

Solubility and spectrochemical characteristics of synthetic chernikovite and meta-ankoleite

LAURENT VAN HAVERBEKE, RENAUD VOCHTEN AND KAREL VAN SPRINGEL

Departement Scheikunde - Experimentele Mineralogie, Universiteit Antwerpen (RUCA), Middelheimlaan 1, B-2020 Antwerpen, Belgium

Abstract

Chernikovite and meta-ankoleite were synthesized with a relatively high crystallinity and the compounds were identified by means of chemical analysis and X-ray diffraction. The infrared spectra were recorded and the bands assigned. From the luminescence spectra, the band-gap energy for both compounds was calculated as 2.35 eV, indicating that they must be considered as insulators. The dependence of the solubilities of these compounds on the acidity of the solution was studied, and the dominant ionic species were determined. The pK_{sp} values of chernikovite and meta-ankoleite were found to be 22.73 ± 0.24 and 24.30 ± 0.81 respectively.

KEYWORDS: chernikovite, meta-ankoleite, solubility, solubility product, infrared spectra.

Introduction

THE tetragonal minerals chernikovite, $(H_3O)(UO_2)(PO_4) \cdot 3H_2O$, and meta-ankoleite, $K(UO_2)(PO_4) \cdot 3H_2O$, belong to the meta-autunite group and occur sparingly as oriented inclusions in secondary uranium minerals (Atencio, 1988). The first studies on chernikovite were carried out by Chernikov (1958) on a sample from an unspecified location in the former USSR. Camargo (1971) studied a sample of chernikovite from Perus, São Paulo, Brazil, which was associated with other secondary uranium minerals. Kashirtseva and Valueva (1979) did a more extensive study of another occurrence in the former USSR. The synthetic phase, obtained by Frondel (1950) and by Ross (1955) was found to be identical to natural chernikovite.

The composition of meta-ankoleite samples found in nature do not agree with the ideal formula. Gallagher and Atkin (1966) studied two meta-ankoleite samples which came from Ankole, S.W. Uganda, and Sebungwe, Zimbabwe, respectively. According to these authors the composition of the Uganda sample was $(K_{1.7}, Ba_{0.2})(UO_2)_2 \cdot (PO_4)_2 \cdot 6H_2O$, whereas the Zimbabwe sample gives the formula $(K_{1.4}, Ca_{0.5})(U_{1.8}O_4)(P_{2.1}O_8) \cdot 6H_2O$. According to the studies of Mrose (1953) and Ross and Evans (1964), meta-ankoleite is isostructural with chernikovite.

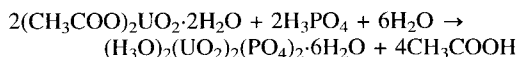
The aim of this paper is to determine the solubility and solubility product of synthetic chernikovite and

meta-ankoleite. Characterization by chemical analysis and X-ray diffraction was carried out, the infrared spectra were recorded and the band-gap energy was calculated from luminescence spectra.

Synthesis

Chernikovite and meta-ankoleite were synthesized using methods similar to those that have been used previously for uranyl phosphates (Vochten *et al.*, 1981), lehnerite (Vochten, 1990), uranyl oxide hydrates (Vochten and Van Haverbeke, 1990), parsonsite (Vochten *et al.*, 1990), meta-uranocircite II (Vochten *et al.*, 1992), liebigite and andersonite (Vochten *et al.*, 1993) and zippeite (Vochten *et al.*, 1995).

Chernikovite was synthesized by mixing solutions of uranylacetate and phosphoric acid according to the method described by Moeller (1957). The reaction can be given as:



The very fine reaction product was filtered off, rinsed with distilled water and subsequently air-dried. In order to obtain a phase with a higher degree of crystallinity, the product was suspended in distilled water and heated for 7 days in a Parr bomb at a temperature of 180°C and a corresponding water vapour pressure of 1 MPa.

