

# THE EFFECT OF MINERAL CONTENT ON THE DEGREE OF DEVIATION FROM RADIOACTIVE EQUILIBRIUM IN THE ANCIENT URANIUM ORES OF THE UKRAINE

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The degree of radioactive nonequilibrium of ores was found to increase in the following order in accordance with the varying mineral content: relatively coarse-grained uraninite ( $\text{UO}_{2 < n < 2.25}$ ) - coffinite ( $\text{USiO}_4$ ), brannerite ( $\text{UTi}_2\text{O}_6$ ) - secondary fine-grained coffinite, brannerite-secondary minerals of thin veins, boltwoodite ( $(\text{Ca,Na,K})(\text{UO}_2)[\text{SiO}_3\text{OH}] \cdot 1.5\text{H}_2\text{O}$ ), and membranous uraninite ( $\text{UO}_{2.25}$ ). This is ascribed to a different loss of radioactive recoil atoms by crystals because of real crystals dimensions and defects and features of ideal atomic structure of minerals.

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## 1. INTRODUCTION

Ores from deposits of sodium-uranium formation in the central part of the Ukrainian Shield where most of the Ukrainian raw uranium is found, are 1.8 to 2.0 billion years of age as inferred from their uranium-lead isotope ratio [1]. However,  $\gamma$ -spectrometry studies of the ores reveal noticeable deviations from the radioactive equilibrium in the  $^{238}\text{U}$  and  $^{235}\text{U}$  decay chains (Table 1).

For equilibrium ores the age equation holds

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \dots = \lambda_n N_n, \quad (1)$$

where  $\lambda$  is the decay constant for nuclei of a given isotope,  $N$  is the number of atoms of a given isotope, and induces 1, 2, 3,  $n$  denote atoms of elements that are members of the decay chains [2].

For a pair of neighboring members it reaches an accuracy of about 97% within a time  $5T_{1/2}$  where  $T_{1/2}$  is the half-life of a longer-lived nuclide. For most members of the  $^{238}\text{U}$  and  $^{235}\text{U}$  decay chains (Table 1),  $T_{1/2}$  is considerably smaller than the geological age of the minerals or the age of the latest possible geochemical transformation of the ore. The exception is relatively long-lived nuclides  $^{234}\text{U}$ ,  $^{230}\text{Th}$ , and  $^{231}\text{Pa}$ . Thus, one may conclude that the radioactive equilibrium which corresponds to the highest radioactivity of the uranium ores, is established within approx. 1.2 million years ( $5T_{1/2}$  for  $^{234}\text{U}$ ; Table 1).

For representative ore samples inside the radioactive chains, we have found nonequilibrium relations:

$$\lambda N_{238\text{U}} > \lambda N_{230\text{Th}} \quad \text{and} \quad \lambda N_{235\text{U}} > \lambda N_{231\text{Pa}}. \quad (2)$$

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The above relations were obtained directly from the  $\gamma$ -spectra of the ores, i.e. by the nuclear-physics technique of determining the radioactive equilibrium. In the case of the  $^{238}\text{U}$  family this observation may be a consequence of the superimposing  $^{234}\text{U}$  and  $^{230}\text{Th}$  loss, so it is important to correlate this result with the  $^{235}\text{U}/^{231}\text{Pa}$  data. If the loss of the above isotopes is fast and complete, the age of this event can be estimated [2-4] from the concentration ratios of the neighboring members in the decay chains. We consider a total nonequilibrium effect occurring between  $^{238}\text{U}$  and  $^{230}\text{Th}$ . These data were mostly correlated with the  $^{235}\text{U}/^{231}\text{Pa}$  ratios for the same samples. The concentrations of the above-mentioned nuclides were found from the radiation intensity of short-lived isotopes coming next in the chain as it was done in [3].

## 2. SAMPLES

Samples were prepared from solid mineralized albitites. Plates of about 0.1 mm thickness were sawed out of each fragment and polished to measure gamma-spectra. The mirror surface of the samples was examined by autoradiography.

