New mineralogical data on uranophane and β-uranophane; synthesis of uranophane

FABIEN CESBRON

LEMI-ESEM, Université d'Orléans, B.P. 6747, 45069 Orléans Cedex 2−LPCE-CNRS, Orléans, France

PHILIPPE ILDEFONSE AND MARIE-CLAUDE SICHERE

Laboratoire de Minéralogie-Cristallographie, associé au CNRS, Université P. et M. Curie, Tour 16, 4 place Jussieu, 75252 Paris Cédex 05, France

Abstract

Uranyl-silicates are widespread minerals in oxidised parts of various uranium deposits, and they frequently contain associations of the polymorphic forms of uranophane. In several recent works devoted to the study of uranium deposits as natural analogues of high-level nuclear waste repository (HLNWR), uranophane is frequently mentioned but without determination of the exact polymorphic species. The existence of two polymorphs presenting different stabilities has to be taken into account when considering the long-term behaviour of these minerals and the use of thermodynamic models for predicting the radionuclide migration in HLNWR. We present here new crystallographic data on beta-uranophane, and preliminary results of synthesis experiments of uranyl silicates. XRD patterns and calculated parameters of beta-uranophane from a Mexican U-deposit are presented. Synthesis experiments succeeded in crystallising uranophane (alpha form) at different pH, Si-, Ca- and Na activities, but beta-uranophane was never obtained. The controlling physico-chemical parameters responsible for the occurrence of these two polymorphic forms are still unknown.

KEYWORDS: uranophane, β-uranophane, synthesis, Mexico.

Introduction

URANOPHANE* $Ca(UO_2)_2(SiO_3OH)_2.5H_2O$ is a monoclinic uranyl silicate fairly common in the oxide zone of most uranium deposits; it was originally described by Websky in 1853. Its beta polymorph, also monoclinic, is much more rare: it was observed for the first time at Jachymov, Bohemia, by Novacek (1935), and was later found in several deposits; the best crystals probably come from Rössing (Namibia) and from the French Massif Central: Bigay (Puy-de-Dome) and Margnac (Haute-Vienne).

Recently, the study of uranium deposits has undergone a renewal of interest (Chapman and McKinley, 1987) because some of these deposits may be used as natural analogues of high-level nuclear waste repositories (HLNWR). In these

* The nomenclature recommended by the Commission on New Minerals and Mineral Names of the International Mineralogical Association will be followed in this paper: the word 'uranophane' will always refer to the alpha form only.

studies, assessments of radionuclide migration is obtained by studying the various generations of uranium-bearing minerals (Ildefonse et al., 1989, 1990). Among them, uranyl silicates are frequently described in oxidised parts of ore bodies. Some authors use the word uranophane to describe the Ca-U-silicate without determination of the polymorphic species; however, the very existence of these two minerals is of great interest when making predictions on the solubilities and speciation of radionuclides under repository conditions. Reliable thermodynamic data are needed for solid phases and respective solubilities of uranophane and beta-uranophane are not accurately known.

Recently, we found beautiful and sometimes abundant crystals in the alteration products of uranium-bearing volcanic tuffs from the Sierra Peña Blanca, Chihuahua, Mexico, and particularly in the Nopal I deposit. This enabled us to resume their crystallographical study and to undertake the synthesis of the two polymorphic forms.

(A)

(B)