TABLE 1. Chemical composition of synthetic chernikovite and meta-ankoleite

	wt.%	chernikovite atomic quantities ($\times 10^4$)	atomic ratio	wt.%	meta-ankoleite atomic quantities ($\times 10^4$)	atomic ratio
UO ₃	65.15	2277	1.09	62.60	2188	1.00
P ₂ O ₅	15.95	1123	1.08	15.22	1072	0.98
K ₂ O	—	—	—	10.15	1077	0.99
H ₂ O	19.15	—	—	12.00	—	—
Total	100.15			99.97		

Meta-ankoleite was obtained by refluxing synthetic chernikovite several times in a 1 M KCl solution until the pH remained at a constant value of 6.5. To obtain a more crystalline phase, the same procedure as mentioned for chernikovite was applied.

Chemical analysis

The air-dried synthetic specimens were dissolved in 6 M HCl. The K₂O content was determined by atomic absorption spectrometry (AAS) using a Philips PU-9200 spectrometer equipped with a potassium hollow cathode tube. The UO₃ was determined spectrophotometrically at 662.5 nm with Arsenazo III as the reagent (Singer and Matucha, 1962), using a Pye Unicam SP8-100 UV-vis spectrophotometer. The phosphorus content was determined spectrophotometrically by means of the vanadomolybdate reagent at 315.0 nm using the same instrument. The H₂O content was measured on separate solid samples by thermogravimetric analysis using a Dupont TGA 951 instrument. Table 1 summarizes the results of these

analyses. From the composition, expressed in terms of oxides, the minimum chemical formulae were calculated by the classical residual oxygen method as (H₃O)_{1.05}(UO₂)_{1.09}(PO₄)_{1.08}·2.75H₂O for chernikovite and as K_{0.99}(UO₂)_{1.00}(PO₄)_{0.98}·3.06H₂O for meta-ankoleite. The idealized formulae can therefore be written as (H₃O)(UO₂)(PO₄)·3H₂O for chernikovite and as K(UO₂)(PO₄)·3H₂O for meta-ankoleite. Scanning electron micrographs of synthetic chernikovite and meta-ankoleite are given in Fig. 1A and B respectively. The outline of both specimens is quadratic and shows a typical layer structure. The largest dimension of the crystals ranges from 0.2 to 0.3 mm.

X-ray crystallography

The X-ray diffraction data were recorded at 40 kV and 20 mA using Cu-K α_1 radiation ($\lambda = 1.54056 \text{ \AA}$). The diffraction patterns were recorded by means of a Guinier-Hägg camera, with a diameter of 100 mm. Silicon powder (NBS 640) was used as an internal standard. The positions and the relative intensities of

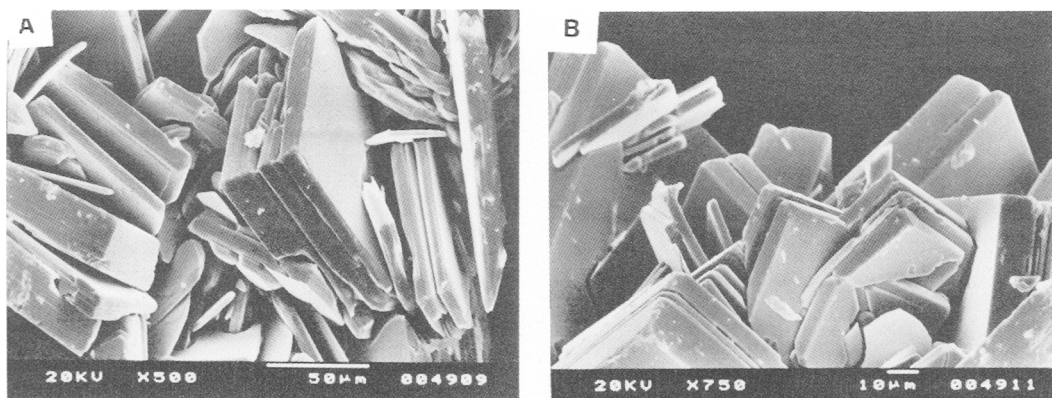


FIG. 1. SEM photographs of synthetic chernikovite (A) and meta-ankoleite (B).

