SBORNÍK NÁRODNÍHO MUZEA V PRAZE

ACTA MUSEI NATIONALIS PRAGAE

Volumen XXX B (1974), No. 1-2

REDAKTOR JIŘÍ ČEJKA

JIŘÍ ČEJKA – ZDENĚK URBANEC National Museum, Prague – Nuclear Research Institute, Řež

ALTERATION OF MINERALS IN MUSEUM COLLECTIONS I

Problem of Alteration of Some Uranium Minerals from the Viewpoint of the Geochemistry of the System U - $O_2 - CO_2 - H_2O$

A variety of minerals have been described belonging to the system $U-O_2-CO_2-H_2O_1$, the superior ones being uraninite UO_{2+x} , ianthinite U_3O_{8+v} . x H₂O or $UO_{2,84}$. x H₂O, schoepite UO_3 . 2 H₂O, sharpite 5 UO_2CO_3 . UO_2/OH_2 . 7 H₂O, and rutherfordine UO_2CO_3 . x H₂O. Ideas of the conditions of formation and existence are not equally extensive with all these minerals. While the published literature on uraninite and its related phases as well as schoepite is voluminous and covers both natural and synthetic phases, less is known of ianthinite and rutherfordine. However, even in these two cases a comparative study may start from the research of synthetic materials; modest natural discoveries also exist. The study of sharpite is difficult because the mineral has not yet been synthetized and even the study of the natural mineral has not been completed because quantities which are available from discoveries at several localities are insignificant and, moreover, most or all the natural material has been consumed during the identification reactions [Banas/1965 and 1968/, Bültemann /1972/, Neumann /1972/, Sainfeld /1972/) and the data on sharpite findings cannot be always regarded as fully proved. No new analysis of the so-called sharpites has been accomplished except the original analysis (Melon /1938/).

Both in nature and in the museum collections, alteration of these minerals, which represent, after all, only intermediate phases of hydration — oxidation weathering of primary minerals of uranium , occurs. These phases are gradually transformed to various uranium minerals according to the conditions to which they are subject. In this case, the conditions of the museum collections will not be so varied, of course, as is the case with the alteration of the uranium minerals in nature (e.g., Frondel /1958/). Some interesting transformations of the mentioned minerals in museum collections have been noticed however (Destas et al. /1958/). Unfortunately, the study of these transformations as well a detailed description of the initial and transformed minerals has not yet been completed (Lepersonne /1972/). We shall therefore try to discuss the problem of alteration of these uranium minerals on the basis of our own experimental material and the available data on the mineralogy and geochemistry of uranium taking regard also to the analysis of the $U-O_2-CO_2-H_2O$ system based on thermodynamic calculations which, in the model form are becoming more important for the mineralogy and geochemistry in general (e.g., Garrels, Christ /1965/, Pačes /1972/, Santoma /1971, 1972/).

The UO_{2+x} [x=0-1] system is essentially unstable from the thermodynamic viewpoint and it is subject to gradual oxidation owing to atmospheric oxygen and humidity; the closer the x to unity, the higher is the oxidation rate (Hostetler, Garrels /1962/, Pourbaix et al. /1956/. Drozdovskaja, Mel'nik /1966/). The mineral ianthinite may obviously form under these conditions as one of the products of moist weathering of uraninite because hydration may also occur in addition to oxidation. Uraninite contains U^{4+} and various amounts of U^{6+} , ianthinite can be described by the formula UO_{2.84}±2.xH₂O (Bignand /1955/, Čejka /1959/, Cordfunke et al. /1968/). Even ianthinite is an unstable phase in the process of hydration — oxidation weathering because it is subject to further oxidation and all uranium involved in ianthinite is transformed to U^{6+} , i.e. uranyl. Phases of a general composition UO_3 . x H₂O are formed, in which x=0-2. A typical representative of this group is schoepite UO_3 . 2 H_2O , which is the primary representative considered in our work. This is the first case of various hydration processes of UO_3 formed which likely depend on the relative moisture content in the sample storage room and, hence, phases of different structures are formed. We have already mentioned the fact that uraninite transforms by a hydration — oxidation reaction to give hydrated uranium trioxide; the intermediate phase can be, and in a variety of cases really is, ianthinite. If the effect of aerial carbon dioxide on the ianthinite transformation is fully excluded from our consideration (which is not quite correct, as will be shown further), we can see that ianthinite is transformed to UO_3 . x H_2O_1 as has been already said. The transformed natural ianthinite corresponds by its composition to UO_3 . 2 H₂O (Frondel, J. W., Cuttitta /1954/, Guillemin, Protas /1959/); the phases described by the mentioned authors are not entirely identical as far as the structure is concerned. This fact follows from Table I where a comparison of the x-ray diffraction diagrams of individual discussed phases has been made. An interesting fact has been shown by J. W. Frondel and F. Cuttitta, i.e. that the product of ianthinite alteration can be compared, from the structure viewpoint, with schoepite I, II, and III, designated so by C. L. Christ and J. R. Clark (Christ, Clark /1960/). It can be assumed that the structure in question is schoepite at different stages of alteration. With synthetic materials, this hydration - oxi-

Schoepite nat. Destas et al. 1958		Schoepite Peters	e synth. 1967	Schoepite Čejka, Ui	Schoepite synth.*) Čejka, Urbanec		synth.**) rbanec
d	Irel	d	Irel	d	Irel	d	I_{rel}
7,36	VVS	7,37 6,65	10 2	7,32	10	7,35 ,	. 10
3,65	MS	3,69	4				
3,56	S	3,59	10	3,55	10	3,56	8
3,47	M	3,52	6	3,469	8	3,456	6
3,20	S	3,235	8	3,190	9	3,22	9
3,13	M	3,17	5	3,135	6	3,133	4
2,93	VW	2,985	1	5			
2,83	W	2,78	1				
		2,58	3				
2,55	MS	2,55	2	2,538	5	2,556	4
2,45	VW	2,455	1			2,464	1
· · ·		2,285	1	5			
2,23	VW	2,26	1			2,205	1
2,15	VW	2,09	2			2,130	1
	a	2,06	3			2,079	2
2,02	MS	2,04		2,008	3	2,030	5
		2,00	2				
1,96	M	1,98	3	1,965	2	1,955	6
		1,849	1				
1,82	VW	1,823	2			1,798	1
1,78	WM	1,802	2			1,785	1
				1,768	2	1,763	3
1,74	W			1,733	1	1,741	2
1,63	W			1,608	1	1,605	1
1,57	W			,		,	
1,45	VW					1,446	1

TABLE Ia X-ray powder data of natural and synthetic schoepites

Notes

*) initial phase

**) after three months air exposure at the room temperature and humidity

dation reaction leading to the formation of schoepite has been successfully performed only in an aqueous suspension, while a hydrate having a composition of 4 UO_3 . 5 H_2O (Bignand /1955/) has been obtained by oxidation of ianthinite in air. The x-ray diffraction diagrams of the natural and synthetic ianthinites are shown in Table II for comparison.