GEOLOGICAL SECTION NE 52° SW

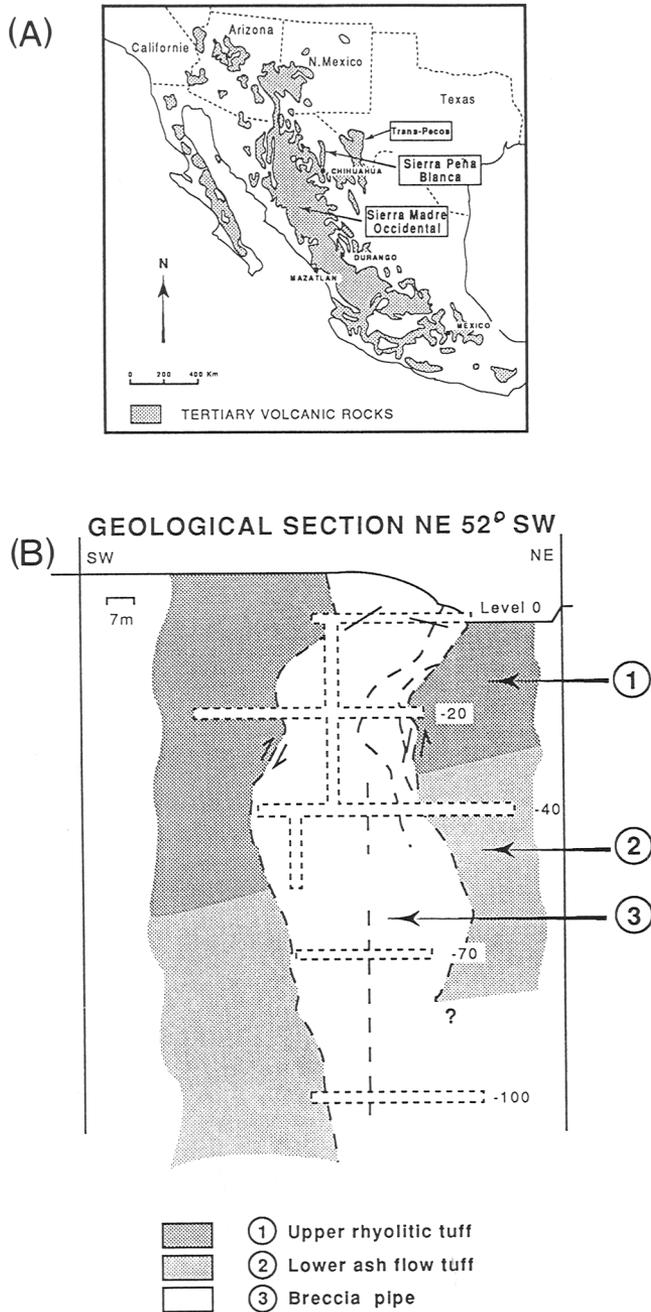| | (1) Upper rhyolitic tuff |
| (2) Lower ash flow tuff |
| (3) Breccia pipe |

FIG. 1. (*a*) Map of Tertiary volcanic rocks in the south part of North America (from Bagby *et al.*, 1976); (*b*) geological vertical section of the breccia pipe of the Nopal I uranium deposit (from Reyes *et al.*, 1980).

Geological setting

In the Chihuahua State of Mexico, more than a hundred radiometric anomalies have been detected in Tertiary volcanic rocks of the Sierra Peña Blanca (Fig. 1*a*), located north-east of Chihuahua City (Uramex, 1980). This Sierra

		UPPER RHYOLITIC TUFF	BRECCIA PIPE	ARGILIZED LOWER TUFF
CLAYEY MINERALS	SMECTITE	– – – – – – – – – –		—————
	KAOLINITE	—————————————		– – – –
	HALLOYSITE		—————	
	HEMATITE	– – – – – – – – – – – – –	—————	– – – – – –
U - BEARING MINERALS	β–URANOPHANE		—————————————	
	α–URANOPHANE		– – – – – – – – – – – – – – –	
	WEEKSITE		—————	
	BOLTWOODITE		—————	
	CARNOTITE		– – – – – –	