TABLE 2. First 25 d_{hkl} -values of synthetic chernikovite and meta-ankoleite and those of their corresponding ICDD-cards

This study	Chernikovite		This study	Meta-ankoleite	
		ICDD card 8-296			ICDD card 29-1061
9.008		9.032	9.029		9.09
5.563		5.556	5.512		5.53
4.964		4.971	4.952		5.02
4.566		4.542	4.323		4.35
4.350		4.360	3.755		3.78
3.763		3.779	3.502		3.51
3.504		3.511	3.250		3.27
3.250		3.270	3.080		3.11
2.944		2.964	2.950		2.96
2.749		2.765	2.747		2.74
2.552		2.576	2.558		2.56
2.470		2.488	2.470		2.47
2.378		2.397	2.380		2.39
2.261		2.267	2.255		2.26
2.210		2.216	2.211		2.22
2.143		2.163	2.150		2.15
2.083		2.075	2.119		2.11
1.893		1.902	2.065		2.07
1.851		1.844	2.029		2.03
1.772		1.789	1.978		1.98
1.747		1.755	1.894		1.89
1.713		1.722	1.832		1.83
1.676		1.697	1.812		1.81
1.647		1.633	1.777		1.78
1.613		1.610	1.749		1.75

the diffraction lines were determined by scanning the film with a Carl Zeiss Jena MD 100 microdensitometer. The d_{hkl} -values of the 25 first lines of the X-ray patterns of synthetic chernikovite and meta-ankoleite are given in Table 2. As can be seen from this table, they show a very good agreement with the ICDD files 8-296 (chernikovite) and 29-1061 (meta-ankoleite) respectively.

Infrared spectroscopy

The infrared spectra of synthetic chernikovite and meta-ankoleite were recorded using an ATI MATTSON GENESIS FTIR spectrometer equipped with a SPECAC diffuse reflection unit, and covers the range from 4000 to 450 cm^{-1} . The spectra are represented in Fig. 2A and B respectively. The two spectra differ from each other by minor wavenumber shifts. Table 3 lists the absorption bands together with their assignment. In agreement with Čejka *et al.* (1985), the UO_2^{2+} -bands are found near 920 cm^{-1} (ν_3) and 820 cm^{-1} (ν_1), whereas the PO_4^{3-} -bands are

found near 1110 and 1000 cm^{-1} (ν_3) and at 545 cm^{-1} (ν_4). The bands between 3500–3000 cm^{-1} , 1650–1750 cm^{-1} and 600–700 cm^{-1} can be attributed to the stretching, bending and libration modes of H_2O and H_3O^+ . The bands between 1990 and 2350 cm^{-1} can be considered as overtones and/or combination bands.

Luminescence spectra

The fluorescence spectra were recorded by means of a Perkin-Elmer MPS44B spectrofluorimeter at 298 K, with an excitation wavelength of 380 nm. Both synthetic specimens fluoresce strongly yellow-green, under both short and long wavelength ultraviolet radiation.

The spectra of chernikovite and meta-ankoleite are similar and are represented in Fig. 3A and B respectively. Both synthetic specimens are characterized by five fluorescence peaks at 505, 526, 550, 575 and 615 nm. The spectrum of meta-ankoleite, however, has a lower fluorescence intensity. Based

