40 kV and 20 mA using Cu-$K\alpha_1$ radiation (λ = 1.5406 Å). The powder diffraction photographs were recorded by means of a Guinier-Hägg camera with a diameter of 100 mm. Si-powder (NBS-640) was used as an internal X-ray diffraction standard. The relative intensities of the diffraction lines were measured with a Carl-Zeiss Jena MD-100 micro-densitometer.

Taking into account the monoclinic lattic parameters of meta-uranocircite II [Khosrawan-Sazedj (1982); a = 9.789(3), b = 9.882(3), c = 16.868(3) Å, β = 89.95(2)°] and the space group $P112_1/a\text{–}C_{2n}^5$, 128 of the 130 diffraction lines could be indexed by applying the computer program of Gabe *et al.* (1989). The first 25 observed and calculated d_{hkl}-values with their indices and relative intensities are given in Table 2.

From these data it is clear that there is good agreement between the observed and calculated d_{hkl}-values for synthetic meta-uranocircite II. A table of all observed and calculated d_{hkl}-values is available upon request. For a cell volume of 1631.7 Å^3 and Z = 4 the density is calculated as 3.970 g/cm^3, where the measured density in toluene by means of a Cahn-RG micro-electrobalance is 3.964 g/cm^3 at 25 °C.

Solubility

The solubility of meta-uranocircite II is relatively high in a strong acidic medium and decreases rapidly with increasing pH. The solubility was determined at 25 °C in aqueous medium in a pH range 1.2–4.0. After equilibration, the suspensions were filtered off and both the uranium concentration and the pH were accurately determined in the filtrate.

The uranium concentration was determined by spectrophotometry using arsenazo III as reagent (Singer and Matuchia, 1962). The dissociation of meta-uranocircite II can be written as:

$$Ba(UO_2)_2(PO_4)_2.6H_2O \rightarrow Ba^{2+} + 2UO_2{}^{2+} + 2PO_4{}^{3+} + 6H_2O, \qquad (2)$$

for which the solubility product is:

$$K_s = [Ba^{2+}][UO_2^{2+}]^2[PO_4^{3-}]^2 \qquad (3)$$

In order to evaluate this equation each of the ions must be related to the H$^+$ or OH$^-$ concentration. Due to the fact that the pH is lower than 4, all barium is present as Ba^{2+}-ions. The phosphate ions are invovled in acid-base equilibria according to:

Table 2. X-ray powder diffraction data of synthetic meta-uranocircite II. Guinier-Hägg camera 100mm, CuK_{α_1}-radiation, 40 kV-20mA. The calculated d–values with their indices, according to the computer program of Gabe, E.J. et al., (1989).

$d_{obs.}$	$d_{calc.}$	I/I_0	hkl
8.508	8.530	20	100
6.430	6.430	15	111, $\bar{1}11$
5.374	5.370	20	112
4.947	4.940	20	020
4.870	4.870	20	$\bar{1}03$
4.361	4.371	5	$\bar{1}13$
4.272	4.268	20	121
4.214	4.217	20	004
3.888	3.893	15	212
3.609	3.607	60	114
3.470	3.470	60	$\bar{1}23$
3.414	3.406	45	221
3.207	3.208	85	024
3.068	3.068	10	032
3.039	3.039	25	$\bar{2}14$
2.9272	2.9280	90	132
2.9006	2.9080	90	$\bar{3}12$
2.6824	2.6800	60	125
2.6065	2.6060	80	$\bar{1}16$
2.5106	2.5100	40	134
2.4959	2.4960	40	$\bar{3}14$
2.4674	2.4700	70	040
2.4581	2.4581	75	$\bar{2}33$
2.4396	2.4390	70	206
2.4171	2.3950	45	140

+ 105 additional lines

$$PO_4^{3-} \xrightarrow{H^+} HPO_4^{2-} \xrightarrow{H^+} H_2PO_4^- \xrightarrow{H^+} H_3PO_4 \quad (4)$$

Since the pH is relatively low, the equilibrium of the acid-base system shifts to the right. The concentration of each phosphate ion can be calculated from:

$$[H_2PO_4^-] = \frac{[H_3PO_4]\,K_{A_1}}{[H^+]^2} \quad (5)$$

$$[HPO_4^{2-}] = \frac{[H_3PO_4]\,K_{A_1}K_{A_2}}{[H^+]^2} \quad (6)$$

$$[PO_4^{3-}] = \frac{[H_3PO_4]\,K_{A_1}K_{A_2}K_{A_3}}{[H^+]^3} \quad (7)$$

The total phosphate concentration $(PO_4)_T$ is to be expressed as:

$$(PO_4)_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \quad (8)$$

The $[PO_4^{3-}]$ can be written as:

$$[PO_4^{3-}] = \frac{[PO_4^{3-}]}{[PO_4]_T} = [PO_4]_T \quad (9)$$

Taking into account expressions (5), (6) and (7) and the fact that $(PO_4)_T = 2C$, equation (9) can be rearranged as:

$$[PO_4^{3-}] = \frac{2K_{A_1}K_{A_2}K_{A_3}C}{[H^+]^3 + [H^+]^2K_{A_1} + [H^+]K_{A_1}K_{A_2} + K_{A_1}K_{A_2}K_{A_3}} \quad (10)$$

