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EVALUATION OF A CALCIUM-RICH URANINITE COMPOSITION BY ELECTRON AND PROTON MICROPROBE

Calcium uraninite, a late stage uranium ore mineral, was collected from the central part of the Ukrainian Shield (Severinovskoje deposit) and has been characterized using SEM-EDX and micro-PIXE techniques. The major (U, Ca) and minor (Si, Na, Al, V) element contents determined by micro-PIXE were found to agree with SEM-EDX data and indicate that the Na, Al and Si contents are due to admixtures of albite ($NaAlSi_3O_8$). In addition, micro-PIXE was used for the first time to detect and quantify trace elements (Pb, Cu, Mg) within the same mineral grains, and assuming radiogenic origin of the lead, allowed an age determination of the calcium uraninite of 137 ± 50 Ma.

Keywords: calcium uraninite, minor elements, trace elements, proton microprobe, electron microprobe.

Introduction. Uraninite with a high calcium content was found in the ores of albitite-uranium deposits in the central part of the Ukrainian Shield by E.V. Kopchenova and co-authors [3]. Investigation by electron microscopy [2] showed that the mineral was homogeneous and had the stoichiometric ratio of Ca : U = 1 : 2. The powder diffraction pattern is the same as for uraninite with some lover meaning of a_0 = 0.537 (±0.001) nm. It is assumed that the mineral has a fluorite type structure [1, 4] and a composition of $CaU_2O_{6.24}$ [2]. This mineral appears to be a new variety of uraninite, uraninite-(Ca), and it is typical for the ores of the sodium-uranium deposits of the central part of Ukraine.

The goal of this investigation was to study the elemental composition of this new variety of uraninite, including the trace element content. In modern mineralogy, the electron microprobe is widely used, while use of the proton microprobe is relatively rare. Our additional goal here was to demonstrate the capabilities of the proton microprobe in ore mineralogy.

Material. We examined ore minerals from the Severinovskoje deposit from the same sample which was studied in [2]. The mineral forms are either a thin film (Fig. 1, *a*) or spherules (Fig. 1, *b*) on the cleavage planes of former potassium feldspars replaced by the albite. Six film fragments of uraninite-(Ca) were separated from the natural substrate using a steel needle (Fig. 2) and analyzed by electron probe microanalysis (EPMA) and proton microprobe using the particle induced X-ray emission (PIXE) technique, in a scanning regime known as micro-PIXE [8].

Methods. The information about morphology, composition and concentration of base elements to include in the six fragments of uraninite-(Ca) was obtained using EPMA Camscan-S4 SEM-EDX (Oxford). The images of all fragments in reflected electrons were received. The fragments revealed to be uraninite-(Ca) with albite inclusions (Fig. 2). The concentrations of elements in uraninite-(Ca) were obtained in 26 points (from 2 to 6 points in each fragment).

Micro-PIXE measurements were carried out at the scanning nuclear microprobe facility of the Institute of Applied Physics of the National Academy of Sciences of Ukraine, Sumy [7]. A proton

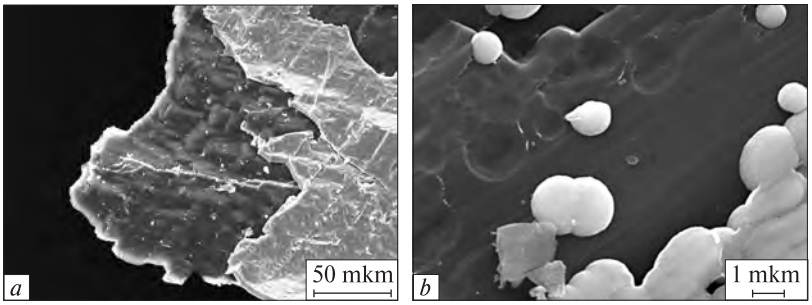

Fig. 1. SEM images in the reflected electrons obtained by the electron microscope JSM 60601A. The scale bars are 50 mkm (*a*) and 1 mkm (*b*). The light areas are uraninite-(Ca), while the grey areas are albite