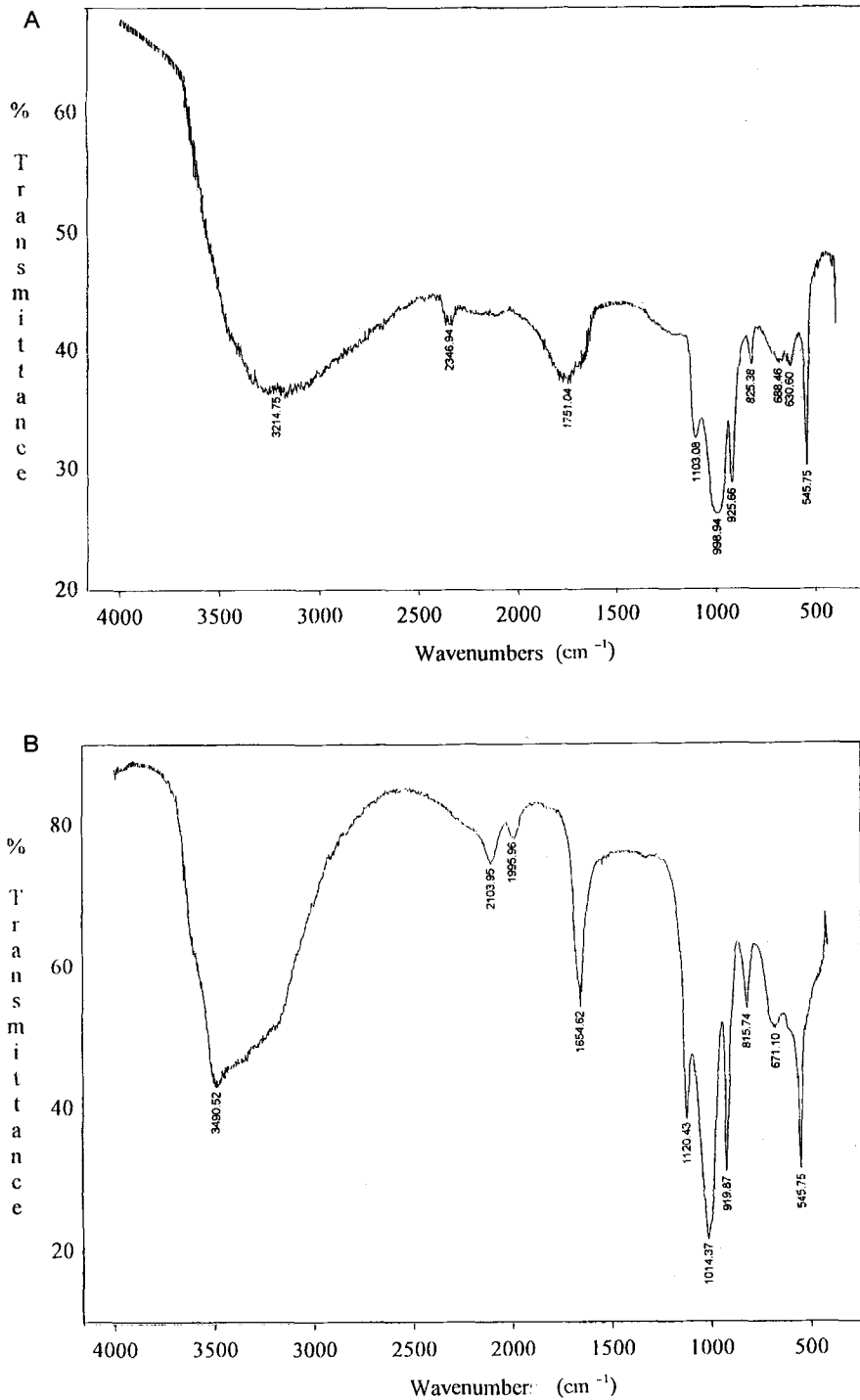


FIG. 2. FTIR spectra of synthetic chernikovite (A) and meta-ankoleite (B).