The samples were taken from ore deposits at different stages of exploitation: Michurinskoye (5/106; 34/132; 82/132), Vatutinskoye (43/163; 50/228; 62/228), reserved Severinovskoye (5/326; 7/326; 12/326) and prospective ore mineralization (5727; 6007; 6025). According to uranium mineralization, all samples can be divided into two unequal groups. One includes sample 12/326 from the Severinovskoye

ore deposit which is characterized by thin (a few tenths of millimeter) veins of "secondary" uranium minerals. The matrix of this sample is responsible for no more than 0.1 of its total radioactivity. The other group comprises all other samples in which the uranium mineralization is present as patches.

**Table 1.** Basic nuclides of  $^{238}\text{U}$  and  $^{235}\text{U}$  families, half-lives  $T_{1/2}$ , principal  $\gamma$ -line energies  $E_\gamma$ , quantum yields  $n_i$

nuclide	$T_{1/2}$	$E_\gamma$ , keV	$n_i$ , %
$^{238}\text{U}$	$4.468 \cdot 10^9$ yr		
$^{234}\text{Th}$	24.1 d		
$^{234m}\text{Pa}$	1.17 m	1001.0	0.837
$^{234}\text{U}$	$2.445 \cdot 10^5$ yr		
$^{230}\text{Th}$	$7.538 \cdot 10^4$ yr	143.9	0.05
$^{226}\text{Ra}$	1600 yr	186.1	3.50
$^{222}\text{Rn}$	3.82 d		
$^{218}\text{Po}$	3.10 m		
$^{214}\text{Pb}$	26.8 m	295.2	18.5
$^{214}\text{Bi}$	19.9 m	351.9	35.8
		609.3	44.8
		768.4	4.80
		934.1	3.09
		1120.3	14.8
		1238.1	5.86
		1377.7	3.92
$^{214}\text{Po}$	164.3 $\mu\text{s}$	1764.5	15.36
$^{210}\text{Pb}$	22.3 yr		
$^{210}\text{Bi}$	5.01 d		
$^{210}\text{Po}$	138.4 d		
$^{206}\text{Pb}$	stable		
$^{235}\text{U}$	$7.038 \cdot 10^8$ yr	143.8	10.96
$^{231}\text{Th}$	25.52 hrs	163.3	5.08
		185.7	57.2
		205.3	5.01
$^{231}\text{Pa}$	$3.276 \cdot 10^4$ yr	300.1	2.47
$^{227}\text{Ac}$	21.77 d	302.7	2.19
$^{227}\text{Th}$	18.72 d	236.0	12.71
$^{223}\text{Ra}$	11.44 d	256.2	7.75
		269.5	13.7
$^{219}\text{Rn}$	3.96 s	271.2	10.8
$^{215}\text{Po}$	1.78 ms	401.8	6.37
$^{211}\text{Pb}$	36.1 m	404.8	3.78
$^{211}\text{Bi}$	2.14 m	351.1	12.91
$^{207}\text{Tl}$	4.77 m		
$^{207}\text{Pb}$	stable		

### 3. EXPERIMENTAL TECHNIQUES

The localization of the uranium minerals was performed autoradiographically by means of a highly sensitive film made by TASMA Holding (Kazan, Russia). At places marked by film blackening, investigations were performed by optic and electron-microscopy techniques; micrograins were extracted for X-radiography and optic studies. The grain fine structure, substructure and composition were examined using scanning electron microscopes-microanalyzers (Camebax-SX-50, France, Camscan-

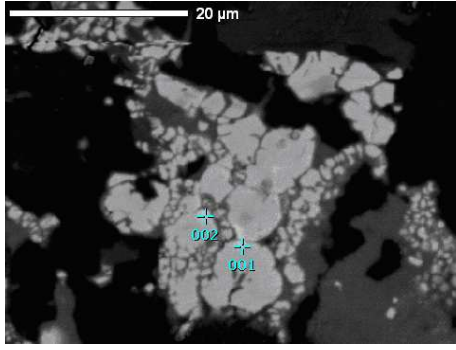
S-4, Oxford, and JSM 60601A, Japan). The gamma-radiation intensities from the ores were measured with a Ge(Li)-detector of  $50 \text{ cm}^3$  volume and  $2.8 \text{ keV}$  resolution for a  $1322 \text{ keV}$  line. In order to reduce the background a special multilayered shield for the detector was used, permitting the amount of the experimental material to be minimized to 1 g, with the intensity measurement accuracy being 5–7% for measurement time 10 hours. The total exposition was for each sample not less than 50 hours. To prevent radon emanation during the experiment the samples were encapsulated in a plastic polymerizing in air.