beam of MeV energy generates many orders of magnitude less brehmsstrahlung radiation than keV energy electron beam, giving PIXE an analytical sensitivity of some orders better than the elemental sensitivity of EPMA. Sections of all six fragments, with a characteristic size of 100—200 μm were scanned using a proton beam with energy $E = 1.5$ MeV. Probe dimensions were about 5×3 μm^2, and variation in the collected charge was $Q = 4—8 \times 10^{-10}$ C/pixel. The scan region was 50×50 pixels^2, with scanning steps of 2 μm and 4 μm. The experimental setup consisted of a Si(Li) X-ray detector with a conventional Be window with an area of 25 mm^2 and a resolution of 190 eV for elements $Z \geq 11$. This micro-PIXE technique allows the characterization of elemental composition and the mapping of element distributions in the sample. The collective PIXE spectra from the scan region of interest were processed using the GUPIXWIN program (ver. 2.2.3) [6]. Although the Si(Li) X-ray detector with conventional Be window does not allow detection of oxygen, it was assumed that all fragments contained oxygen and was therefore included in the fitting procedure for the sample model as an "invisible" element. In the following results we compared conventional microanalysis by EPMA with the above micro-PIXE technique which is utilized at the Sumy scanning nuclear microprobe facility.

Results and discussion. Six fragments of uraninite-(Ca) film were analyzed. Grain morphology and elemental composition were determined by SEM-EDX. Elemental distribution and determination of major and trace elements were accomplished by micro-PIXE. The results for fragment 2 (Fig. 2) are presented in detail.

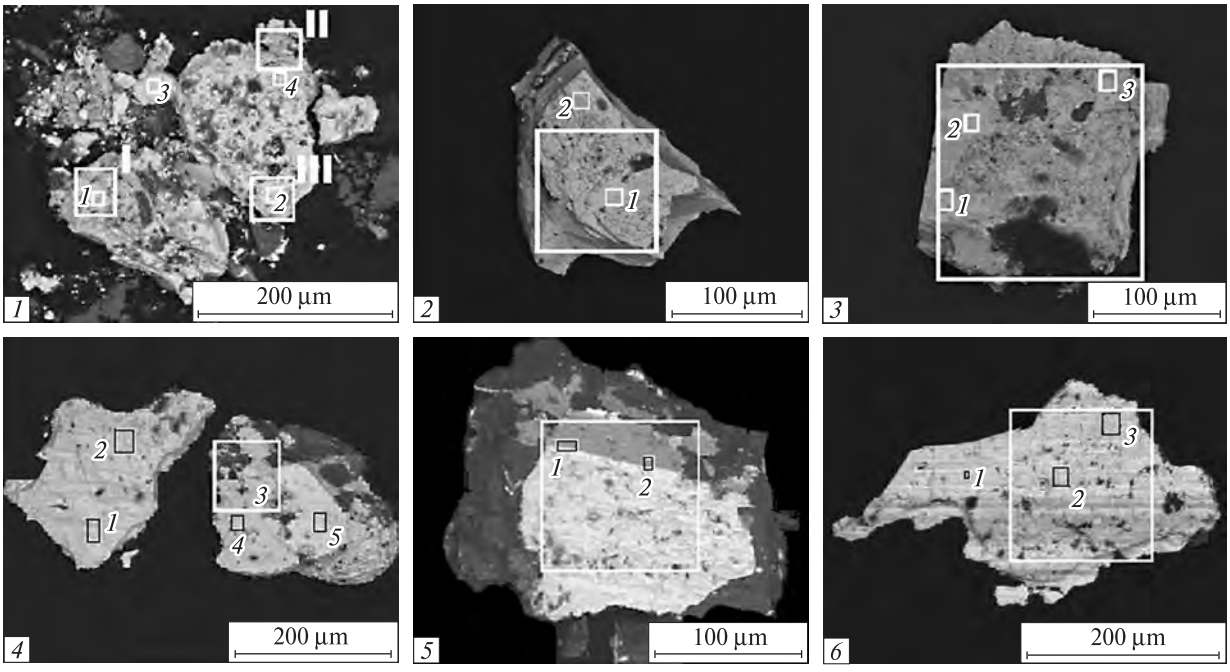

Fig. 2. The SEM images of analyzed uraninite-(Ca) grain fragments. The numbers of fragments (left corners of photos) and locations of analyzed areas are shown. The larger squares show areas scanned by micro-PIXE and the smaller rectangles show areas analyzed by EPMA. The numbers of electron spectra are also shown. One can see the growth of uraninite-(Ca) (light) and albite (dark grey). Uraninite-(Ca) forms the thin layers on the albite (No 2, 5 and others)