TABLE 3. IR absorption bands (in cm^{-1}) of synthetic chernikovite and meta-ankoleite

Chernikovite	Meta-ankoleite	Assignment
3500–3000 (s,b)	3500-3000 (s,b)	ν_{OH}
2346 (w)	2103 (w)	
	1995 (w)	
1751 (s)	1654 (s)	δ_{OH}
103 (m)	1120 (m)	
998 (s)	1014 (vs)	$\nu_3\text{PO}_4$
925 (s)	920 (vs)	
825 (w)	816 (m)	$\nu_3\text{UO}_2$
688 (w)	671 (w)	$\nu_1\text{UO}_2$
630 (w)		H_2O librations
545 (vs)	545 (vs)	
		$\nu_4\text{PO}_4$

s = strong, m = medium, w = weak, v = very, b = broad.

on the relation $E = hc/\lambda$ ($hc = 1.9863 \cdot 10^{23} \text{ Jm}$; $1 \text{ eV} = 1.6021 \cdot 10^{19} \text{ J}$), E can be expressed in eV as $1.24 \times 10^{-6}/\lambda$. Using this relation, the band-gap energy E_g between the conduction and valence band was calculated for both synthetic species at the most intensive peak (526 nm) at 298 K, and a value of 2.35 eV was obtained. This value indicates that chernikovite and meta-ankoleite must be considered as species with well-pronounced insulator properties.

Solubility

The solubility of both synthetic chernikovite and meta-ankoleite was investigated as a function of the pH. Therefore, 100 mg of the product was placed in 50 ml of distilled water. The pH was adjusted to the desired value by means of HClO_4 . The closed vessel was shaken under a N_2 atmosphere at 25°C . The total U content in the solution was determined spectrophotometrically every 5 days using Arsenazo III as the reagent (Singer and Matucha, 1962). After 30 days, equilibrium was reached. The solubilities of both compounds, expressed in mol./l, are given in Table 4.

From Table 4 we can conclude that chernikovite has a relatively high solubility at low pH values. The solubility rapidly decreases with increasing pH. Above $\text{pH} = 1.5$, the solubility is lower than the detection limit for uranium. Similar behaviour is observed for meta-ankoleite. However, solutions with a pH-value below 2.5 show the presence of a precipitate other than chernikovite. Chemical analysis and X-ray diffraction identify this compound as $(\text{UO}_2)_3(\text{PO}_4)_2$. The solubility of the solutions above $\text{pH} = 5.50$ is also below the uranium detection limit.

In an aqueous solution, chernikovite and meta-ankoleite dissociate into their ions according to the following schemes:

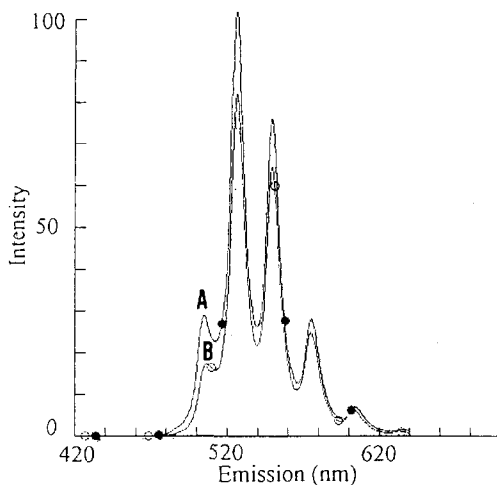
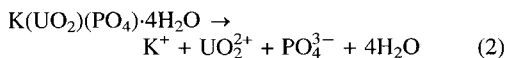
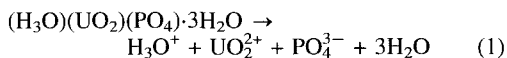
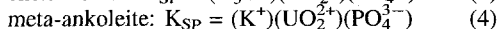
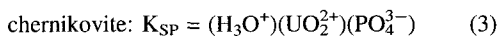


Fig. 3. Fluorescence spectra of synthetic chernikovite (A) and meta-ankoleite (B).



With these dissociations, the following solubility products can be associated:



The K^+ ion concentrations can be derived directly from the measured solubility data. The concentrations of the H_3O^+ ions can be calculated from the pH value. The actual concentrations of (UO_2^{2+}) and (PO_4^{3-}) , however, cannot be derived directly from the solubility data. The reason for this is the large number of equilibrium reactions in which these ions are involved, in solution. One of this series is the well-known dissociation equilibrium of H_3PO_4 (Smith and Martell, 1989)



At the time of dissolution, chernikovite and meta-ankoleite introduce tertiary phosphate ions in solution. Due to the relative acidity of the solutions, the majority of the phosphate species will be transformed into H_3PO_4 and/or H_2PO_4^- .