Basic data for determining the concentration ratios of radionuclides from the  $^{238}\text{U}$  family were measured intensities of the  $1001 \text{ keV}$  line from  $^{234m}\text{Pa}$  and the strongest lines from  $^{214}\text{Bi}$  and  $^{214}\text{Pb}$  (Table 1). Relative efficiency of the detector -  $D_{ef}$  has been constructed on  $^{214}\text{Bi}$  and  $^{214}\text{Pb}$  lines as  $\ln D_{ef} \approx \ln E_\gamma$ . The deviation from intensity of  $1001 \text{ keV}$  line ( $^{234m}\text{Pa}$ ) was determined and served as a criterion for value of nonequilibrium for the  $^{238}\text{U}$  family. Half-lives of  $^{222}\text{Ra}$  (3.82 days),  $^{218}\text{Po}$  (3.10 minutes) and  $^{214}\text{Pb}$  (26.8 minutes) being considerably smaller than the  $^{230}\text{Th}$  half-life, were neglected. The inclusion of the  $^{226}\text{Ra}$  half-life (1600 years) had no appreciable effect on the final result either. Thus, the shift of equilibrium between  $^{238}\text{U}$  ( $^{234}\text{U}$ ) and  $^{230}\text{Th}$  was determined.

### 4. RESULTS FROM A COMPARATIVE STUDY OF THE PHASE NATURE OF THE URANIUM MINERALIZATION AND THE DEVIATIONS FROM RADIOACTIVE EQUILIBRIUM

Measurements (Table 2) of the degree of radioactive nonequilibrium as against the phase composition of the uranium carriers show that most closely the equilibrium is approached by ores with relatively large individual uraninite crystals (Fig.1): ore mineralization (samples 5727; 6007; 6025) and sample 50/228 from Vatutinskoye ore deposit. From the lead-uranium concentration ratio in the samples with allowance for the average isotope composition of lead ores [1] the age of the uraninite crystals was estimated which proved to be quite probable ( $t \approx 2.05 \cdot 10^9 \text{ years}$ ), indicating a relatively closed isotope system within a mineral grain since the uraninite formation.

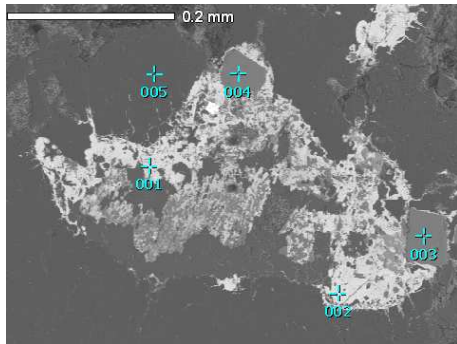
Somewhat farther from equilibrium are essentially coffinite ores: 34/132 (Michurinskoye deposit), 62/228 (Vatutinskoye deposit), 7/326 (Severinovskoye deposit, Fig.2) and low-uranium matrix of sample 12/326 from the same deposit where uranium is both bound mostly in zircon and scattered, as well as one sample of the brannerite ore (5/326, Severinovskoye deposit). The next group comprises two samples of brannerite ore (82/132, Fig.3 and 5/106, Michurinskoye deposit) and one sample of fine-grained coffinite ore (43/163, Vatutinskoye deposit).



**Fig.1.** Uraninite formation and composition in albitite (ore mineralization, sample 6025)

for Fig.1.