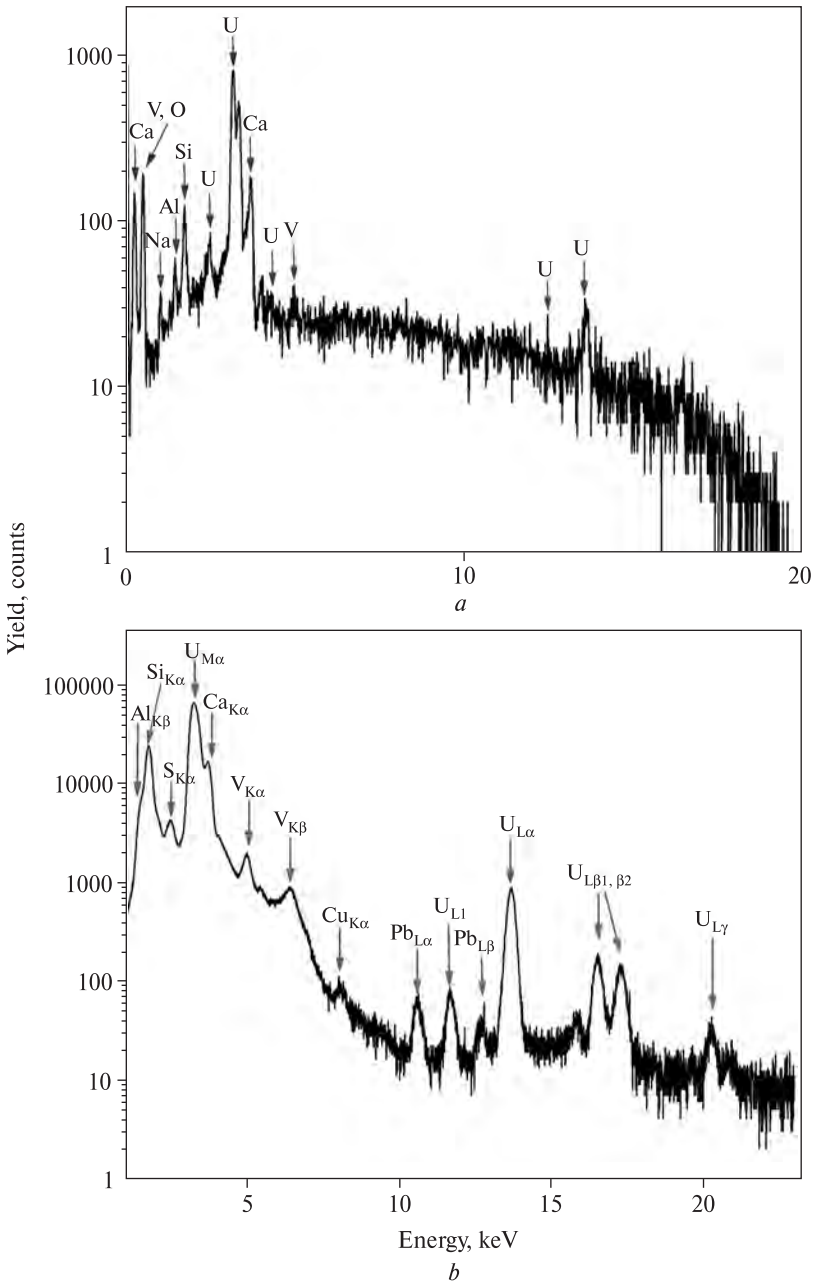

Fig. 3. SEM-EDX (*a*) and micro-PIXE (*b*) spectra (in log scale) obtained from the squares of fragment 2 shown on Fig. 2

Table 1. **The concentrations of elements in fragment 2, obtained by EPMA and micro-PIXE, mass %**