The uranyl ions behave in a similar way by forming uranyl-hydroxo complexes according to the following scheme (Djogic *et al.*, 1986):

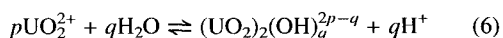


TABLE 4. Solubility, dominant species and solubility product of synthetic chernikovite and meta-ankoleite for different pH-values

pH	Solubility	$[\text{UO}_2^{2+}]$	$[(\text{UO}_2)(\text{OH})^+]$	$[(\text{UO}_2)(\text{OH})_2]$	$[(\text{UO}_2)_2(\text{OH})_2^{2+}]$	$[(\text{UO}_2)(\text{H}_2\text{PO}_4)^+]$	$[(\text{UO}_2)(\text{H}_2\text{PO}_4)_2]$	pK _{sp}
chernikovite:								
0.98	$1.22 \cdot 10^{-2}$	$6.40 \cdot 10^{-3}$	$6.12 \cdot 10^{-7}$	$3.69 \cdot 10^{-12}$	$4.11 \cdot 10^{-9}$	$5.29 \cdot 10^{-3}$	$4.90 \cdot 10^{-4}$	22.46
1.12	$6.30 \cdot 10^{-3}$	$3.72 \cdot 10^{-3}$	$4.91 \cdot 10^{-7}$	$4.09 \cdot 10^{-12}$	$2.65 \cdot 10^{-9}$	$2.40 \cdot 10^{-3}$	$1.74 \cdot 10^{-4}$	22.81
1.38	$3.21 \cdot 10^{-3}$	$2.02 \cdot 10^{-3}$	$4.85 \cdot 10^{-7}$	$7.34 \cdot 10^{-12}$	$2.58 \cdot 10^{-9}$	$1.11 \cdot 10^{-3}$	$6.87 \cdot 10^{-5}$	22.91
meta-ankoleite:								
2.60	$2.26 \cdot 10^{-4}$	$1.95 \cdot 10^{-4}$	$7.78 \cdot 10^{-7}$	$1.95 \cdot 10^{-10}$	$6.64 \cdot 10^{-9}$	$2.96 \cdot 10^{-5}$	$5.02 \cdot 10^{-7}$	23.20
4.13	$4.70 \cdot 10^{-6}$	$4.12 \cdot 10^{-6}$	$5.57 \cdot 10^{-7}$	$4.74 \cdot 10^{-9}$	$3.40 \cdot 10^{-9}$	$1.67 \cdot 10^{-8}$	$7.58 \cdot 10^{-12}$	25.07
4.90	$2.26 \cdot 10^{-6}$	$1.22 \cdot 10^{-6}$	$9.72 \cdot 10^{-7}$	$4.87 \cdot 10^{-8}$	$1.04 \cdot 10^{-8}$	$2.32 \cdot 10^{-9}$	$4.93 \cdot 10^{-13}$	24.71
5.24	$2.15 \cdot 10^{-6}$	$7.81 \cdot 10^{-7}$	$1.35 \cdot 10^{-6}$	$1.49 \cdot 10^{-7}$	$2.03 \cdot 10^{-8}$	$1.48 \cdot 10^{-9}$	$3.12 \cdot 10^{-13}$	24.21

Solubility and species concentration expressed in mol/l.

With these reactions, complex formation constants β_{pq} can be associated and are defined as:

$$\beta_{pq} = \frac{[(\text{UO}_2)_2(\text{OH})_q^{2p-q}][\text{H}^+]}{[\text{UO}_2^{2+}]^p} \quad (7)$$

Several uranyl-hydroxo complexes are known. Djogic *et al.* (1986) list 11 of these complexes with their formation constant. Because of the dependence of the formation reactions on the pH, it is clear that the relative contributions of the different uranyl-hydroxo complexes to the total uranyl concentration vary considerably with the pH and the total uranyl concentration (Van Haverbeke and Vochten, 1992).