El.	001 wt.%	002 wt.%	001 at.%	002 at.%
Na	1.02	0.82	1.26	0.71
Mg	0.26		0.31	
Si	0.33	7.03	0.34	4.98
K	0.71	0.76	0.51	0.38
Ca	1.55	1.85	1.10	0.92
Fe		0.47		0.17
Sr	0.86	1.03	0.28	0.23
Cs		0.47		0.07
Pb	22.7	18.7	3.12	1.80
U	58.5	49.1	7.06	4.14



**Fig.2.** SEM- photograph and microanalysis data for the fine-grained essentially coffinite ore from Severinovskoye deposit, sample 7/326. Elastically scattered electrons. Analysis 1 and 2: fine-grained coffinite attached to other silicates; analysis 3 and 4: crystals of Nb-bearing rutile; analysis 5: albite

for Fig.2.

El.	001	002	003	004	005
Na, at.%	0.07	0.08	0.03	0.02	3.20
Mg, at.%	0.04	0.18			
Al, at.%	0.36	0.73	0.02	0.05	3.29
Si, at.%	3.81	6.49	0.04		8.68
K, at.%				0.01	0.03
Ca, at.%	9.16	0.57	0.01	0.01	0.00
Ti, at.%			11.8	11.8	
Nb, at.%			0.11	0.11	
Fe, at.%	0.10				0.08
Zr, at.%	0.25	0.33			
I, at.%	0.04	0.01			
Pb, at.%			0.01	0.00	
U, at.%	2.35	3.38			

The brannerite composition is in satisfactory agreement with theoretical predictions:  $(U, Ca)(Ti, Fe)_2O_6$  (Table 3). The composition of the mineral (mineral mixture) in the central regions of the grains cannot be interpreted unambiguously. In this group a sample of fine-grained coffinite ore from Vatutinskoye deposit (sample 43/163) is represented by colloform zoned formations with fine-grained coffinite (Fig.4). The central regions of the globules are constituted by potassium feldspar with fine patches of acicular aggregates of minerals for which the sum of atomic quantities of cations is  $(U + Pb + Sn + Sr + Ca + K) \approx Si$ . A margin with a high atomic number is fine-grained coffinite (atomic ratio  $U + Ca \approx Si$ ) followed by kaolinite-carbonate and then by feldspar with a high  $Cr$  content.

These formations are secondary, i.e. they are deposited from reactions between intergranular solutions and some primary minerals.

The farthest from radioactive equilibrium are boltwoodite (Fig.5) and membranous uraninite (Fig.6) of secondary thin veins in sample 12/326 from Severinovskoye deposit. A typical boltwoodite composition is characterized by atomic ratios  $U : Si : \sum(Na + K) = 1 : 1 : 1$  and composed of light elements which were differently interpreted:  $H, OH, H_2O, H_3O$ . According to the latest data on the boltwoodite structure [5], the ideal formula of the mineral is  $(K, Na)[(UO_2)(SiO_3)(OH)] \cdot 1.5H_2O$ . The characteristic property of boltwoodite from Ukrainian deposits discussed earlier [2,6,7] is that it has a high varying content of calcium or sometimes lead. As was shown in [6] and confirmed by our electron-microscopy studies, these elements are uniformly distributed in the mineral.

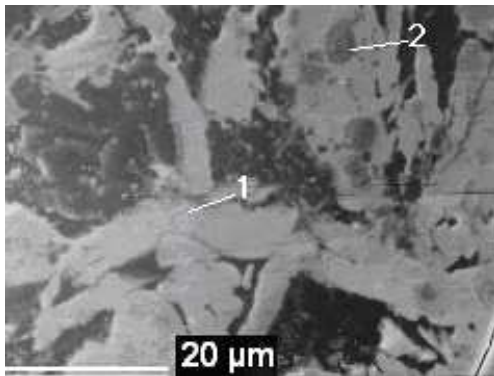
Our investigations of boltwoodite revealed its varying cation composition and some features in X-ray powder pattern (Table 3) suggesting the existence of alternating uranophane and boltwoodite layers in the mineral crystals. On the average, in 10 runs atomic ratios in the  $K : Ca : Na$  mineral were roughly 1:2 and 3:3 (with the mean error of about 10% for each value). Another series of 6 analyses demonstrated approximately equal atomic contents of calcium and sodium, but the absence of potassium.