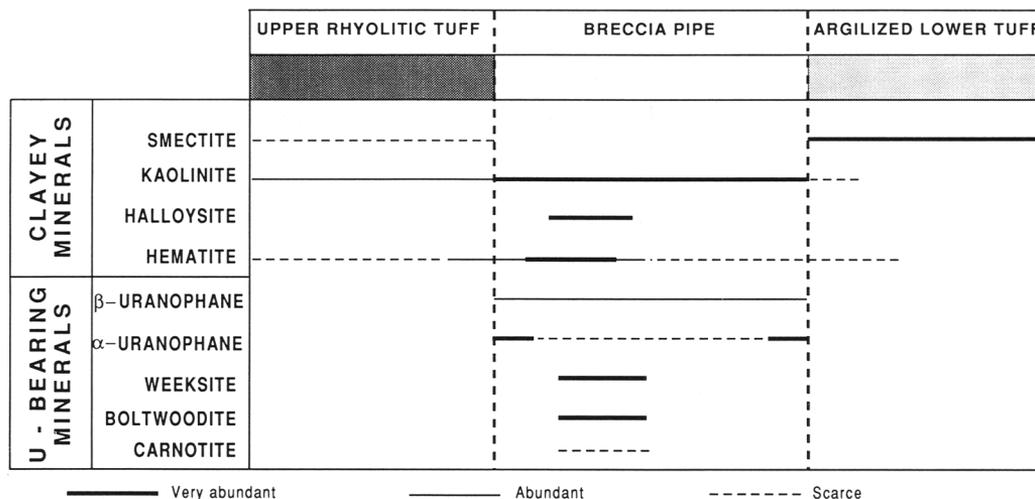————— Very abundant   ————— Abundant   – – – – – – Scarce

FIG. 2. Nature, location and relative abundance of the main secondary minerals in the Nopal I deposit.

consists of a gently dipping Tertiary volcanic pile which covers a calcareous basement of Cretaceous age (Calas, 1977; Goodell, 1981). The studied uranium-deposit (Nopal I) is hosted by the two members of the Nopal formation (upper welded rhyolitic tuffs and lower weakly welded ignimbritic tuffs) dated at 44 Ma by Alba and Chavez (1974). In the Nopal-I deposit, the ignimbritic tuffs have been highly altered under hydrothermal conditions (Calas,1977; Aniel and Leroy, 1985; Ildefonse et al., 1990). Uranium mineralisation is strictly located within a breccia pipe structure (100 m high, 20 × 40 m wide) at the intersection of several faults (Reyes et al., 1980) which bring into contact the upper rhyolitic tuff and the lower argilised tuff (Fig. 1b).

In the Nopal-I deposit, a reduced U^{4+}-mineralisation has been described by Calas (1977) and Aniel and Leroy (1985). Just now, the major part of the deposit consists of an oxidised U^{6+}-ore, the reduced mineralisation being limited to some dense and massive black decimetric cores made of uraninite associated with pyrite (Ildefonse et al., 1989). This mineral assemblage shows that uranium has been early acccumulated in a reducing environment. Around the uraninite cores, the yellow oxidised mineralisation is composed of soddyite, an uranyl silicate associated with uranophane, and minor quantities of hydrated oxides belonging to the becquerellite group.

In the numerous fracture fillings inside the breccia pipe, uranium-bearing minerals are uranyl silicates which are subsequent to kaolinite which they recover. The distribution of these silicates is ordered both in space and time

(Ildefonse et al., 1988):

—in space: potassic uranyl silicates (weeksite, boltwoodite) and minor potassic uranyl vanadates (carnotite) in the centre of the pipe, while calcic uranyl silicates (uranophane) are located at its periphery (Fig. 2);

—in time: the previous phases can be recovered by beta-uranophane crystallisations. This later can in turn be covered by ultimate precipitates of uncolored or greenish-yellow opal which mimics the prismatic crystals of beta-uranophane (Fig. 3a).

Crystallographic properties

Crystals of beta-uranophane (Fig. 3b) from Nopal can reach 2–3 mm in size; they are prismatic along [100] and slightly flattened on {001} contrary to Rössing and Margnac crystals which are usually flattened on the perfect cleavage {010}. The (001) face is finely striated in a parallel direction to this cleavage, as also (100) which is usually well developed; (201) always seems to be missing. Very frequently, the crystals are more or less leached with a fibrous structure appearing on {010} and the prisms are not terminated (Fig. 3c). Fig. 4a represents a typical Nopal crystal, compared to Rössing (Fig. 4b) and Margnac (Fig. 4c) crystals.

