

TO MINERALOGY OF TETRAVALENT URANIUM

Olga A. Doynikova

*IRAS Institute of geology of ore deposits, petrography, mineralogy and geochemistry
RAS (IGEM), Moscow, doa@igem.ru*

Galina A. Sidorenko

FGUP All-Russian Research Institute of Mineral Resources, Moscow, vims@df.ru

On the basis of the author experimental data and analysis of literature, modern state of mineralogy of tetravalent uranium is considered. New and little known results are obtained due to utilization of local methods of analytical electron microscopy (AEM). More thorough mineralogical investigations from optical level to electronic level not only widened range of U^{4+} minerals, showing possibility of existence of U^{4+} -phospho-silicates, but also allowed us to say more definitely about structural relation of Ca and U^{4+} in these minerals.

5 figures, 1 table, 28 references.

Keywords: minerals of tetravalent uranium, U^{4+} -phosphates.

Introduction

In mineralogical data base are noted about 200 mineral species, in which uranium is structure-forming element. From all big quantity of uranium minerals we know less than ten minerals of tetravalent uranium. Among them are wide known: uraninite, coffinite, brannerite. By these three mineral species of U^{4+} , as a rule, the interest of geologist to mineralization of primary (non oxidized) uranium ores is restricted. U^{4+} phosphates – ningyoite and three minerals of lemontovite group are less known. Such approach does not simply “impoverish” mineralogy of uranium ores, but is not always correct. Moreover, incomplete mineralogical study of the ores might result in erroneous interpretation of their genesis, on the one hand, and incorrect assessment of physical – chemical (technological) properties of ore, on the other hand. As far as these problems have very important significance, the necessity arises for consideration of modern status of mineralogy of tetravalent uranium.

Uranium as chemical element has such structure of outer electronic shell ($5f^36d7s^2$), which allows him to form ions of different valency – from 2^+ to 6^+ . As a result, uranium in each valent state forms definite, corresponding only to this state specific compounds. Under natural conditions compounds of U^{4+} and U^{6+} are stable.

During many years in mineralogy it was considered, that U^{5+} cannot form stable compounds and therefore there are not in nature minerals of pentavalent uranium. At present moment publications about existence of minerals with U^{5+} in their composition are already known, but the problem of definite determina-

tion of such valent state of uranium is not solved. The presence of U^{5+} in composition of nature uranium oxides was established due to data of X-ray photoelectronic spectroscopy (XPhES), however taken as standards natural samples, by our opinion, were not sufficiently studied (Teterin *et al.*, 1981). Later the data were published regarding synthesis of stable compound of pentavalent uranium U^{5+} , and then also about finds of natural mineral wyartite (Burns, Finch, 1999), in whose composition enters U^{5+} . Proof of presence of pentavalent uranium in composition of this water-bearing calcium-uranium uranyl-carbonate, obtained during determination of mineral structure, is indirect – crystallochemical. It is based on geometry of polyhedrons and sum of valency bonds of one of uranium positions in structure, requiring presence here of U^{5+} for electrically neutral balance of valencies. The other valence states of uranium are displayed only in laboratory syntheses. Thus, under natural conditions at present are trustworthily known compounds of tetra- and hexavalent uranium.

Speaking about uranium mineralogy, it worths first of all to underline, that behaviour of this element in geological processes is in principle different for its different valence states. Minerals of tetravalent uranium U^{4+} are formed under reduction geochemical environment, and minerals of U^{6+} – under oxidized one.

By their chemical properties ions of U^{4+} and U^{6+} are so different, that each of them forms compounds on principle different type both by crystal structure, morphology and by physical-chemical properties. During mineral formation U^{4+} behaves as typical cation, demonstrating isomorphism with Th and REE,

more rarely with Ca. Differing from it, cation U^{6+} is not typical and usually is represented in nature as linear ion $(U^{6+}O_2)^{2+}$ – uranyl. It is unique ability of U^{6+} to create specific uranyl-ion that determines individuality of its compounds. As a result it is necessary to consider independently and separately mineralogy of tetravalent and hexavalent uranium.

Mineralogy of uranyl (U^{6+}) differs by very wide spectrum of mineral species (about 170), formed as a result of its contrast and energetic water migration under conditions of hypergenesis. These exogenic (so called secondary) minerals of hexavalent uranium strongly reflect conditions of ore formation (Sidorenko, Doynikova, 2009).