When comparing the x-ray diffraction diagrams shown in Tables I and II, we can see the identity of the natural ianthinite and the synthetized phases U_3O_8 . x H_2O as well as the fact that ianthinite appears to transform most likely into schoepite by a hydration — oxidation process proceeding at a sufficient humidity at the room temperature. Under the normal conditions, schoepite may be therefore considered to be a relatively stable phase, which corresponds also with thermodynamic calculations of the equilibrium between individual hydrates (Garrels /1955/, Hostetler, Garrels /1962/, Drozdovskaja, Mel'nik /1966, 1967/), even though a certain equilibrium state with separate hydrates

Schoepite- epiianthinite Guillemin, Protas 1959		UO3 . 2 H2O*) Bignand 1955		4 UO ₃ . 5 H ₂ O**) Bignand 1955		Alteration product of ianthinite, Frondel, Cuttitta 1954***)	
d	Irel	d	Irel	d	Irel	d	Irel
7,37	VS	7,35	S	5,23	VS	7,63 5,37	10 2
3,69	W			4,34 3,80	MS S	4,13 3,78	4 9
3,59 3,51	MS M	3,55 3,47	MS MS	3,52	S	3,60 3,36	3 7
3,23	S-VS(d)	3,20 3,14	M	3,27	м	3,20	ð
				2,74	М	2,90 2,67 2,60	5 1
2,56	WM(d)	2,55 2,45	M VW			2,51 2,38	54
						2,29 2,24 2 14	2
2,08 2.03	vvw w	2,08 2,01	VW MS	2,09	MW	2,06	2
1,963	W	1,96	М	1,94	М	1,978 1,950 1,915 1,889	2 2 2 4
1,840 1,789	vvw vw	1,77	MW	1,76	w	1,833 1,783 1,756	231
1,739	vvw	1,74	W			1,734 1,673	2 4
1,632	VVW(d)	1,62 1,61	VW VW	1,64	MW	1,632 1,615 1,595	2 2 2
1,562	vvw					1,574	5

TABLE Ib X-ray powder data of the oxidation products of natural and synthetic ianthinites

Notes

*) the phase formed by the atmospheric oxygen oxidation of the U_3O_8 . x H_2O water suspension at the room temperature and humidity.

**) the phase formed by the atmospheric oxygen oxidation of the $U_3 O_8$. $x \; H_2 O_{\cdot}$

***) alteration product of ianthinite, composition UO_3 . 2 H₂O.

can be admitted when considering the changes in free enthalpy $\triangle G^{\circ}_{298}$ of hydration reactions according to Garrels [Garrels /1955/]:

$UO_2/OH/_2$. 2 H_2O	4	UO_2/OH_2 . $H_2O + H_2O$	(1)
$\triangle G^{\circ}_{298} = 0$			
$UO_2/OH/_2$. H_2O	4	$UO_2/OH/_2 + H_2O$	(2)
$\triangle G^{\circ}_{298} = 0$			
$UO_2/OH/_2$	<u>7</u>	$UO^{3} + H^{2}O$	(3)
$\triangle G^{\circ}_{298} = 13.2 \text{ Kcal}$			

Ianthinite Guillemin, Protas 1959		anthinite UO _{2,84} . x H ₂ O in, Protas 1959 Bignand 1955		UO _{2,86} . Cordfunke	x H ₂ O et al. 1968
d	I _{rel}	d	I _{rel}	d	I _{rel}
7,63 5,90 5,35	VS VVW VVW	7,59	VS	7,516 5,923 5,315 5,07 4,28 4,022	100 4-7 6-10 2 4
3,81 3,59 3,35 3,24	M WM WM M	3,76 3,57 3,34 3,26	M M MW	3,763 3,558 3,316 3,219 3,173	30-32 78-100 51-53 78-100 57
2,95	VW	2,95	W	2,958 2,920	6 20
2,69 2,61	VW W	2,86	w	2,840 2,644 2,586	3-8 11-16 16
2,53	W	2,53	MS	2,512 2,49	7 5
2,39	VW	2,35	vw	2,3835 2,363 2,2735	3 9 2
2,24	VVW	2,22	vw	2,2735 2,262 2,219 2,1695	2 3 7 3
2,15	VW	2,15	MW	2,1575 2,129	5 10
2,07 2,03 1,992 1,956 1,929 1,899	VW W VW VW VVW W-VW			2,053 2,041 2,005 1,972 1,935 1,908 1,878	10 5 29-32 30 6 16 8-14
1,842 1, 794 1,746	VVW W-VW W-VW			1,822 1,779 1,770 1,731 1,723	12 28-43 9 28-33 10
1,681 1,582	w vw			1,68 1,661 1,622 1,6085 1,585	3 15 6 10-13 6

TABLE II X-ray powder data of natural and synthetic ianthinites

The separate hydrates of uranium trioxide (we use this simplified formulation although the real state is more complicated because the "hydrates" are hydrated hydroxocomplexes of uranyl) will have according to Garrels, no excessive tendency to mutual transformation and one can judge that they can exist together for a certain time as a

metastable phase. New experimental data on the thermodynamics of the UO₃ — H₂O system have been recently published by Nikitin and coworkers (Nikitin et al. /1972/). Another situation appears, for example, with amorphous uranium trioxide, the existence of which is very unlikely under the conditions considered by us — the positive value of ΔG°_{298} of the mentioned dehydration reaction (3) confirms the stability of the monohydrate in comparison with anhydrous UO₃. Synthetic amorphous UO₃, even in a dry state, is hydrated to give UO₃. x H₂O, where the x reaches very quickly a value of about 0.2 (Drobnic', Kolar /1966/), and gradually 2, i.e., practically UO₃. 2 H₂O is formed. In our experiments (Čejka, Urbanec /1971/ /1973/, Čejka /1970/), no more significant change was found during air exposure of UO₃. 2 H₂O (a synthetic material, structurally identical with the natural schoepite), which could be connected with eventual dehydration or further hydration:

Composition of the	Molar ratios of				
followed- up phases	UO_3	CO_2	H_2O		
a) initial phase	1	0.05	1.93		
b) after three months	1	0.04	2.01		

The small differences which we have found may be — especially from the viewpoint of the water content — affected by the accuracy of the analysis, although the content of CO₂, especially its decrease when exposing a specimen to air, is very interesting. It may be connected with the process of hydrolysis. The presence of carbon dioxide in the system cannot be really avoided because the used UO_3 . 2 H_2O has been obtained by hydration of amorphous UO₃ in an aqueous suspension under the normal conditions; absorption of carbon dioxide from air may really occur, which will be further shown. Owing to the fact that this hydration proceeds for a relatively short time, the absorption of CO_2 from air is unlikely, however. More accurately, the absorption of carbon dioxide from air already during the preparation of uranium peroxide UO_4 . 2 H_2O , from which amorphous UO_3 has been prepared by thermal decomposition, cannot be avoided; this fact has been studied already by Hoekstra and Siegel (Hoekstra, Siegel /1961/). If uranyl carbonate forms during the mentioned processes, as referred to by these authors, unfortunately without defining the formed uranyl carbonate more precisely, the carbonate phase need not decompose completely in the range of temperatures of the thermal decomposition of uranium peroxide giving amorphous UO₃, i.e., at 300-400 °C (Vlasov et al. (1972). If this were a type of uranyl carbonate corresponding to UO_2CO_3 prepared by a hydrothermal method, the decomposition would have proceeded only at temperatures above 500 °C, in the optimal case, at 600 °C (Čejka /1969, 1970/, Čejka, Urbanec /1973/). The presence of carbonate in the hydrated uranium oxide has not affected the hydroxide structure in any way and therefore we assume that a solid solution is formed. A detailed study of schoepite specimens (Christ, Clark /1960/) has led to a finding that also alteration of schoepite occurs. The authors have described even three phases, which they have