Unit-cell parameters were calculated, using a least-squares unit-cell refinement program, from an X-ray powder diagram obtained with a Guinier-de Wolff camera using Cu-$K\alpha_1$ radiation and quartz as an internal standard. They are com-
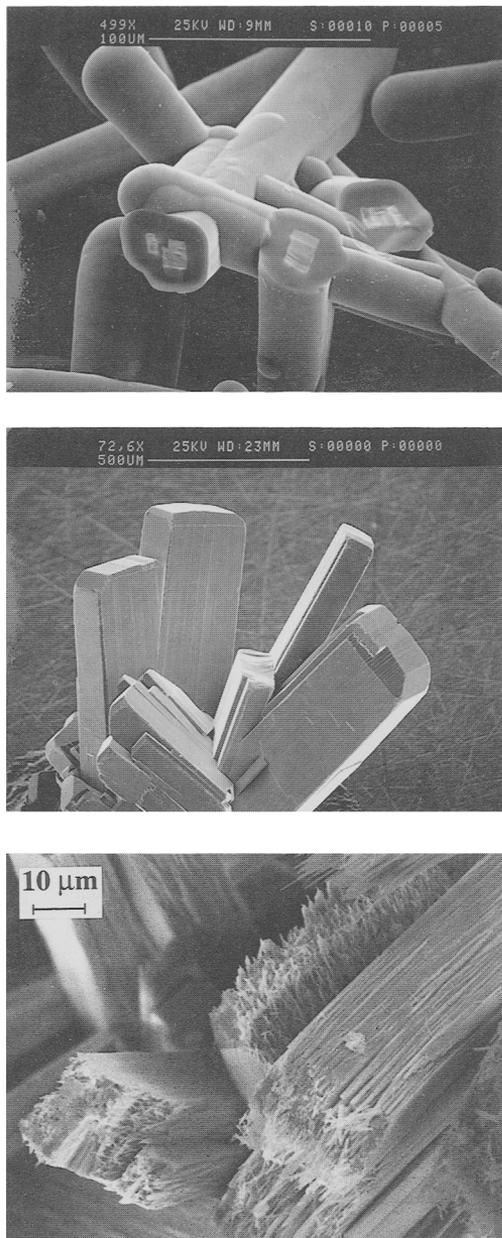
by a similar method, are also given. We do not think necessary to give the powder diagram of uranophane as our data differ only very slightly from those recently published in the JCPDS 39-1360 file.

The powder pattern of beta-uranophane, with many additional reflections, is given in Table 2 and compared with the one from JCPDS 8-301 file (indices *h* and *l* were permuted in order to comply with the crystallographic orientation of Stohl and Smith, 1981). Intensities were visually estimated and differ in magnitude from those obtained with an X-ray diffractometer, where reflections of different orders on $\{010\}$ are strongly prominent.

It must be emphasised that the powder patterns of the two polymorphic species present some lines in common, owing to the fact that both minerals are monoclinic and have quite similar parameters, with the exception of the beta-uranophane *b* parameter (15.488 Å) which is more than twice as long as that of uranophane ($7.027 \times 2 = 14.054$ Å). Both diagrams however are easily distinguishable when using these new data.

Synthesis of beta-uranophane

Some fifty hydrothermal syntheses were performed at 150 °C in steel autoclaves with a Teflon internal lining, in order to obtain the uranyl silicates found at Nopal I and to understand their conditions of formation. Only weeksite $K_2(UO_2)_2Si_6O_{15}.4H_2O$, sodium-boltwoodite $(H_3O)Na(UO_2)SiO_4.H_2O$ and its K- and (NH_4)-equivalents, and uranophane were obtained. Beta-uranophane could never be synthesised, even for various pH and for temperatures as low as 60 °C.