Besides the differentiation of the uranyl and phosphate species caused by the acidity of the solution, there exist several complexes that are formed between UO_2^{2+} and one or more of the phosphate species. According to Mathur (1991), the only significant species that we may expect to be present are $(\text{UO}_2)(\text{H}_2\text{PO}_4)^+$ and $(\text{UO}_2)(\text{H}_2\text{PO}_4)_2$. The formation constants of these complexes are defined as:

$$\beta_{\text{UP1}} = \frac{[(\text{UO}_2)(\text{H}_2\text{PO}_4)^+]}{[\text{UO}_2^{2+}][\text{H}_2\text{PO}_4^-]} \text{ and } \beta_{\text{UP2}} = \frac{[(\text{UO}_2)(\text{H}_2\text{PO}_4)_2]}{[\text{UO}_2^{2+}][\text{H}_2\text{PO}_4^-]} \quad (8)$$

and their values are given by Baes (1956).

Using these equilibria and their formation constants, the UO_2^{2+} and PO_4^{3-} concentrations could be calculated as easily as the concentrations of all the different species involved. Table 4 lists the concentrations of these species that are present in non-negligible concentrations. It is clear that the free uranyl species is always the dominant uranyl species present in very acidic solutions. When going towards less acidic solutions, however, the uranyl-hydroxo species $(\text{UO}_2)(\text{OH})^+$, $(\text{UO}_2)(\text{OH})_2$ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$, become more and more important. A similar trend is observed for the uranyl-phosphate complexes. In particular, the concentration of the uranyl-monophosphate complex increases very spectacularly when the solution becomes strongly acidic. In solutions with a very high acidity, the concentration of this species even approaches the concentration of the free uranyl ion.

Table 4 also contains the values of the solubility products for chernikovite and meta-ankoleite, calculated starting from the concentrations obtained for each individual solution. No attempt was made to correct the concentrations used for the ionic strength of the solution. The reason for this is the relatively high ionic strength of some of these solutions. In these high ionic media, the relations that calculate the activity coefficient are not very accurate. Moreover, extrapolation of the solubility constant to zero ionic strength cannot be done accurately, because measurements in solutions of low ionic strength are lacking. We did, however, determine an average solubility product:

chernikovite: $\text{p}K_{\text{sp}} = 22.73 \pm 0.24$; meta-ankoleite: $\text{p}K_{\text{sp}} = 24.30 \pm 0.81$

It appears that the solubility products of the two compounds are very close to one another. The difference in solubility can be explained by the fact that the K^+ concentration is determined by the solubility itself, whereas the H^+ concentration is imposed by the acidity of the solution and may differ from the K^+ by 1 or more orders of magnitude.

Acknowledgements

The authors are indebted to the Belgian National Fund for Scientific Research, for financial support of this study. They also thank Mr J. Eysermans of the Institute of Electron Microscopy for Material Research (EMAT, RUCA) for taking the SEM photographs.