denoted as schoepites I. II. and III. It is not known whether schoepite I transforms directly into schoepite III and what is the role of schoepite II At all events the process in question is dehydration whose extent and consequences have not been verified and quantitatively evaluated fully, of course, Nevertheless, one may judge that the natural schoepite can be dehydrated under the normal conditions: one of the studied specimens is reported by Christ and Clark to contain also UO₃. H₂O according to the x-ray phase analysis; by comparison with the standard values, it could be $\alpha - UO_3$. H₂O. This phase is always an intermediate product of dehydration of UO_3 , 2 H₂O, as we have already found out in the study of dehydration (Urbanec, Imrišová /1963/). As far as the structure is concerned, schoepite can be visualized by a hexagonal bipyramid having the uranyl oxygen atoms at its apexes and six hydroxyls in the uranyl plane. As these structures are stratified, it is assumed that the remaining water is interlayer one. According to Evans (Evans /1963/). Christ suggests (Christ /1965/) that during the mentioned dehydration a structural re-arrangement about uranyl and a change in the coordination number of uranyl from six to five occur, i.e., that a pentagonal arrangement about uranyl and, consequently, a pentagonal bipyramid, which is more stable, forms, For a more detailed expansion of these thoughts especially a quantitative experimental proof is lacking, which is also true when considering the dehydration of schoepite under the normal conditions.

When summing up all facts discussed hitherto, hydration-oxidation weathering of minerals containing U⁴⁺ and gradual formation of phases containing only U^{6+} in the form of uranyl occur in the uraninite ianthinite - schoepite system under the normal conditions. The rate of these oxidation processes depends on the ratio of UO_2 : UO_3 in separate phases and it increases with increasing quantity of UO_3 . The observed phenomena agree entirely with thermodynamic calculations of the change in the free enthalpy ΔG°_{298} of individual reactions which may occur in the mentioned systems. So far, all processes discussed here can be regarded as entirely unambiguous. However, it should be respected that the effect of carbon dioxide on the course of the hydration-oxidation weathering of uranium minerals was entirely knowlingly neglected. As we know that the equilibrium constant of the oxidation processes of the natural uranium oxides is, under ideal conditions, only a function of the partial pressure of oxygen (at the normal temperature) one may suppose for simplification that, at such low pressures, the fugacities of oxygen and carbon dioxide are equal to their partial pressures — all these processes will obviously also depend on the partial pressure of carbon dioxide in air which can be absorbed by the system. the result being a formation of phases which will be here, for simplicity, denoted untill further notice by uranium carbonates. The partial pressure of aerial carbon dioxide varies within a considerable range. the average value for our conditions is reported to be $10^{-3.8}$ atm. As the development of industry and motorism leads, especially in larger towns, to a considerable increase in the carbon dioxide concentration

in air, this fact must be obviously reflected also on the course of the alteration of various minerals in museum collections which are installed in such areas. Naturally, this is true not only for the uranium minerals. A majority of papers dealing with the evaluation of the UO₃ — CO₂ — H₂O system start from the conclusions of Bullwinkel (Bullwinkel /1954/) who suggests that UO₃ . 2 H₂O absorbs carbon dioxide in air (obviously in an aqueous suspension, see below) and uranyl carbonate gradually forms. Unfortunately, no experimental proof is given in the cited paper. The calculations are based on the reaction

 $UO_3 \cdot 2 H_2O + CO_2 \qquad \rightleftharpoons \qquad UO_2CO_3 + 2 H_2O \tag{4}$

 $UO_3 \cdot 2 H_2O + H_2CO_3 \Rightarrow UO_2CO_3 + 3 H_2O$ (5)

The possibility of eventual formation of solid solutions is entirely neglected. Therefore, the equilibrium constant of the above reactions is a function of the partial pressure of carbon dioxide (e.g., Garrels /1957/, Hostetler, Garrels /1962/, Letowski, Niemiec /1966/, Garrels, Christ /1959 and 1965/, Drozdovskaja, Mel'nik /1967/, Needes /1970 and /1971/, Babko, Kodenskaja /1960/, Naumov /1959 and 1961/, Naumov and Mironova /1960/, Perez-Bustamante et al. /1962/). The values of the partial pressure of carbon dioxide necessary for the formation of uranyl carbonate in the given system that individual authors suggest differ from paper to paper, however. In our experiments with synthetic materials, which we have performed within the scope of our systematic study on the UO₃ — CO₂ — H₂O system with the aim of a verification of the mentioned data in literature, the following items have been followed-up:

a) the effect of aerial carbon dioxide and oxygen on UO_3 . 2 H_2O and U_3O_8 at the normal temperature and pressure. Whilst it has not been proved that absorption of carbon dioxide by uranium oxide dihydrate has occurred, as discussed above, we have found out that U_3O_8 prepared by a thermal decomposition of uranium peroxide at 800 °C for 2 hours is very slowly gradually oxidized in air and, simultaneously, absorbtion of carbon dioxide from air occurs, which we have proved by means of the i.r. spectroscopy. It should be emphasized, however, that the process in question is a very slow one and it is not by far finished even after two years. Naturally, a significant factor can be here the reactivity of the prepared U_3O_8 which depends on the purity of the used compounds as well as on the conditions of its preparation. In any case, these facts are worth considering because especially in natural processes this increased reactivity of uranium oxides UO_x (x < 3) can manifest itself during the formation of secondary minerals of uranium more expressively than the transformation into UO_3 . x H_2O , which is considered to be one of the main intermediate phases of the hydrationoxidation processes in the zone of hypergenesis. As hydrated phases of uranium oxides can appear in nature, e.g., of the ianthinite type $(U_3O_8$. x H_2O), their significance during wheathering in the zone of hypergenesis especially as the intermediate products giving rise to a variety of further secondary minerals of uranium cannot be neglected. The

increased reactivity of U_3O_8 . x H_2O in comparison with UO_3 . x H_2O has been already proved by us during the preparation of uranyl carbonate (Čejka /1959 and 1960/). However, the absorption of aerial carbon dioxidate by uranium trioxide dihydrate connected with the formation of uranyl carbonate of the rutherfordine type proceeding in the system gas — solid phase, that is without any aqueous phase, has not been proved in our experiments.