Uranophane was obtained using aqueous solutions of uranyl acetate, calcium acetate and sodium metasilicate as starting materials. Tetra-ethyl-orthosilicate $Si(OC_2H_5)_4$ was also tested but did not give good results; uranophane was sometimes produced, but always badly crystallised. The pH was adjusted using NH_4OH and HCl, its value ranging from 1.5 to 13; it was measured at the autoclave opening, when the equilibrium between liquid and precipitate was achieved.

With an atomic Ca : U : Si ratio equal to 2 : 1 : 1, uranophane was synthesied for pH values ranging from 9.5 to 3.5; X-ray diffraction lines were quite broad for values of pH between 9.5 and 6, but good crystallinity was obtained at pH lower than 5. At a pH of 5, uranophane was also precipitated for atomic U/Si ratios ranging from 1/1 to 1/6; yet crystallinity was not very good for high silica concentrations.

Finally the influence of sodium concentration

FIG. 3 (*a, top*) Opal covering prismatic crystals of beta-uranophane; (*b, centre*) euhedral prismatic crystals of beta-uranophane from Nopal 1; (*c, bottom*) beta-uranophane crystal presenting etching features along [010].

pared in Table 1 with those given by Stohl and Smith (1981) and Smith and Stohl (1972). Unit-cell parameters of Nopal uranophane, obtained
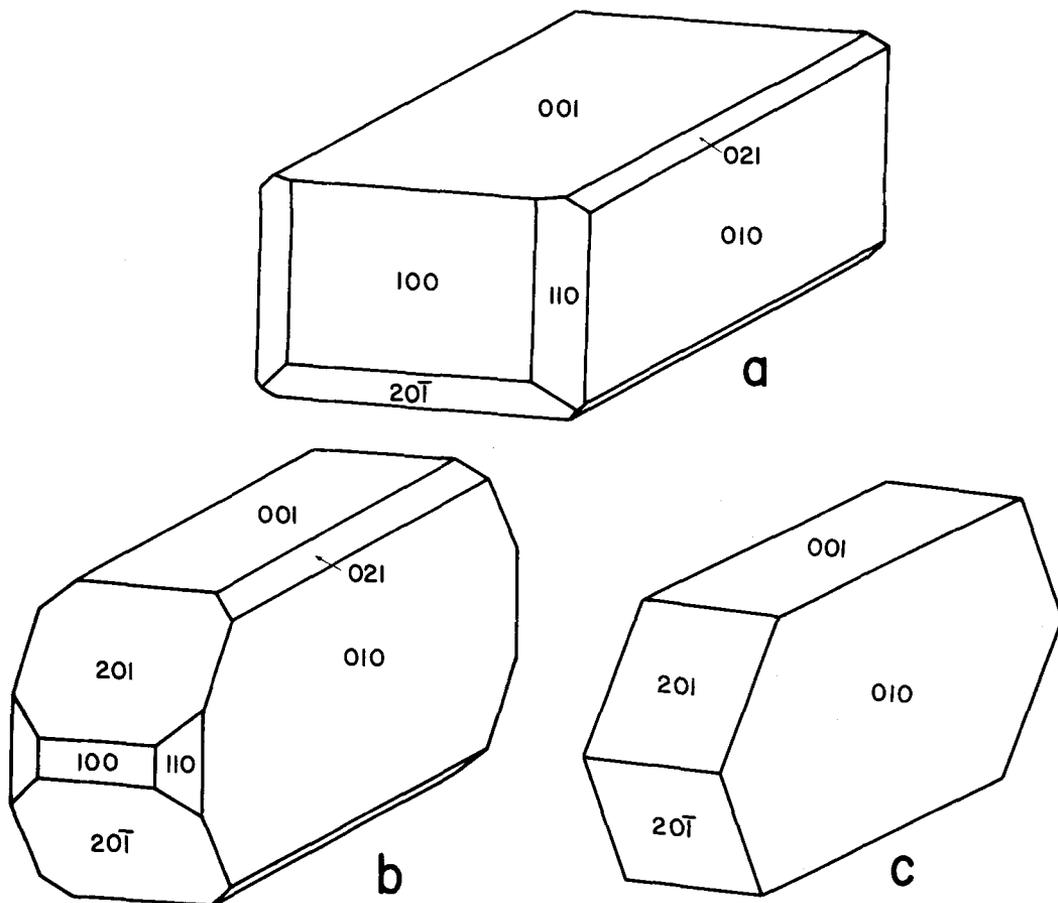
FIG. 4. Idealised crystal drawings of beta-uranophane from: (*a*) Nopal I (Mexico); (*b*) Rössing (Namibia); (*c*) Margnac (France).