	O	Na	Al	Si	S	Ca	V	Pb	U	Cu
SEM-EDX, area 1	24.06	0.55	0.42	1.75	—	4.74	—	—	68.48	—
Statistical error, %	0.81	0.21	0.15	0.16	—	0.22	—	—	0.82	—
SEM-EDX, area 2	27.56	0.8	0.51	2.14	—	4.68	—	—	64.31	—
Statistical error, area 2, %	0.77	0.2	0.14	0.16	—	0.21	—	—	0.77	—
Micro-PIXE	18.11	—	0.61	2.2	0.5	8.3*	0.8	1.4	67.5	0.11
Statistical error, %	1.18	—	3.84	0.73	5.54	1.24	6.01	8.24	1.18	4.39

N o t e.* One can see in both Table 1 and Table 2 that the concentration of Ca determined by micro-PIXE is much higher than the same determined by EPMA. This is possibly the peculiarities in the GUPIXWIN program which does not correctly resolve the Ca_K and U_M lines due to differences between the theoretical and experimental cross-sections for the uranium *M*-line.

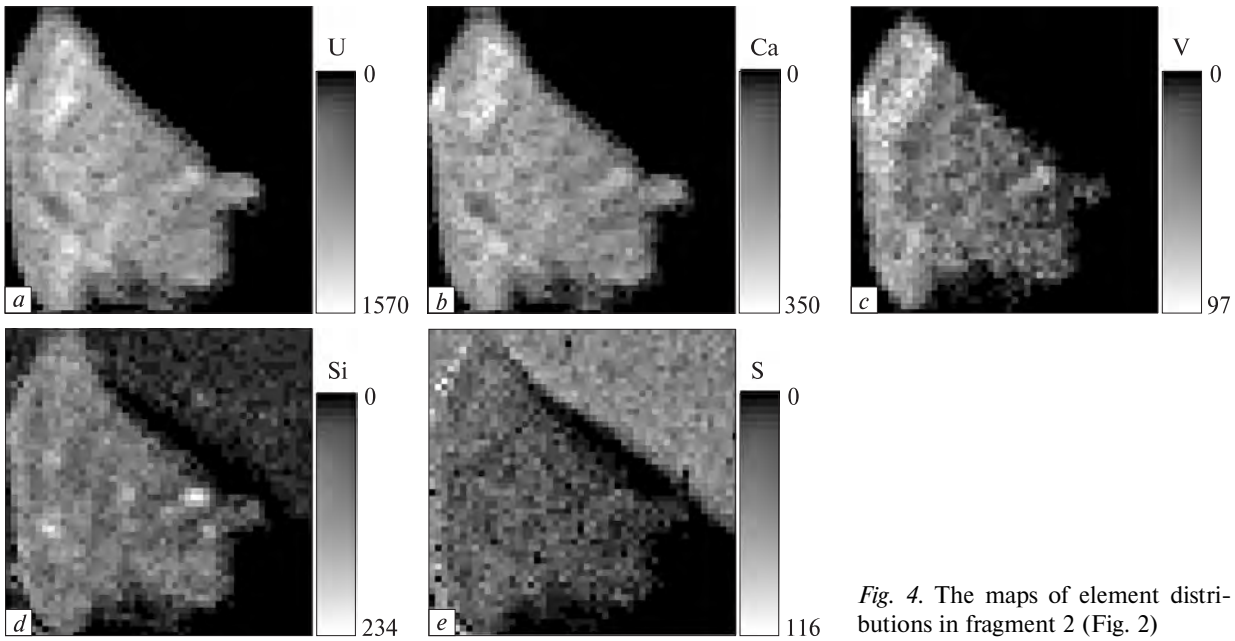

Fig. 4. The maps of element distributions in fragment 2 (Fig. 2)

Fig. 3 shows the X-ray spectrum obtained by proton activation of fragment 2. For the other fragments, results are presented in Tables.

The distributions of U, Ca, V, Si, and S were also determined and the element maps are shown in Fig. 4, where the scale indicates the X-rays counts in each pixels which is proportional to element concentration.