b) the effect of aerial carbon dioxide and oxygen on aqueous suspensions of amorphous UO₃, UO₃, $2 H_2O_3$, and U_3O_8 at the normal temperature and pressure. We can assume that also in the case of the mentioned Bullwinkel's experiments, absorption of aerial carbon dioxide by an aqueous suspension of UO_3 . 2 H_2O has occurred (p. 31 of the cited paper: "It is also observed that long exposures of UO_3 . 2 H₂O suspensions to air result in the gradual formation of UO_2CO_3 "; in preceding paragraphs, aqueous suspensions were really dealt with). Our experiments have shown that if uranium oxides or their hydrates in aqueous suspensions are exposed to air (and aerial carbon dioxide), absorption of carbon dioxide and a gradual formation of uranyl carbonate really occur (besides eventual oxidation of U⁴⁺ by aerial oxygen). The processes proceed even quicker with U_3O_8 than with UO_3 . x H₂O. It cannot be excluded that the relatively quicker transformation giving carbonate depends on the formation of a soluble hydroxouranyl complex, its carbonation in the solution, and only then on the separation of uranyl carbonate in a crystalline form. Bullwinkel is right when stating that the UO_3 . 2 H_2O suspensions (if he means the aqueous suspensions) absorb aerial carbon dioxide and that UO_2CO_3 is gradually formed (this formulation is not already entirely correct). Unfortunately, the mentioned author has not studied the formed phase more thoroughly. We have found out during our experiments that uranyl carbonate of the composition UO_2CO_3 . 2.27 H_2O has formed. This carbonate, however, entirely differs from uranyl carbonate of the rutherfordine type as follows from the chemical, thermal, and x- ray analyses as well as from the i.r. spectra of the studied samples. (Čejka /1970/, Čejka, Urbanec (1971/, (1973/). The phase in question is entirely a new phase which has not been described in the literature. A comparison of the x-ray diffraction diagrams of rutherfordine and this phase with x-ray diffraction diagrams of sharpite and schoepite is given in Table III. The DTA curves of a hydrothermally prepared uranyl carbonate, schoepite, and the carbonate phase identified by us are shown in Fig. 1. It should be noted that no serious DTA curve of rutherfordine has been published, as discussed in detail earlier by us (Čejka /1969/, Čejka, Urbanec /1973/). A thorough study of the mineral rutherfordine has been already started by us. From the presented Tables it follows unambiguously that, as we have already pointed out, the phase in question is really a new one. An interesting fact is worth noting, i.e., that this phase has been synthetized in an institute in Roudnice on L., while in the NRI, Řež, this synthesis has failed to be successful. Unfortunately, the values of the partial pressures of aerial CO_2 in both workplaces

UO2 CO3 . 2,27 H2O Čejka, Urbanec		Ruther	Rutherfordine Sharpite Destas et al. 1958			Sharpite Neumann 1972		Schoepite Destas et al. 1958	
d	Irel	d	Irel	d	Irel	d	$\mathbf{I}_{\mathrm{rel}}$	d	$I_{\rm rel}$
7,67	8			11,0 7,85	W VW	7,80	20	7,36	VVS
4,95 4,91	6 10	5,11	VW	5,34	W	5,3	30		
4,44 4,22 3,95	1 1 6	4,61 4,29 3,91	VS VS S	4,49 4,30 3,93	S W WM	4,50 4,29 3,92	20 100 30		
3,72 3,56 3,42	1 6 1			3,67	VVW	3 31	5	3,65 3,56 3,47	MS S M
3,18	8	3,22	S-VS	3,18	W	5,51	5	3,20 3,13	M M
2,96 2,85	1 4 1			2,99	WM	2,99	30	2,93 2,83	w
2,62	9	2,64 2,59	M W	2,62	W	2,62	60	2,55	MS
2,49 2,42 2,34	1 1 4	2,50 2,42	VW W	2,447	WM	2,45	40	2,45	vw
2,21	1	2,230	M	2,237 2,153	VW W	2,30 2,24 2,15	10 10	2,23 2,15	VW VW
2,01 1,93	3 5	2,025 1,948 1,922	MS VW W	2,071 1,990 1,899	W VW W(d)	2,06 2,00 1,90	50 30 30	2,02 1,96	MS M
1,84	1	1,872	WV (d)			1,83 1,78	50 20	1,82 1,78	VW WM
		1,694 1,660	VW VW VW					1,63	w
		1,589	VW VW			1,52	20	1,57	W
						1,50 1,44	10 10	1,45	vw

TABLE III X - ray powder data of the phase UO_2CO_3 . 2,27 H₂O, rutherfordine, sharpite and schoepite

during the synthesis or, more precisely, during studying the absorption of aerial CO_2 by aqueous suspensions of U_3O_8 and $UO_3 \cdot x H_2O$ cannot be compared.

First we have discussed the alteration of ianthinite connected with the formation of schoepite or the UO_3 . x H_2O phase under conditions of obviously very low partial pressures of aerial carbon dioxide. Now we are going to try to compare our experimental results obtained under the conditions of hydration - oxidation or hydration processes of uranium oxides connected with the formation of a new carbonate phase with the alteration of uraninite and ianthinite leading also to the formation of





The DTA curves of the phases in the $UO_3 - CO_2 - H_2O$ system

1 — UO₃.2H₂O

- 2 UO₃.0,4 CO₂.2,03 H₂O
- $3 UO_3 . 0,052 CO_2 . 2,19 H_2O$
- 4 UO₂CO₃. 2,27 H₂O
- $5 UO_3 . 0,80 CO_2 . 1,06 H_2O$
- $6 UO_3 . 1,06 CO_2 . 0,28 H_2O$
- $7 UO_3 . 1,09 CO_2 . 0,59 H_2O$

Notes concerning the conditions of preparation see in Tab. $\ensuremath{\mathrm{V}}.$

a carbonate phase. In the book "Minéraux d'uranium du Haut Katanga", which has been already cited, facts are reported that fully comply with our experimental results:

a) ... "Il est, de plus, probable que des minéraux néogénes se développent sur les spécimens des collections. On a remarqué récemment sur des échantillons d'uraninite des Musées de Tervuren et du Katanga de petites formations fibro-radiées d'un carbonate d'uranium. Il serait étonnant que ce minéral ait échappé à l'observation lors de leur récolte...". The transformation of uraninite into a phase containing carbonate ions and, hence, into uranyl carbonate of a certain type has been verified with the natural material.

b) "La ianthinite ... La première forme est transformée en épiianthinite dans un temps assez court (quelques années); la seconde par contre peut se transformer lentement en sharpite (comme le montre un échantillon de la collection du Katanga, partiellement modifié) ... Les cristaux plats donnent une effervescence à l'acide. Cependant on ne peut pas en conclure que se minéral renferme CO_2 depuis sa formation. Le carbonate peut être présent par suite d'un début de transformation en sharpite ...". The x - ray diffraction diagrams of epiianthinite are practically identical with the x - ray diffraction diagrams of schoepite.

Unfortunately, no more detailed information about the observed facts described in the cited book is available. The study on these materials has not yet been finished (Lepersonne /1972/). Owing to the fact that we have succeeded in observing similar processes with synthetic materials, the course of the hydration - oxidation weathering of uranium oxides. e.g., uraninite or ianthinite (which is, in fact, a product of uraninite weathering), connected with simultaneous absorption of aerial carbon dioxide resulting in the formation of the x UO_3 . y CO_2 . z H_2O phase both of the sharpite type and of other carbonate type — can be regarded as fully proved. That even another type of carbonate may form has been confirmed not only by our experiments but also by Bültemann who has reported that the found uranium carbonate (Kruth, France), insufficiently described and provisionally denoted as sharpite [Chervet /1960/, Chervet, Branche /1955/) is, in fact, not identical with the original sharpite described by Mélon (Bültemann /1972/). We may judge that under various conditions various carbonate phases may form in the system $UO_3 - CO_2 - H_2O$ of various composition and various structure. When we now disregard the complex dioxo-carbonatouranates (VI) containing various cations (e.g., Na, K, Ca, Mg, Cu) which form an important group of secondary uranium minerals, a mineral called wyartite of the composition UO_2 . 6 UO_3 . 3 CaO. (12–14) H₂O containing also carbon dioxide and U^{4+} together with U^{6+} (Bignand /1955/, Guillemin, Protas (1959) is to be mentioned in connection with ianthinite and sharpite. Wyartite also transforms, even if not so easily as ianthinite, and a phase containing anly U⁶⁺ gradually forms; simultaneously, a partial dehydration occurs. This problem has not yet been worked out in more detail (Clark /1960/).