was also investigated. At a pH value of 5 and with U:Si = 1:1, uranophane was obtained for Ca:Na:U ratios ranging from 0.5:2:1 to 4:2:1, boltwoodite can be synthesised only if calcium is virtually absent.

Recently, Nguyen *et al.* (1991) prepared two

TABLE 1. Refined unit-cell parameters for beta-uranophane and uranophane.

	1	2	3	4
a =	13.964 (8)	13.898 (11)	15.927 (10)	15.858 (15)
b =	15.488 (10)	15.394 (14)	7.027 (6)	6.985 (7)
c =	6.628 (4)	6.609 (5)	6.625 (4)	6.641 (5)
ß =	91.40° (3)	91.42° (2)	97.52° (4)	97.55° (2)
space group		$P2_1/a$		$P2_1$

1 - beta-uranophane, Nopal I; present study.
2 - beta-uranophane; Smith and Stohl (1972).
3 - uranophane, Nopal I; present study.
4 - uranophane; Stohl and Smith (1981).

TABLE 2. X-ray powder diffraction data for natural beta-uranophane (Nopal I).

	present study			JCPDS n° 8-301	
I/I_o	$d_{obs.}$	$d_{calc.}$	hkl	$d_{obs.}$	hkl
1	10.38	10.37	110		
10	7.75	7.74	020	7.83	020
2	6.64	6.63	001	6.66	001
3	6.10	6.09	011	6.15	011
<1	5.65	5.63	$\overline{1}11$		
<1	5.55	5.54	111		
3	5.05	5.03	$0\overline{2}1$	5.07	$\overline{0}21$
3	4.876	4.865	$\overline{2}01$	4.85	$\overline{2}01$
1	4.756	4.764	$\overline{1}21$		
2	4.650	4.642	$\overline{2}11$		
5	4.546	4.539	211	4.55	211
2	4.128	4.120	221		
1	4.074	4.072	031	4.11	031
1	4.050	4.048	$\overline{2}21$		
<1	3.988	3.989	320		
4	3.870	3.872	040	3.90	$\overline{0}40$
<1	3.728	3.731	$\overline{1}40$	3.75	$\overline{3}11$
<1	3.543	3.541	$\overline{2}31$		
7	3.489	3.490	400	3.51	400
3	3.405	3.405	410	3.41	321
2	3.343	3.343	041	3.35	041
<1	3.315	3.313	002		
1	3.241	3.242	141		
		3.240	012		
6	3.182	3.182	420	3.19	$\overline{1}12$
<1	3.142	3.139	112		
<1	3.119	3.119	$\overline{4}01$		
3	3.057	3.058	$\overline{4}11$	3.04	$\overline{2}41$
		3.057	401		
5	3.023	3.024	150		
		3.022	$\overline{2}02$		
4	2.965	2.966	$\overline{2}12$		
		2.965	202	2.99	202
2	2.913	2.912	212	2.91	212
1	2.890	2.891	430		
1	2.841	2.844	421		
4	2.815	2.815	$\overline{2}22$	2.83	$\overline{2}22$
3	2.768	2.769	222	2.78	222
<1	2.744	2.746	151		
		2.745	$\overline{1}32$		
<1	2.667	2.670	$\overline{4}31$		
<1	2.627	2.630	312		
		2.626	520		
2	2.590	2.592	440		
1	2.577	2.580	350		
		2.575	$\overline{3}22$	2.59	$\overline{3}22$
1	2.569	2.571	232		232
<1	2.513	2.517	511		
<1	2.427	2.429	441		
<1	2.398	2.399	441	2.41	
1	2.380	2.382	242		