The boltwoodite was unambiguously identified by the powder diffraction pattern (Table 4). As compared with standard data, it should be noted that the strong  $\approx 3.40 \text{ \AA}$  line is absent. This line is also absent in the Ca-boltwoodite patterns given in [6]. According to modern approach [9] it can be interpreted as structure disorder along the a-axis, i.e. normal to the layers.

Uraninite in the form of thin veins is observed in albite crystals to develop frequently along the cleavage planes. Sometimes inside the veins calcite is present. At the boundary between the uraninite and accommodating albite one can discern zones of yellow mineral - uranophane or Ca-boltwoodite. The nature of the uraninite vein is seen in electron micrographs (Fig. 6).

**Table 2.** The Degree of Nonequilibrium and Phase Composition of the Uranium Mineralization of Samples Examined

No	Ore deposit Sample No	Pre- sence Th 232	Nonequili- brium by $^{238}\text{U}$	Uranium minerals	Estimated mini- mum crystal- lite size, $\mu\text{m}$
1	Vatutinskoye, 43/163	+	$0.870\pm 0.028$	Margins of fine-grained mica-coffinite aggregates around the potassium feldspar	1
2	ibid., 50/228	-	$0.939\pm 0.024$	Fine-grained uranite and sorbed uranium	10
3	ibid., 62/228	-	$0.897\pm 0.029$	Fine growth of coffinite, boltwoodite and relict uraninite	10
4	Severinovskoye, 5/326	-	$0.907\pm 0.023$	Brannerite in association with apatite and zircon	0.5
5	ibid., 7/326	-	$0.907\pm 0.025$	Coffinite, haiweeite	1
6	ibid., 12/326	+	$0.903\pm 0.028$	Uranium addition in zircon, scattered uranium in iron oxides and pyrite	40
6b	ibid., 12/326	-	$0.787\pm 0.028$	Microveins of boltwoodite	0.00007
6u	ibid., 12/326	-	$0.787\pm 0.023$	Microveins of secondary uraninite	0.5
7	Michurinskoye, 5/106	-	$0.866\pm 0.026$	Fine-growth of brannerite with non-metalliferous minerals	3
8	ibid., 34/132	-	$0.913\pm 0.026$	Coffinite	10
9	ibid., 82/132	+	$0.812\pm 0.026$	Growth of brannerite with U-bearing titanosilicates of calcium and lead	5
10	Ore mineralization, 5727	-	$0.958\pm 0.027$	Uraninite	10
11	ibid., 6007	+	$0.985\pm 0.028$	Fine-grained uraninite	10
12	ibid., 6025	+	$0.947\pm 0.037$	Fine-grained uraninite	10



**Fig. 3.** SEM-photograph of the brannerite ore, sample 82/132, Michurinskoye ore deposit. Elastically scattered electrons. 1: light elongated crystals of brannerite; 2: overgrowing mineral inclusions with a smaller average atomic number

At the albite - uraninite boundary there are microspherules ( $0.5-3\ \mu\text{m}$ ) of uranium mineral. Atomic - molecular ratios in the spherules are approximately as follows:  $U : Si : (Ca + Na) \approx 1 : 1 : 1$ . On the albite surface, under spherical particles there are

small pits of depth roughly equal to half-diameter of the droplets - traces of albite corrosion by the ore solution (Fig.6).

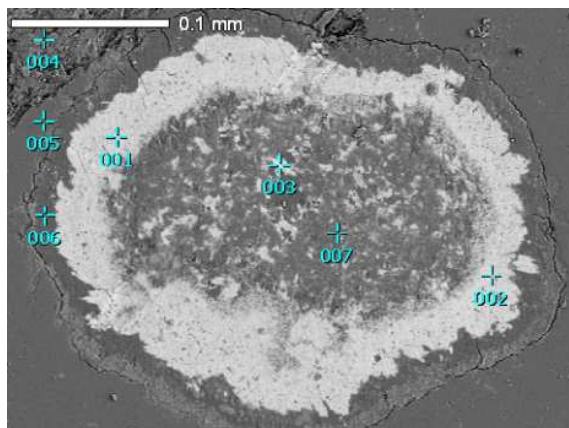
**Table 3.** Average composition of U minerals in sample 82/132 from Michurinskoye ore deposit. Brannerite (Fig.3;1), Titanosilicates of Ca, Fe, and Pb (Fig.3;2)