$UO_3 \cdot 2 H_2O$ synth.			UO3.	UO ₃ .0,4 CO ₂ .2,03 H ₂ O*) UO ₃ .0,52CO ₂ .2,19			2,19H ₂ O**)
d (A)		Irel	(1(A)	Irel	d (A)	I _{rel}
7.42 7.20	}	10		7.67) 7.20 J	10	7.60 7.20	10
				6.42	0.5	6.66 6.09	1
						5.20 4.80	1
				4.47	0.5		
3 55		10		3 56	8	3 54	10
3 50		8		3.47	5	3 46	3
3.19		g		3 20	g	3 18	8
3 11		6		3 13	6	3 12	3
2.56	}	5		2.54	4	2.54	2
	,			2.07	1	2.07	1
2.02	1	F					
2.00	Î	5		2.02	1	2.02	1
				1.99	1	1.99	1
1.935		2		1.947	1	1.947	3
1.770		2		1.770	1	1.769	2
1.728		1		1.722	1	1.722	2
				1.708	1	1.658	0.5
1.616	}	1		1.616 }	1	1.611	1
1.000	,			1.569	1		

TABLE IV

X-ray powder data of the phases formed by the atmospheric carbon dioxide absorption in the water suspensions of the amorphous UO_3 and UO_3 . $2H_2O$

Notes

*) The starting material was a water suspension of the $UO_3 \cdot 2 H_2O$

**) The starting material was a water suspension of the amorphous UO3

Both compounds are formed after one year exposing to the atmospheric carbon dioxide.

In the system $UO_3 - CO_2 - H_2O$ which is characterized by its adjoined compounds, the mineral schoepite $UO_3 \cdot 2 H_2O$ and rutherfordine UO_2CO_3 x H₂O, solid solutions are formed whose structure is $UO_3 \cdot 2 H_2O$ at a relatively low content of carbon dioxide, as follows from the x - ray phase analysis (Table IV); the differences palpable from the infrared spectrum (Table V) and the DTA curve (Fig. 1) give evidence of a formation of a new structure. With increasing content of carbon dioxide, a new structure of hydroxocarbonato complex of uranyl gradually forms. The structure depends on the conditions of its formation. At a low partial pressure of carbon dioxide and at the normal temperature, phases are formed that contain molecular water and they are, therefore, hydrates, among which also sharpite might be placed. At a higher pressure of carbon dioxide and at a higher temperature (under hydrothermal conditions), eventually at a higher pressure and the normal temperature, phases of

UO3.: syn	2 H ₂ O th.	UO ₃ . 0,4 2,03 H	CO ₂ . 2 O *)	U	D3 . 0,5 2,19 H2	2 CO ₂ . 20*]	UO ₂ C 2,27 H ₂	O3. 0**)
442	М	449	м		449	м	413 420	} M
192	141	(485)	M		(485)	IVI IVI	440	VVVI
		525	Mb		528	M	525	М
546	М						020	
					(605)	VW	601	W
		678	W		667	W	662	M
					785	VW	781	VWb
0.40	147 -	825	VW		826	W	828	W
840	VV O				040	TIMO	040	TIMO
					870	VWO	049 870	Wo
912	vw				070	v vv0	070	WU
	a. a t	931	S		931	S	930	S
958	S							
989	vw							
1010	W	The Harman and a	805740		100000000		ELM SECON	
		1020	W		1021	W	1025	VW
		1147	W		1145	W	1151	M
		1300	VV 17117		1300	VVO	1300	VV O
		1430	V VV		1430	VVVD		
		1472			1472			
		1553	W		1560	W	1558	М
1590	r							
		1619	М		1618	М	1612	W
1623	М							
3180	Mb	(3050)	161		0075	01	(0000)	
2265	Mb	[3250]	IVID		32/5	SD	[3300]	MD
3305	VV D	3430	Mo		3435	М	3430	So
3541	Mo	3535	W		0100	141	0100	
	1000		6-3X		3580	М	3572	М
3590	Wo						ALCO NUC	
3625	Wo							

TABLE V The infrared spectra of the phases in the $UO_3 - CO_2 - H_2O$ system

Notes

*) The phases formed by the atmospheric carbon dioxide absorption in the water suspension of the $\rm UO_3$ $.2~\rm H_2O$ and the amorphous $\rm UO_3$ respectively.

.

**) The phase formed by the atmospheric oxygen oxidation and sorption of the atmospheric carbon dioxide by the water suspension of U_3O_8 at the room temperature and humidity.

Abbreviations used in Tables:

S strong, M middle, W weak, VW very weak, VVW very very weak, b broad, r shoulder, o sharp

UO3.0,80 CO2. 1,06 H2O***)	UO ₃ . 1,06 (0,28 H ₂ O**	CO2. ***)	UO ₃ . 1,09 0,59 H ₂ O*	0 CO2 . *****]
(233) r	224	Wo	222	Wo
(253) M	259	M	259	S
352 W	354	М	355	M
(390) r				
467 W				
(493) r				
(520) r				
* (545) W				
658 VW				
704 Wo	(697)	r		
767 VW0	704	Mo	703	Mo
784 Mo			, 66	
806 Mo	783	So	784	So
(815) r	806	Мо	805	So
* 840 VW				
849 VW				
868 VW			852	VW
898 VWo	865	VW	865	VW
* (905) r * 017 We				
917 WU				
534 5	978	S	968	S
* (1007) VW	0/0	0	500	0
(100))	1105	VVWo		
1113 VWo	1113	VWo	1114	VWo
1315 VW				
1426 S	1423	S	(1413)	S
(1510) Wr	1517	S	(1510)	S
1543 S			(1540)	r
1666 Mo	1700	* 7 * 1 *	1700	* ***
	1/90	VW	1/90	VW
	1032	VWO	1001	VWO
	(2510)	VVV	(2510)	VVV
(2628) VW	2630	VWo	2628	VW
(2665) VW	2000	1110		
2720 VW				
* (3185) r				
3402 Mo			3380	W
	(3450)	Wb		
* (3540) r				
* (3590) r				
[3620] r				

TABLE V (cont.) The infrared spectra of the phases in the $UO_3 - CO_2 - H_2O$ system

Notes

*) The band associated with the $UO_3 . 2 H_2O$ phase. ***) The phase formed by passing a vigorous stream of CO_2 through the water suspension of $UO_3 . 2 H_2O$ (prepared by the atmospheric oxygen oxidation of the $U_3O_8 \cdot x H_2O$ suspension) at the room temperature (8 hours).

****) The phase prepared under hydrothermal conditions, 200 °C/24 hours, 0,5 g of solid carbon dioxide per ml of the free volume.