The distributions of U, Ca and V are similar (Fig. 4, *a*—*c*) and these elements are important components of uraninite-(Ca). Differences of visible element concentrations are likely caused by differences in the film thickness of the mineral. The Si distribution (Fig. 4, *d*) shows some additional maxima not seen in the U, so the Si distribution likely reflects a fragment of albite substrate or inclusion, not uraninite-(Ca). The S distribution (Fig. 4, *e*) shows the maximum concentration beyond the contour of the uraninite-(Ca) grain and reflects the composition of the backing plate.

A comparison of element concentrations for fragment 2 by SEM-EDX and micro-PIXE are presented in Table 1.

The data obtained by these methods show satisfactory agreement with the exception of Ca (see note in Table 1).

The lower background of the micro-PIXE technique allows determination of trace elements Cu and Pb. Table 2 shows the average results of quantitative elemental analysis of uraninite-(Ca) by micro-PIXE and EPMA. In addition to the main mineral elements (U, O, Ca), small amounts of Na, Al and Si were detected in both EPMA and micro-PIXE. This was probably caused by the capture of enclosed albite owing to breaks in the thin

Table 2. **The average concentration of elements in uraninite-(Ca)**

Element	SEM-EDX		Micro-PIXE	
	C, mass %	Statistical error, %	C, mass %	Statistical error, %
Na	0.80	0.23	—	—
Al	0.40	0.1	0.93	0.16
Si	1.67	0.23	3.77	0.55
S	—	—	0.25	0.07
Ca	4.82	0.19	8.88*	0.74
V	0.66	0.12	1.06	0.1
Fe	—	—	0.07	0.03
Pb	—	—	1.26	0.11
U	63.26	0.76	63.87	0.99
Cu	—	—	0.08	0.03

N o t e.* See note to Table 1.

Table 3. **The U/Pb age estimation for uraninite-(Ca)**

Number fragment	Pb	U	*t*, Ma
	mass %		
1	0.78	61.2	91 ± 7
2	1.40	67.5	147 ± 12
3	1.84	64.0	202 ± 13
4	1.14	68.3	118 ± 8
5	1.23	61.4	142 ± 6
6	1.15	62.5	130 ± 7

uraninite film. Vanadium was detected by both techniques: 0.66 ± 0.12 mass % by SEM-EDX and 1.06 ± 0.1 mass % by micro-PIXE. From this, we conclude that this element is a regular admixture in this mineral.

The PIXE technique in which characteristic X-ray radiation is stimulated by protons appears to be more sensitive for determination of low concentration elements. In all spectra obtained by micro-PIXE the lead contents were found to be from 1.27 to 1.84 mass %. But lead was only detected once using SEM-EDX, at 1.42 mass %.

Assuming a radiogenic origin for the lead, we used the micro-PIXE measurements to estimate the age of the mineral. The isotopic composition of lead in ore deposits in this region support this assumption [5]. The age of the uranium mineral was calculated using the ratio of uranium and lead, using the following constants: ^{238}U isotope content of uranium is $k_1 = 0.9927$, and the ^{235}U isotope is $k_2 = 0.0072$, with half-lives of $T_1 = 4.47 \cdot 10^9$ years and $T_2 = 0.7040 \cdot 10^9$ years, respectively. If the content of uranium is U ppm (g/t), then the number of atoms of ^{238}U is proportional to $U_1 = k_1 \cdot U/238$, and ^{235}U is proportional to $U_2 = k_2 \cdot U/235$. For time t, the number of atoms formed from ^{238}U decaying to ^{206}Pb is proportional to $Pb_1 = U_1 [\exp(\lambda_1 \cdot t) - 1]$ and the atoms of ^{207}Pb formed from the decay of ^{235}U is proportional to $Pb_2 = U_2 [\exp(\lambda_2 \cdot t) - 1]$ where $\lambda_1 = \log 2/T_1 = 0.1551 \cdot 10^{-9}$ years^{-1}, $\lambda_2 = \log 2/T_2 = 0.9846 \cdot 10^{-9}$ years^{-1}. Assuming negligible ^{204}Pb and Th (^{208}Pb) in this ore, $Pb = 206 \cdot Pb_1 + 207 \times Pb_2$. This equation with one unknown allows us to define t using measured values of U and Pb. One of the numerical solutions for determining the interval $\Delta t = t_2 - t_1$ where the function $f(t) = 206 \cdot Pb_1 + 207 \cdot Pb_2 - Pb$ changes the sign and the further shortening of the interval to divide half up to the required accuracy of t determination. Using the above coefficients, this equation is:

$$f(t) = [0.8593 \cdot \exp(0.1551 \cdot t) + 0.0063 \times \exp(0.9846 \cdot t) - 0.8656] \cdot U - Pb = 0,$$

where t is expressed in billions of years.

The age calculations for the six uraninite-(Ca) fragments studied by micro-PIXE are presented in Table 3. Excluding the two outliers, the average age of uraninite-(Ca) grains was $t = (137 \pm 50)$ million years old. This value is the estimation of the age of these mineral grains only but not the age of the deposit as a hollow.

Conclusions. The analysis of uraninite-(Ca) by EPMA and micro-PIXE techniques was shown. The main element concentrations obtained by both methods are similar. Some portion of the Ca content determined by micro-PIXE one can be explained by the defect of the spectrum analytical program GUPIXWIN which does not resolve the $Ca_{K\alpha}$ and $U_{M\alpha}$ lines.

For the first time vanadium was shown as a characteristic admixture element of the mineral. There are clear advantages in using micro-PIXE including the detection of the trace elements Mg, Pb, and Cu in uraninite-(Ca).

Assuming a radiogenic origin, lead determination allowed an age estimate of mineral formation of $t = (0.137 \pm 0.05)$ billion years old for the uraninite-(Ca).

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ДОСЛІДЖЕННЯ СКЛАДУ БАГАТОГО НА КАЛЬЦІЙ УРАНІНІТУ ЗА ДОПОМОГОЮ ЕЛЕКТРОННОГО І ПРОТОННОГО МІКРОЗОНДУВАННЯ

Кальцієвий уранініт, що є пізнім мінералом уранових руд, був відібраний з Северинівського родовища в центральній частині Українського щита і досліджений за допомогою методів сканувальної електронної мікроскопії та мікроаналізу (СЕМ-ЕМА) і протонного мікроаналізу (мікро-ПІКСІ). Значення концентрації головних (U, Ca) і елементів-домішок (Si, Na, Al, V), визначених цими методами, узгоджуються. Карти розповсюдження елементів за площинами зразків вказують, що вміст Na, Al і Si пов'язаний із включеннями альбіту ($NaAlSi_3O_8$). Завдяки методу мікро-ПІКСІ в тих самих мінеральних зернах вперше визначено кількість домішкових елементів (Pb, Cu, Mg). Припускаючи радіогенне походження свинцю, визначили вік мінералу — 137 ± 50 млн рр.

Ключові слова: кальцієвий уранініт, малі елементи, домішкові елементи, протонне мікрозондування, електронне мікрозондування.

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ИЗУЧЕНИЕ СОСТАВА БОГАТОГО КАЛЬЦИЕМ УРАНИНИТА С ПОМОЩЬЮ ЭЛЕКТРОННОГО И ПРОТОННОГО МИКРОЗОНДИРОВАНИЯ

Кальциевый уранинит — поздний минерал урановых руд, был отобран из Севериновского месторождения в центральной части Украинского щита и исследован с помощью методов сканирующей электронной микроскопии и микроанализа (СЭМ-ЭМА), протонного микроанализа (микро-ПИКСИ). Значения концентрации главных (U, Ca) и элементов-примесей (Si, Na, Al, V), определенные этими методами, согласуются. Карты распределения элементов по площади образцов показывают, что содержание Na, Al и Si связано с подложкой и включениями альбита ($NaAlSi_3O_8$). Благодаря методу микро-ПИКСИ в тех же минеральных зернах впервые определено количество примесных элементов (Pb, Cu, Mg). Предполагая радиогенное происхождение свинца, определили возраст минерала — 137 ± 50 млн лет.

Ключевые слова: кальциевый уранинит, малые элементы, примесные элементы, протонное микрозондирование, электронное микрозондирование.