Component	Fig.3; 1 content	Fig.3; 2 content
PbO, wt.%	$6.17\pm 0.18$	$17.5\pm 0.65$
UO <sub>2</sub> , wt.%	$39.2\pm 2.1$	$0.77\pm 0.23$
CaO, wt.%	$3.15\pm 0.12$	$5.44\pm 0.95$
SiO <sub>2</sub> , wt.%	$2.31\pm 0.87$	$33.3\pm 1.23$
TiO <sub>2</sub> , wt.%	$24.5\pm 2.68$	$28.6\pm 1.13$
FeO, wt.%	$2.08\pm 0.27$	$4.01\pm 0.26$
Pb, rel.at.abun.	$1.64\pm 0.07$	$2.45\pm 0.92$
U, rel.at.abun.	$8.81\pm 0.88$	$0.09\pm 0.03$
Ca, rel.at.abun.	$3.37\pm 0.04$	$3.06\pm 1.15$
Si, rel.at.abun.	$2.32\pm 0.18$	$17.3\pm 6.52$
Ti, rel.at.abun.	$17.8\pm 1.14$	$11.1\pm 4.2$
Fe, rel.at.abun.	$1.67\pm 0.16$	$1.75\pm 0.66$

The secondary minerals are extremely fine-grained being formed under the action of fluids, which can also facilitate the loss of recoil atoms.

The X-ray pattern of an uraninite microfraction only exhibits lines based on the structure of this mineral, the uraninite having a lower unit cell parameter,  $a_0 = 5,37 \text{ \AA}$ , corresponding to an oxidized uraninite variety with approx. Composition  $UO_{2.25}$ . Microprobe analyses of the uraninite composition reveal three components:  $U - Ca - O$ . On the average, the Ca content obtained from 20 measurements is roughly 35 at.%. The presence of  $Ca$  in the composition of geological young uraninites from deposits of the sodium - uranium formation in Ukraine was first suggested by G.V. Kopchenova et al. [10]. These authors also found a lower unit cell parameter ( $a_0 = 0.537 \text{ nm}$ ) for a mineral from Severinovskoye ore deposit.

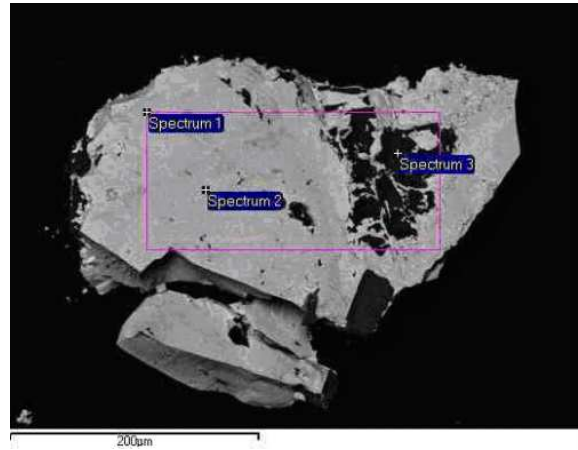
Experimental data [11] are consistent with a possible calcium component in the uraninite structure, though certain very high calcium content is likely to indicate a mineral calcite addition.



**Fig.4.** Fine-grained coffinite ore from Vatutinskoye deposit (sample 43/163). Analysis at points 001 and 002 correspond to the coffinite composition with carbonate additions. See details in the text

for Fig.4.