*****) The phase prepared under hydrothermal conditions, 220 °C/22 hours, 0,2 g of solid carbon dioxide per ml of the free volume.

the rutherfordine type are formed having a spatial arrangement in the form of a hexagonal bipyramid with a coordination number of uranyl equal to six. Phases formed at the normal temperature contain molecular water, phases formed under hydrothermal conditions contain only hydroxogroups or they approach by their composition anhydrous UO_2CO_3 (Čejka, Urbanec /1973/). All discused phases crystallize in the orthorhombic crystal system. It is interesting that also among phases prepared under hydrothermal conditions clean-cut differences exist. As we have already mentioned, we have isolated, on the one hand, hydroxocarbonates of the $[UO_2(CO_3)_{1-x}(OH)_{2x}]$ type which we can regard as solid solutions having the rutherfordine structure and, on the other. phases that approach the ideal anhydrous uranyl carbonate UO_2CO_3 . Also in these cases, however, according to the x - ray analysis, the structure is identical with the structure of rutherfordine. In like manner, the phases prepared under the normal conditions containing, besides hydroxogroups, also molecular water have, according to the x - ray analysis, the rutherfordine structure. We can regard them, in fact, as hydrated hydroxocarbonates of uranyl having a general formula $[UO_2(CO_3)]_{1-x}$ $(OH)_{2x}$, yH_2O . It is therefore again a solid solution of the rutherfordine type. The effect of composition manifests itself, of course, during the thermal analysis, in which, e.g., endothermic peaks on the DTA curves appear corresponding to dehydration, release of OH- groups and, finally, to the decomposition of the carbonate. We have synthetized, under the normal conditions by saturing aqueous suspension of UO_3 . 2 H_2O with carbon dioxide, a phase having a composition of $[UO_2]$ $(CO_3)_{0.80}[OH_{0.39}]$. 0.67 H₂O (with the use of UO₃ . 2 H₂O obtained by oxidation of U_3O_8 . x H_2O in an aqueous suspension with aerial oxygen), which has - according to the x - ray diffraction diagram - a structure of rutherfordine; from the evaluation of the i.r. spectra, the presence of non-equivalent carbonate groups follows; the thermal analyses (DTA, DTG, and TGA as well as an isothermal heating) and the chemical analysis of intermediate products have shown that this phase is not only dehydrated through several stages but also that at least twostage decarbonation occurs, the first stage occurring at a temperature as low as about 325°, while the remaining carbon dioxide releases in the range of decarbonation of uranyl carbonate prepared hydrothermally. It is also very interesting that the first decarbonation is associated with an exothermal reaction, as follows from the DTA curve, which is comparable from the viewpoint of both the heat of the reaction and the temperature with the decarbonation of phases formed during absorption of aerial carbon dioxide by aqueous suspensions of uranium oxides [Fig. 1] and even with the decarbonation of sharpite, as described by Mélon. A thorough analysis of these experimental results is outside the scope of this work and it will be published separately (Čejka, Urbanec /1973/).

These facts are important from the viewpoint of the genesis of the discussed minerals. The evaluation of individual studied phases has been accomplished by means of the chemical, x - ray phase, and thermal analyses and by the i.r. spectroscopy. Our last research shows that the

effect of the conditions on the formation of phases of the rutherfordine type is considerably more pronounced than it was supposed because from the analysis of especially the i.r. spectra significant differences in the structural arrangement of phases prepared under hydrothermal conditions and at the normal temperature (at the normal pressure as well as at a higher pressure of carbon dioxide) follow. An interesting finding is, for example, that the asymetric vibration of the uranyl group with phases prepared at the normal temperature has practically the same value as with UO_3 . 2 H₂O, i.e. about 960 cm⁻¹, while with the hydrothermal phases, the value varies between the range of about 965-985 cm^{-1} . No expressive connection between this shift and the experimental conditions has been proved. Besides, from the viewpoint of the preparation, also the influence of the structure of the used forms of uranium trioxide (Urbanec, Čejka /1972/), which is in a good agreement with the presumptions ($\tilde{C}e_{jka}$ /1960/ and /1970/), appears. The problem of the different structure of phases of the so-called rutherfordine type has not vet been discussed in the literature. Even eventual differences in the structure of rutherfordine when it comes from different localities cannot be excluded from our considerations.

We have tried to discuss objectively, on the basis of the literature and our own experimental data, the problem of alteration of uranium minerals which might be met with in the museum collection material whose nature differs somewhat from the common types of dehydration processes proceeding, for instance, with uranium micas or with some other uranium minerals. The orientation of the hydration - oxidation processes depends primarily on the partial pressure of carbon dioxide and on the relative humidity of air. Measurement of these values is quite a problem owing to the fact that the weathering processes proceed very slowly, they last a number of years and, therefore, also the outer climatic conditions can vary within a larger range. Defining accurate values of the partial pressure of carbon dioxide and the relative humidity of air that are needed for the transformation of uraninite or ianthinite into schoepite on the one hand and into sharpite or another uranium carbonate on the other is, therefore, very difficult and it has not been done as yet. However, we can regard as proved that under the conditions considered by us, rutherfordine can only very difficultly form. Conceivably, a number of further factors exist which can affect the kinetics of these processes so that the measurement of small differences which obviously set forth during the reactions in one direction or in the other is no easy problem (Wey /1965/). We believe that our analysis has shown the complexity of deceivingly simple alterations occurring with the museum collections, that it has indicated which methods should be used when studying these problems, and that it has confirmed the necessity of comparative experiments with synthetic materials even when studying the natural minerals. The result of such a complex analysis are then directly applicable also to natural processes.

BABKO A. K., KODENSKAJA V. S. (1960): Izučenija ravnovesij v rastvorach karbonatnych kompleksov uranila. Ž. neorgan. chimii 5, 2568-2574.

BANAS M. (1965 and 1968): Private communication.

BIGNAND C. (1955): Sur les propriétés et les synthèses de quelques minéraux uranifères. Bull. Soc. franç. Minér. Crist. 78, 1-26.

BULLWINKEL E. P. (1954): The chemistry of uranium in carbonate solutions. US AEC Report RMO 2614, 59 pp.

BÜLTEMANN Hw: (1972): Private communication.

ČEJKA J. (1959): Herstellung von Uranylcarbonat. Coll. Czechoslov. Chem. Commun. 24, 3180-81.

ČEJKA J. (1960): Uhličitan uranylu. Chem. listy 54, 124-128.

ČEJKA J. (1969): To the chemistry of andersonite and thermal decomposition of dioxotricarbonatouranates. Coll. Czechoslov. Chem. Commun. 34, 1635-1656.

ČEJKA J. (1970): Příspěvek k chemii a geochemii rutherfordinu. Kandidátská disertační práce. VŠCHT Praha, 164 str.

ČEJKA J., URBANEC Z. (1971): Příspěvek k chemii uhličitanu uranylu I. VII. celostátní konference o anorganické chemii, Csl. společnost chemická při ČSAV, Praha.

ČEJKA J., URBANEC Z. (1973): The chemistry of uranyl carbonates I. The system rutherfordine-sharpite-schoepite. Coll. Czechoslov. Chem. Commun. 38, 2327-46.

CHERVET J. (1960):Les minéraux secondaires. Les minerais uranifères français et leur gisements (publié sous la direction de Marcel Roubault), T. 1er, p. 89-296. Institut National des Sciences et Techniques Nucléaires, Saclay et Presses Universitaires de France, Paris.

CHERVET J., BRANCHE G. (1955): Contribution à l'étude des mineraux secondaires d'uranium français. Sciences de la Terre 3, 1-190.

CHRIST C. L. (1965): Phase transformations and crystal chemistry of schoepite. Am. Mineralogist 50, 235-239.

CHRIST C. L., CLARK J. R. (1960): Crystal chemical studies of some uranyl oxide hvdrates. Am. Mineralogist 45, 1026-1061.