TABLE 2–continued

2	2.352	2.354	$\bar{2}42$	2.36
<1	2.314	2.317	450	
<1	2.278	2.280	261	2.29
2	2.210	2.212	601	2.21
3	2.185	2.187	013	2.20
		2.185	170	
2	2.154	2.157	432	2.17
		2.156	541	
		2.152	113	
2	2.125	2.127	621	2.13
		2.124	023	
<1	2.099	2.101	$\bar{2}13$	2.11
		2.099	071	
		2.097	621	
1	2.089	2.091	203	
		2.090	512	
1	2.071	2.072	213	2.08
2	2.043	2.045	223	2.04
2	2.029	2.031	033	
2	2.017	2.019	223	
		2.016	133	
2	2.004	2.003	133	2.01
<1	1.969	1.972	461	1.98
		1.969	$\bar{5}51$	
1	1.960	1.962	$\bar{2}33$	
		1.961	313	
<1	1.945	1.947	262	
<1	1.931	1.931	720	
2	1.925	1.926	$\bar{6}02$	1.93
1	1.917	1.918	043	
		1.918	180	
1	1.909	1.911	$\bar{6}12$	
		1.908	$\bar{7}11$	
		1.908	371	
<1	1.885	1.887	$\bar{5}42$	
		1.884	452	
1	1.879	1.882	602	1.877
		1.877	$\bar{3}33$	
3	1.866	1.866	$\bar{7}21$	
		1.866	280	
1	1.837	1.840	243	1.841
		1.840	072	
2	1.831	1.833	413	
		1.830	$\bar{5}61$	
1	1.826	1.827	$\bar{1}72$	
<1	1.802	1.802	$\bar{7}31$	1.807
1	1.795	1.796	423	
1	1.777	1.779	$\bar{1}53$	1.778
<1	1.770	1.770	$\bar{4}62$	
1	1.766	1.768	632	
<1	1.741	1.742	$\bar{5}13$	
<1	1.736	1.738	433	
2	1.731	1.730	$\bar{3}81$	1.734
		1.728	660	
1	1.722	1.722	381	
		1.722	$\bar{7}41$	
1	1.700	1.702	$\bar{8}20$	1.701

batches of synthetic uranophane using the same starting chemicals but by a slightly different method: the precipitates obtained at 90 °C and pH 8 were washed, dried, transferred into a Teflon-lined Parr bomb and reacted at 118 °C with water in order to improve the crystallinity. Beta-uranophane was not obtained.

Discussion and conclusion

Uranophane and beta-uranophane are two Ca-uranyl silicates which have distinctly different crystallographic data and stabilities. Differences in stability are demonstrated by our synthesis experiments. We never succeeded in preparing beta-uranophane, while uranophane crystallisation was controlled by the following active parameters:

—acid pH < 5 is most efficient in obtaining good crystallinity;

—the U : S ratio is not an intense parameter because uranophane crystallised for U : Si ranging from 1 : 1 to 1 : 6. Besides, for the highest Si-activity, crystallinity decreases.

—uranophane may crystallise for a range of Ca : Na ratios in solutions from 0.5 : 2 to 4 : 2; at low Ca-activity, boltwoodite is the stable phase. The activity of Ca and Na thus governs the respective stability of Ca- and Na-uranyl silicates.