El.	001	002	003	004	005	006	007
Na, at.%				2.1	1.8		
Al, at.%				2.8	2.4	3.6	2.6
Mg, at.%		0.8	0.9				
Si, at.%	5.6	5.4	7.5	9.1	7.6	8.8	8.9
K, at.%			0.3				2.3
Ca, at.%	2.3	3.1	0.4		0.2		
Cr, at.%					2.4		
Fe, at.%		0.1			0.1	0.3	
Sr, at.%	0.4	0.3	0.1	0.2	0.1	0.3	0.1
Sn, at.%			0.5				
Pb, at.%	0.7	0.7	1.1	0.3	0.3	0.5	0.3
U, at.%	3.8	3.2	2.2	0.0	0.0		0.3



**Fig.5.** An essentially boltwoodite particle from a vein (photographed using elastically scattered electrons) and point microanalysis data. Note: Spectrum 1: Ca - boltwoodite; spectrum 2: uraninite; spectrum 3: albite

for Fig.5.

El.	S1 wt.%	S2 wt.%	S3 wt.%	S1 rel.at.	S2 rel.at.	S3 rel.at.
C		7.75	4.73			
O	33.4	24.6	58.6			
Na	2.34		8.13	0.47		1.39
Al	2.27		7.13	0.39		1.04
Si	6.61	1.36	21.4	1.09	0.18	3.0
Ca	3.76	4.41		0.43	0.43	
Pb		0.98			0.05	
U	51.6	60.9		1	1	

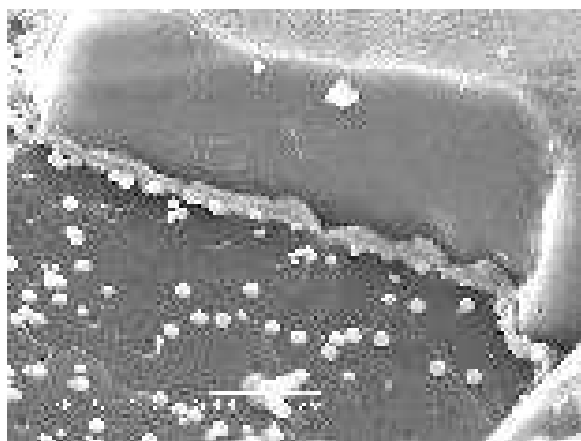
**Table 4.** Calculations and interpretations of the boltwoodite (BW) power pattern. Note: \*, addition, interplanar lines correspond to the most pronounced b-uranophane maxima: (020) and (040)+(131), respectively, \*\*, indices in [9]

BW I	examined d/n, A	BW I	from[8] d/n, A	hkl**
1	7.63*	2	7.53*	
7	6.71	10	6.81	100
		5	6.4	001
1	5.4	5	5.45	101
5	4.72	4	4.74	011
1	4.31	4	4.32	111
		2	4.11	101
2	3.9*	1	3.91	
		1	3.75	
5	3.53	7	3.54	020
		9	3.40	200
1	3.14	5	3.13	120
10	2.92	8	2.92	112, 012

## 5. DISCUSSION

All samples examined were found to deviate from radioactive equilibrium for two possible reasons: (1) young geologic age of the ore which has not yet reached equilibrium and (2) geochemical transforma-

tions of the ore with addition or loss of the above-mentioned isotopes ( $^{234}\text{U}$ ,  $^{230}\text{Th}$ , and  $^{231}\text{Pa}$ ) or new portions of "primary uranium".



**Fig.6.** Membranous uraninite (light) developing on albitite (grey). SEM-photograph. Scale is  $10\ \mu\text{m}$

The first reason cannot be accepted for all samples except membranous uraninite because of a considerable content of lead which, according to the literary data on the isotope composition [1], has a radiogenic origin. Estimating the age of minerals by the lead content, one obtains values in excess of billion years. Since the mineralogical studies do not permit any conclusions concerning the addition of "primary" uranium, the most probable cause for the departure from radioactive equilibrium is the loss of recoil atoms. The  $\alpha$ -decay in a host crystal is accompanied by excitation of atoms in the volume of about  $1\ \text{nm}^3$  [12]. The probability that a recoil atom from this decay event as well as such atoms produced earlier, would escape from the crystal, depends on the initial position of the atom with respect to the crystal surface or structural inhomogeneity (e.g. interlayer distance along which water or other fluids can flow facilitating a removal of the recoil atom from the crystal). The most favourable structure for the loss of recoil atoms from crystals is that of boltwoodite where parallel (100) layers of uranium and silicon-oxygen polyhedrons are bonded by large  $K$ ,  $Na$ , or  $Ca$  cations. The interlayer space with large cations, as is well known from studies of mica and other layered silicates, is a place where ion-exchange phenomena occur.