CORDFUNKE E. H. P., PRINS G., VLAANDEREN P. Van (1968): Preparation and properties of the violet "U₃O₈ hydrate". J. Inorg. Nucl. Chem. **30**, 1745-50. DESTAS A., VAES J. F., GUILLEMIN C. (1958): Minéraux d'uranium du Haut Katanga.

Les Amis du Musée royal du Congo Belge, Tervuren, 81 pp.

DROBNIC M., KOLAR D. (1966): Calorimetric determination of enthalpy of hydration of UO₃. J. Inorg. Nucl. Chem. 28, 2833.

DROZDOVSKAJA A. A., MEL'NIK Ju. O. (1966): Nekotoryje termodinamičeskije dannyje ob ustojčivosti uraninitov peremennogo sostava v gipergennych uslovijach. Atomnaja energija 21, 483-92.

DROZDOVSKAJA A. A., MEL'NIK Ju. P. (1967): Termodinamičeskij analiz ustojčivosti okislov urana v nizkotemperaturnych karbonatnych vodach. Atomnaja energija. Deponnirovannaja staťja. Annotacija mapečatana v t. 22, vyp. 5, str. 407.

EVANS H. T., Jr. (1963): Uranyl ion coordination. Science 141, 154-158.

FRONDEL C. (1958): Systematic mineralogy of uranium and thorium. U. S. Geol. Survey Bull. 1064, 400 pp.

FRONDEL J. W., CUTTITTA F. [1954]: Studies of uranium minerals (XVI): An alteration product of ianthinite. Am. Mineralogist 39, 1018-1020.

GARRELS R. M. (1955): Some thermodynamic relations among the uranium oxides and their relation to the states of the uranium ores of the Colorado Plateaus. Am. Mineralogist 40, 1004-1021.

GARRELS R. M. (1957): Some free energy values from geologic relations. Am. Mineralogist 42, 789.

GARRELS R. M., CHRIST C. L. (1959): Behavior of uranium minerals during oxidation. Geochemistry and mineralogy of the Colorado Plateau uranium ores. U. S. Geol. Survey Profess. Paper 320, 81-89.

GARRELS R. M., CHRIST C. L. (1965): Solutions, minerals and equilibria. Harper and Row, New York, 450 pp.

GÜILLEMIN C., PROTAS J. (1959): Ianthinite et wyartite. Bull. Soc. franç. Minér. Crist. 82, 80-86.

HOEKSTRA H. R., SIEGEL S. (1961): The uranium-oxygen system U₃O₈ - UO₃. J. Inorg. Nucl. Chem. 18, 154-165.

- HOSTETLER P. B., GARRELS R. M. (1962): Transportation and precipitation of uranium and vanadium at low temperatures with special reference to sandstone-type uranium deposits. Econ. Geology **57**, 137-167.
- LEPERSONNE J. (1972): Private communication.

ŁETOWSKI F., NIEMIEC J. (1966): Diagramy równowag elektrochemicznych układu U-H₂O-CO₂ w 25°. Nukleonika 11, 13-28.

- MÉLON J. (1938): La Sharpite, nouveau carbonate d'uranyle du Congo Belge. Bull. Inst. Royal Colon. Belge **9**, 333—336.
- NAUMOV G. B. (1959): K voprosu o karbonatnoj forme perenosa urana v gidrotermal'nych rastvorach. Geochimija, 6—19.
- NAÚMOV G. B. (1961): Nekotoryje fiziko-chimičeskije osobennosti povedenija urana v gidrotermaľnych rastvorach. Geochimija, 115—132.
- NAUMOV G. B., MIRONOVA O. F. (1960): Okislitel'no-vosstanovitel'noje ravnovesije v sisteme uran-železo v karbonatnoj srede i jego značenije v geochimii. Geochimija, 241-246.
- NEEDS C. R. S. (1970): The calculation of the equilibrium distribution of metal-ion complexes in multicomponent aqueous systems. Nat. Inst. Metall., Johannesburg, S. A., Report No. 1093, 14 pp.
- NEEDS R. C. S. (1971): Three-dimensional predominant -area and solubility diagrams for the uranyl carbonate and uranyl sulphate systems. Nat. Inst. Metall., Johannesburg, S. A., Report No. 1144, 18 pp.
- NEUMANN H. (1972): Private communication.
- NIKITIN A. A., SERGEJEVA E. I., CHODAKOVSKIJ I. L., NAUMOV G. B. (1972): Gidroliz uranila v gidrotermal'noj oblasti. Geochimija, 297-307.
- PAČES T. (1972): Chemické rovnováhy v přírodním systému voda-hornina-atmosféra. Ústřední ústav geologický v nakl. Academia Praha, 196 str.
- PEREZ-BUSTAMANTE J. A., POLONIO J. B., CELLINI R. F. (1962): Contribucion al estudio de los carbonatos complejos de uranilo I. Nueva reacción de hidroxilo de uranilo el ácido carbónico como paso intermedio en la obtencion del carbonato de uranilo. Anal. Real. Soc. Espan. Fís. Quí m., Ser. B-Química 58, 677-704.
- PETERS J. M. (1967): Synthèses et étude radiocristallographique d'uranates synthetiques du type oxyde double d'uranyle. Mém. Soc. Roy. Sc. Liège, 5e série, T. 14, Fasc. 3, 58 pp.
- POURBAIX M., DELTOMBE E., ZOUBOV N. de (1956): Comportement électrochimique de l'uranium. Diagramme d'équilibre tension-pH du système U—H₂O à 25 °C. Centre Belge d'Etude de la Corrosion, Bruxelles, Rapport, Techn. No. 31, 20 pp.
- POURBAIX M. (1963): Atlas d'équilibres électrochimiques à 25 °C. Gauthiers-Villars, Paris, p. 200, 203, 204, 209.
- SAINFELD P. (1972): Private communication.
- SANTOMA JUNCADELLA L. (1971): Los minerales secundarios de uranio y su ambiente geológico de formacion. Energía Nuclear 15, 375—380.
- SANTOMA JUNCADELLA L. (1971): Ambientes físico-quimicos de formacion de los minerales de uranio. Publ. del I. Congreso Hispano-luso-americano de Geol. Economica. 4, 341-358.
- SANTOMA JUNCADELLA L. (1972): Programa VODAM para tratamiento de datos de fisico-quimica mineral. Ejemplo de aplicacion al caso del uranio. Junta de Energia Nuclear, J. E. N. 237, 38 pp.
- URBANEC Z., ČEJKA J. (1971): Příspěvek k chemii uhličitanu uranylu II. VII. celostátní konference o anorganické chemii, Čsl. společnost chemická při ČSAV, Praha.
- URBANEC Z., ČEJKA J. (1972): Studium systému UO₃ CO₂ H₂O. 28. celostátní sjezd Čsl. společnosti chemické při ČSAV, Pardubice.
- URBANEC Z., IMRIŠOVÁ D. (1963): Pyrolyseprodukte des Urantrioxydmonohydrats. I. Reflexionsspektren der pulverförmiger Uranverbindungen. Z. anorg. allg. Chem. **323**, 300-307.

VLASOV V. G., ŽUKOVSKIJ V. M., TKAČENKO E. V., BEKETOV A. R. (1972): Kislorodnyje sojedinenija urana. Atomizdat Moskva, 256 str.

WEY R. (1965): Private communication.