Further work is necessary to understand the reason why beta-uranophane has not been synthesised in these experiments. It is a major problem to measure the stability field of this phase because in the Nopal I deposit, it represents the ultimate U-bearing mineral which trapped uranyl ions. The long-term stability of this mineral phase is thus an important parameter to be determined in order to assess the availability of this phase as a retarding effect on radionuclide migration in HLNWR.

References

Alba, L. A. and Chavez, R. (1974) K–Ar ages from volcanic rocks from the Central Peña Blanca, Chihuahua, Mexico. *Isochron West*, **10**, 21–3.

Aniel, B. and Leroy, J. (1985) The reduced uraniferous mineralizations associated with the volcanic rocks of the Sierra Peña Blanca (Chihuahua, Mexico). *Amer. Mineral.*, **70**, 1290–7.

Bagby, W. C., Cameron, K. L., Cameron, M., and Gill, J. B. (1976) Petrology of tertiary ash flow tuffs and

related volcanics from Barranca de Batopilas and Gell regions of the Sierra Madre Occidentale, Chihuahua, Mexico. *Geol. Soc. Am., Abst.* with programs, vol. **8**, 5, p. 566.

Calas, G. (1977 Les phénomènes d'altération hydrothermale et leur relation avec les minéralisations unranifères en milieu volcanique: le cas des ignimbrites tertiares de la Sierra Peña Blanca, Chihuahua, Mexico. *Sci. Geol. Bull.*, **30**, 3–18.

Chapman, N. A. and McKinely, I. G. (1987) *The geological disposal of nuclear waste*. John Wiley and Sons, Chichester, 280 pp.

Goodell, P. C. (1981) Geology of the Peña Blanca uranium deposits, Chihuahua, Mexico. In *Uranium in volcanic and volcaniclastic rocks* (Goodell, P. C. and Waters, A. C., eds.), AAPG Studies in Geology, **13** 275–91.

Ildefonse, Ph., Muller, J. P., Cesbron, F., and Sichere, M. C. (1988) Mineralogy of uranium concentrations and associaed hydrothermal alteration minerals in ignimbritic tuffs, Sierra Peña Blanca, Chihuahua, Mexico. *Geol. Soc. Amer. Abs. Progrs.*, **20**, A336.

——Cesbron, F., Muller, J. P., and Calas, G. (1989) *Study of alteration systems in the light of nuclear waste repository safety. 1—Element remobilization in hydrothermally altered tuffs*. Proc. EUG V Congress, Strasbourg, 1989, *Terra Abs.*, **1**, 111–2.

——Muller, J. P., Clozel, B., and Calas, G. (1990) Study of two alteration systems as natural analogues for radionuclide release and migration. *Engineering Geol.*, **29**, 413–39.

Novacek, R. (1935) Study of some secondary uranium minerals. *Vestnik Kral. Ceske. Spol. Nauk.*, **II**, no. 7, 36 pp, 2 pls.

Nguyen, S. N., Silva, R. J., Weed, H. C., and Andrews, J. E. Jr., (1991) *Standard Gibbs free energies of formation at 30 °C of four uranyl silicates: soddyite, uranophane, sodium boltwoodite and sodium weeksite.* Lawrence Livermore National Laboratory, Internal Report UCRL-JC-106032.

Reyes, C. M., Cruz, B. R., and Guerrero, P. S. (1980) *Descripcion petrographica de las muestras obtenidas de los niveles cero y cuarenta del yacimiento Nopal I, Sierra Peña Blanca, Municipio de Aldama, Chihuahua.* URAMEX Internal Report: Informe 10.

Smith, D. K. and Stohl, F. V. (1972) Crystal structure of beta-uranophane. *Geol. Soc. Amer. Mem.*, **135**, 281–8.

Stohl, F. V. and Smith, D. K. (1981) The crystal chemistry of the uranyl silicate minerals. *Amer. Mineral.*, **66**, 610–25.

Uramex (1980) *Nopal I, Las Margaritas, Puerto III.* Unpublished Internal Reports.

Websky, M. (1853) *Zeits. Geol. Gesselschaft*, **5**, 427.