References

- Atencio, D. (1988) Chernikovite, a new mineral name for $(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ superseding 'hydrogen autunite'. *Mineral. Rec.*, **19**, 249–52.
- Baes, C. F. Jr. (1956) A spectrophotometric investigation of uranyl phosphate complex formation in perchloric acid solution. *J. Phys. Chem.*, **60**, 878–83.
- Camargo, W.G.R. (1971) Minerais uraníferos de Perus. *SP. Bol. Inst. Geociências e Astronomia da Univ. São Paulo*, **2**, 83–201.
- Čejka, J. Jr., Muck, A. and Čejka, J. (1985) Infrared spectra and thermal analysis of synthetic uranium minerals and their deuteroanalogues. *Neues Jahrb. Mineral., Mh.* **1985**, 115–26.
- Chernikov, A.A. (1958) New data on some uranium and uranium-bearing minerals. *Proceedings of the 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy*, **2**, 298–9.
- Djogic, R., Sipos, L. and Branica, M. (1986) Characterization of uranium (VI) in seawater. *Limnol. Oceanogr.*, **31**, 1122–31.
- Frondel, C. (1950) Studies of uranium minerals (V): Phosphuranylite. *Amer. Mineral.*, **35**, 756–63.
- Gallagher, M.J. and Atkin, D. (1966) V -Meta-ankoleite, hydrated potassium uranyl phosphate. *Bull. Geol. Surv. Gt. Brit.*, **25**, 49–54.
- Kashirtseva, M.F. and Valueva, A.A. (1979) On some properties of hydrogen autunite. *Novye Dannye o Mineralakh, SSSR*, **28**, 178–82.
- Mathur, J.N. (1991) Complexation and thermodynamics of the uranyl ion with phosphate. *Polyhedron*, **10**, 47–53.
- Moeller, T. (1957) In *Inorganic Syntheses*, vol.V. McGraw-Hill, New York, 150–2.
- Mrose, M.E. (1953) Studies of uranium minerals (XIII): Synthetic uranospinites. *Amer. Mineral.*, **38**, 1159–68.

- Ross, M. and Evans, H.T., Jr. (1964) Studies of the torbernite minerals (I): The crystal structure of abernathyite and the structurally related compounds $(\text{NH}_4)(\text{UO}_2\text{AsO}_4) \cdot 3\text{H}_2\text{O}$ and $\text{K}(\text{H}_3\text{O})(\text{UO}_2\text{AsO}_4) \cdot 6\text{H}_2\text{O}$. *Amer. Mineral.*, **49**, 1578–602.
- Ross, V. (1955) Studies of uranium minerals (XXI): Synthetic hydrogen-autunite. *Amer. Mineral.*, **40**, 917–9.
- Singer, E. and Matucha, M. (1962) Erfahrungen mit der Bestimmung von Uran in Erzen und Gesteinen mit Arsenazo III. *Z. Anal. Chem.*, **191**, 248–53.
- Smith, R.M. and Martell, A.E. (1989) *Critical stability constants*. Plenum Press, New York.
- Van Haverbeke, L. and Vochten, R. (1992) A computer program for the calculation and visualisation of the contribution of uranyl-hydroxo complexes. *Proc. 29th Int. Geol. Cong.*, Kyoto, Japan, 957.
- Vochten, R. (1990) Transformation of chernikovite and sodium autunite into lehnerite. *Amer. Mineral.*, **75**, 221–5.
- Vochten, R. and Van Haverbeke, L. (1990) Transformation of schoepite into the Uranyl oxide hydrates: becquerelite, billietite and wolsendorfite. *Mineral. Petrol.*, **43**, 65–72.
- Vochten, R., Piret, P. and Goeminne, A. (1981) Synthesis, crystallographic data, solubility and electrokinetic properties of copper, nickel and cobalt uranylphosphate. *Bull. Mineral.*, **104**, 457–67.
- Vochten, R., Van Haverbeke L. and Van Springel, K. (1990) Transformation of Chernikovite into Parsonsite and study of its solubility product. *Neues. Jahrb. Mineral., Mh.*, 551–8.
- Vochten, R., Van Haverbeke, L. and Van Springel, K. (1992) Transformation of Chernikovite into meta-uranocircite II, $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ and study of its solubility. *Mineral. Mag.*, **56**, 367–72.
- Vochten, R., Van Haverbeke, L. and Van Springel, K. (1993) Synthesis of liebigite and andersonite and their solubility in aqueous medium. *Can. Mineral.*, **31**, 167–71.
- Vochten, R., Van Haverbeke, L., Van Springel, K., Blaton, N. and Peeters, O.M. (1995) The structure and physicochemical characteristics of synthetic zippeite. *Can. Mineral.*, **33**, 1091–101.

[Manuscript received 20 October 1995;
revised 18 January 1996]