JIŘÍ ČEJKA a ZDENĚK URBANEC

ALTERACE MINERÁLŮ V MUSEJNÍCH SBÍRKÁCH I

Otázka alterace některých minerálů uranu z hlediska geochemie systému U – $0_2 - C0_2 - H_20$

V práci, která je prvním sdělením v plánované řadě studií o alteraci minerálů v musejních sbírkách, se autoři zabývají problémem některých minerálů uranu a konfrontují vlastní experimetální výsledky studia synthetických minerálů s literárními údaji alterace minerálů uranu, přičemž při hodnocení výsledků studia aplikují současně modelovou aplikaci thermodynamických hodnot změn volné energie \bigtriangleup G°298 jednotlivých diskutovaných reakcí vedle využití chemické, rentgenometrické analysy, thermické analysy a infračervené spektroskopie. Pozornost byla soustředěna především na systém U – O2 – CO2 – H2O se zřetelem na sekundární minerály uranu, které mohou v zoně hypergenese, tj. hydratačně – oxidačního větrání vznikat a podléhat dalším změnám – především ianthinitu UO2,84 . x H2O, schoepitu UO3 . 2 H2O, sharpitu UO2CO3 . H2O resp. 5 UO2CO3 . UO2(OH)2 . 7 H2O a rutherfordinu UO2CO3.

Uvažuje-li se jako typický představitel primárních minerálů uranu uraninit, pak v zoně hydratačně - oxidačního větrání nelze považovat tuto fázi za stabilní, protože podléhá oxidaci a současné hydrataci, rychlost tohoto procesu je tím větší, čím více obsahuje uraninit U⁶⁺. Jedním z prvních produktů alterace uraninitu je ianthinit, velmi nestabilní a rychle se přeměňující minerál obecného složení U₃O₈. xH₂O. Alterace tohoto minerálu může probíhat dvěma směry. Vytváří se buď UO₃ . $x H_2O$, kde x se blíží nebo i rovná dvěma, tj. vznikají fáze, které svou strukturou odpovídají schoepitu, UO3 . 2 H2O, případně vzniká hydrát s jinou strukturou (viz tab. I), nebo může současně dojít vedle hydratačně oxidačního procesu i ke karbonisaci, která je spojena se vznikem uhličitanu uranylu. V literatuře byl popsán jak vznik schoepitu UO3 . 2 H2O, tak sharpitu 5 UO2CO3 . UO2(OH)2 . 7 H2O z ianthinitu. V rámci této práce byly sledovány vzájemné relace mezi schoepitem, sharpitem a rutherfordinem na synthetických fázích, připravených v systému $UO_3 - CO_2 - H_2O$. Pokusy se synthetickým schoepitem ukázaly, že tato fáze je za normální teploty velmi stálá a nepodléhá žádným výraznějším změnám. Ovšem je nutno respektovat skutečnost, že byla zaznamenána alterace přírodního schoepitu a byly identifikovány tři fáze schoepit I, II a III, dokonce vedle dehydratací vzniklého monohydrátu $lpha - UO_3$. H₂O (Christ, Clark /1960/). I mezi zmíněnými třemi fázemi schoepitu existuje podle citovaných autorů vztah, podmíněný částečnou dehydratací, spojenou současně, jak uvádí Christ (Christ /1965/) s přeskupením prostorového uspořádání schoepitu ve formě hexagonální bipyramidy s kyslíky uranylu v jejích vrcholech a šesti hydroxyly v rovině uranu se zbývající mezivrstvovou vodou a koordinačním číslem uranylu šest na pentagonální bipyramidu s koordinačním číslem uranylu pět, toto uspořádání je podle Evanse (Evans /1963/) stabilnější. V suchém stavu nedochází u fází typu UO3. x H₂O k absorpci kysličníku uhličnatého ze vzduchu. Pomocí infračervené spektroskopie byla prokázána hydratačně – oxidační reakce spojená se současnou absorpcí CO2 ze vzduchu u U3O8, ovšem toto je velmi pomalý dlouhodobý proces. Ve vodných suspensích dochází k absorpci vzdušného kyslíku jak U3O8, tak i fázemi UO3 . x H2O. Proces hydratačně – oxidačního větrání vodné suspense U3O8 spojené s absorpcí vzdušného kysličníku uhličitého je relativně rychlejší než absorpce vzdušného CO₂ vodnými suspensemi UO3 . x H2O. Ve všech případech vzniká jako konečný produkt karbonátová fáze, UO2CO3 . x H2O, která není identická s uhličitanem uranylu typu rutherfordinu. V našem případě jsme izolovali fázi složení UO2CO3 . 2,27 H2O, u níž, na základě rozboru infračervených spekter, lze předpokládat prostorové uspořádání hydroxylů v rovině uranylu a mezivrstvové vody, jiné než u fází typu rutherfordinu. Lze soudit, že i přírodní sharpit vzniká podobným procesem, jak bylo zjištěno při alteraci ianthinitu (Destas et al /1958/), čímž se právě sharpit odlišuje od rutherfordinu z hlediska genese. Bylo prokázáno, že v systému UO $_3$ — CO $_2$ — H $_2$ O dochází ke vzniku tuhých roztoků, které při relativně nízké koncentraci kysličníku uhličitého mají podle rentgenometrické analysy uspořádání uranové submřížky totožné s UO₃. 2 H₂O, rozdíly jsou patrné na křivce DTA a infračerveném spektru. Za nor-mální teploty dochází působením vzdušného kysličníku uhličitého k postupnému

vzniku karbonátové fáze, kterou možno považovat za hydratovaný hydroxokarbonát uranylu se strukturou odlišnou od rutherfordinu. Do této skupiny karbonátových fází uranylu možno zařadit i minerál sharpit. Naproti tomu při normální teplotě a nadbytku kysličníku uhličitého resp. v hydrothermálních podmínkách vznikají tuhé roztoky, hydroxokarbonáty uranylu se strukturou uranové submřížky, odpovídající uspořádání rutherfordinu. V těchto podmínkách je konečným produktem uhličitan uranylu se strukturou rutherfordinu UO2CO3 . x H2O kde x≧O. Rychlost těchto reakcí je závislá na použitých vstupních modifikacích kysličníku uranového a jeho hydrátů a na jejich reaktivitě. V každém případě možno považovat za prokázané, že v podmínkách hypergenese může jen těžko vznikat rutherfordin, pro který jsou příznivější podmínky vyššího tlaku kysličníku uhličitého případně vyšší teplota. Naproti tomu za normální teploty a působení vzdušného kysličníku uhličitého dochází v námi diskutovaných systémech ke vzniku uhličitanu uranylu resp. hydratových hydroxokarbonatokomplexů uranylu typu sharpitu. Z uvedeného vyplývá, že v musejních sbírkách jsou produktem alterace fází typu UOx . y $\rm H_{2}O$ primárně ianthinit UO $_{2,86}$. x $\rm H_{2}O$ a dále pak buď hydratovaný hydroxo-komplex uranylu UO₃ . xH₂O (x=2) nebo hydratovaný hydroxo karbonát uranylu obecného vzorce [UO₂(CO₃)_{1-x}(OH)_{2x}] . y H₂O. Provedený rozbor současně prokázal, že je nezbytné při studiu chemie, mineralogie a geochemie mineralogických systémů kombinovat výsledky, získané pomocí chemické, thermické, rentgenometrické fázové analysy a infračervené spektroskopie, příp. jiných metod, aby se dospělo k objektivním závěrům.