In membranous uraninite which is as nonequilibrium as boltwoodite, there are no obvious structural features favouring a removal of decay products. Its composition has two distinctive characteristics: presence of high calcium content and absence of lead. Hence one may suggest that this mineral is geologically young and the structurally unexplainable high calcium content is due to thin calcite ingrowths providing a very developed surface of the mineral. The closest approach to radioactive equilibrium of relatively large uraninite grains can be given a reasonable explanation from two points of view: (i) "closed" coordination atomic structure of the mineral and (ii) grain size exceeding by at least 4 decimal orders the

dimensions of mineral structure regions "activated" by the  $\alpha$ -decay. The intermediate value of nonequilibrium is characteristic of ores composed of coffinite and brannerite, with the extent of deviation for coffinite ores being normally lower than that for brannerite. This may be attributed to a more "closed" nature of the coffinite structure which is, on the whole, near to isotropic. At the same time, the brannerite structure is of a layer type produced by alternating octahedral  $\text{TiO}_6$  layers interlaid by more "loose" uranium octahedron layers. Supposedly this anisotropic structure facilitates the migration of "activated" recoil atoms along the "loose" layers.

## 6. CONCLUSIONS

1. Ancient uranium ores from the Ukrainian Shield were found to have appreciable deviations from radioactive equilibrium. An oversight of this fact may negatively affect the uranium content data measured by radiometric methods.

2. The extent of the deviation from radioactive equilibrium correlates with the mineral composition of the ores. A possible explanation is that the minerals grain permeability to fluids facilitating the removal of intermediate decay products, depends on the particular atomic structure and defects in real crystals.

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### **ВЛИЯНИЕ МИНЕРАЛЬНОГО СОСТАВА ДРЕВНИХ УРАНОВЫХ РУД УКРАИНЫ НА СТЕПЕНЬ НАРУШЕНИЯ РАДИОАКТИВНОГО РАВНОВЕСИЯ**

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Установлено, что степень радиоактивной неравновесности руд растёт вдоль следующего тренда изменения минерального состава: относительно крупнозернистый уранинит ( $UO_{2 < n < 2,25}$ ) - коффинит ( $USiO_4$ ), браннерит ( $UTi_2O_6$ ) - вторичные мелкозернистые коффиниты, браннерит - вторичные минералы тонких прожилков - болтвудита ( $(Ca, Na, K)(UO_2)[SiO_3OH] \cdot 1.5H_2O$ )), плёночный уранинит ( $UO_{2.25}$ ). Это объяснено различной степенью потери кристаллами радиоактивных атомов отдачи, что определяется как особенностями реальных кристаллов, так и атомной структурой минералов.

### **ВПЛИВ МІНЕРАЛЬНОГО СКЛАДУ ДРЕВНІХ УРАНОВИХ РУД УКРАЇНИ НА СТУПІНЬ ПОРУШЕННЯ РАДІОАКТИВНОЇ РІВНОВАГИ**

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Установлено, що ступінь радіоактивного порушення рівноваги руд росте уздовж слідуючого тренду зміни мінерального складу: відносно грубозернистий уранініт ( $UO_{2 < n < 2,25}$ ) - коффініт ( $USiO_4$ ), бранерит ( $UTi_2O_6$ ) - вторинні дрібнозернисті коффініти, бранерити - вторинні мінерали тонких прожилків - болтвудиту ( $(Ca, Na, K)(UO_2)[SiO_3OH] \cdot 1.5H_2O$ )), плівковий уранініт ( $UO_{2.25}$ ). Це пояснюється різним ступенем втрати кристаллами радіоактивних атомів віддачі, що визначається як особливостями реальних кристалів, так і атомною структурою мінералів.