In this equation C represents the solubility of synthetic meta-uranocircite II in mol/L and K_{A_i} the *i*-th acid dissociation constant of H_3PO_4. The UO_2^{2+}-ions form several complexes with OH^--ions, governed by the equilibrium reaction:

$$pUO_2^{2+} + qH_2O \leftrightharpoons (UO_2^{2+})_p(OH)_q^{(2p-q)+} + qH^+, \quad (11)$$

with corresponding formation constant β_{pq}:

$$\beta_{pq} = \frac{[(UO_2^{2+})_p(OH^-)_q^{(2p-q)+}][H^+]^q}{[UO_2^{2+}]^p} \quad (12)$$

The β_{pq} values of the most significant uranyl-hydroxo complexes we substracted from Sillen and Martell (1964), Perrin (1984), Högfeldt (1982) and Djocić *et al.* (1986). Since the concentrations of the different phosphate species are very low, the formation of UO_2^{2+}-phosphate complexes may be neglected. Using the different β_{pq} values, the UO_2^{2+}-ion concentration was calculated at each pH and corresponding solubility.

From these values and the Ba^{2+} and the PO_4^{3-} concentrations we could obtained a weighted mean pK_s value of 51.79 ± 0.21. Table 3 summarizes the solubility data and the calculated pK_s values of meta-uranocircite II at different pH values and 25 °C. As mentioned in an earlier study (Vochten, 1990), the distribution of the different uranyl species was calculated as function of the pH. From these data it is clear that in the studied pH range (pH < 4) the UO_2^{2+}-ion is the dominant ion in solution.

Discussion

Comparing the pK_s-value of meta-uranocircite II ($pK_s = 51.79$) with those of meta-torbernite, $Cu(UO_2)_2(PO_4)_2.8H_2O$, ($pK_s = 12.8$); nickel-uranylphosphate, $Ni(UO_2)_2(PO_4)_2.8H_2O$, ($pK_s = 9.5$) and the cobalt analogue ($pK_s = 9.2$) (Vochten *et al.*, 1984), it is clear that meta-uranocircite II is less soluble, with the consequence that this mineral can be formed in the vicinity of primary uraninite. If the phosphorus source is of mineral origin, such as apatite, the alteration of this mineral is to be considered first in the genesis of uranyl-phosphate minerals.

The alteration in the presence of CO_2, H_2O and O_2 can be represented as:

$$\underset{\text{apatite}}{2Ca_5(PO_4)_3(F,Cl,OH)} + 5H_2O + 8CO_2 + O_2 \rightarrow 6H_2PO_4^- + Ca^{2+} + 2Cl^- + \underset{\text{calcite}}{8CaCO_3\downarrow} + CaF_2\downarrow$$

Depending of the pH of the reacting medium, the UO_2^{2+}-ions formed by the alteration of the primary ore, reacts with the HPO_4^{2-}-ions, resulting in the formation of chernikovite.

Table 3. Solubility data of synthetic meta-uranocircite II at different pH–values at 25°C.

pH	Solubility mol/L.10^6	pKs
1.37	300.0	51.51
1.55	156.4	51.91
1.97	61.4	51.69
2.38	20.7	52.05
3.79	1.5	51.77

$$2HPO_4{}^{2-} + 2UO_2{}^{2+} + 8H_2O \rightarrow \underset{\text{chernikovite}}{(H_3O)_2(UO_2)_2(PO_4)_2.6H_20}$$

The H_3O^+-ions can further be exchanged with bivalent cations X^{2+}, such as Ba^{2+} and Ca^{2+}, resulting in the formation of uranocircites, autunites and Ba-Ca uranyl-phosphate hydrates according to the general reaction:

$$\underset{\text{chernikovite}}{(H_3O)_2(UO_2)_2(PO_4)_2.6H_2O} + X^{2+}$$

$$\xrightarrow{(n-6)H_2O} \underset{X^{2+}\text{-uranylphosphate}}{X(UO_2)_2(PO_4)_2.nH_2O} + 2H_3O^+.$$

The first reaction can give a plausible explanation of the fact that in some primary deposits of uranocircite, fluorite is accessory (Wilmarth *et al.*, 1952). The water content of the meta-uranocircite species ranges between the two hydrates I and II in a reversible way and is affected by the partial water pressure of the ambient atmosphere.

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