Mineralogy of uranium U^{4+} is rather limited as regards a number of mineral species composing it (until now less than 10, and real number of mineral species of U^{4+} might be greater, but their revealing requires utilization of modern methods of mineralogical analysis). However exactly minerals of tetravalent uranium are practically the most important components of mineral raw material for atomic industry. Therefore just mineralogy of U^{4+} attracts special attention.

Up till now this division of mineralogy was restricted only by three mineral species. They are – oxide *uraninite* and its morphological varieties: collomorphic *nasturan* (pitchblende) and highly dispersed powder *uraninite*, silicate *coffinite* and titanate *brannerite*. At the end of 20th century these commercially significant mineral species were added by Ca- U^{4+} -phosphate *ningyoite* (Doynikova, 2007). Besides there were discovered U^{4+} -phosphates (Belova *et al.*, 1998) – *lermontovite*, *vyacheslavite*, *orfoite*, later united into mineral group of *lermontovite* (Doynikova, 2005), they are represented by separate single finds. It is noteworthy to recall also earlier single finds of *sedovite* and *mourite*, known as molybdates of U^{4+} (Sidorenko, 1978), which are not still sufficiently studied and represent only scientific interest. Coexisting in their structure simultaneously of reduced (U^{4+}) and oxidized (U^{6+}) uranium forms, as well as the most oxidized form of molybdenum Mo^{6+} , seems to be geochemical groundless. Taking into consideration high dispersion of this formations, at present it is necessary to do their additional study using modern methods.

While considering of mineral species, composing the class of minerals of tetravalent uranium, we shall expose only new or little known information, which adds known handbook data. Such information was obtained

during last decades as a result of developing of mineralogical investigations and transferring from the level of optical microscopy to the level of electronic one. Analytical electronic microscopy (AEM) allows us to study both composition of the finest mineral formations and diffraction characteristics of micron particles (microdiffracton of electrons). Study of complex for traditional diagnostics uranium ores with the help of highly local methods of AEM (transmission and scanning), in fact – investigation of micromineralogy, led to accumulation of new knowledge about U^{4+} -minerals, to refinement of their isomorphic transformations.

About well known minerals of tetravalent uranium

Uraninite – a single representative of uranium oxides in nature. All above mentioned its morphological varieties have the simplest cubic crystal structure of fluorite type with idealized crystallochemical formula UO_2 . Some varieties are known with isomorphic admixtures of rare earth elements of cerium group (cleveite) or thorium Th (to uranothorianite).

During study of exogenic (so called black's) ores with the help of transmission AEM it was observed very wide spectrum of degree of uraninite crystallization in them. Finely dispersed character of uranium oxide segregation in composition of uranium blacks facilitates in its quick oxidation. Process of oxidation decreases degree of particles crystallinity at the expense of increase of structure dislocations during oxidation (without uranyl forming). According to patterns of electron microdiffraction (from spot to circle ones) one can observe decreasing of structural perfection of uranium-oxide substance right up to electron amorphous state (Fig. 1a). Electron amorphous segregations of uraninite occur in natural samples rather often. In such case mineral is diagnosed by means of element composition of particles, determined directly under electron microscope. In composition of poorly crystallized dispersed uraninites (with diffused circular reflections) rather often is present admixture of silicon; alongside with decrease of crystallinity degree quantity of Si increases. Entering of Si in composition of the mineral in this case is caused by high sorption properties of dispersed matter, it should not be related to uraninite structure.

At a number of deposits uranium-oxide substance was found as mineraloid, glass-like

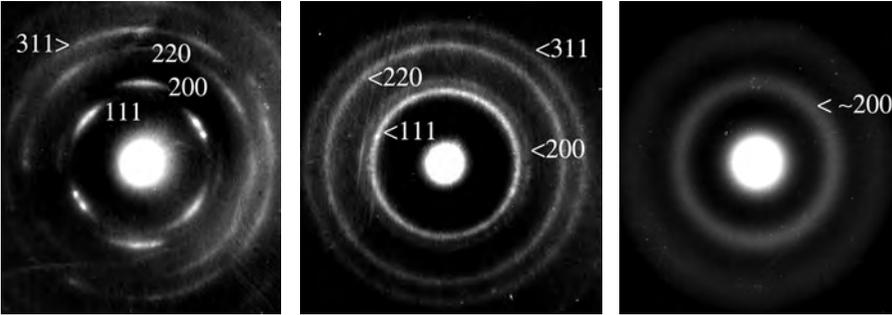
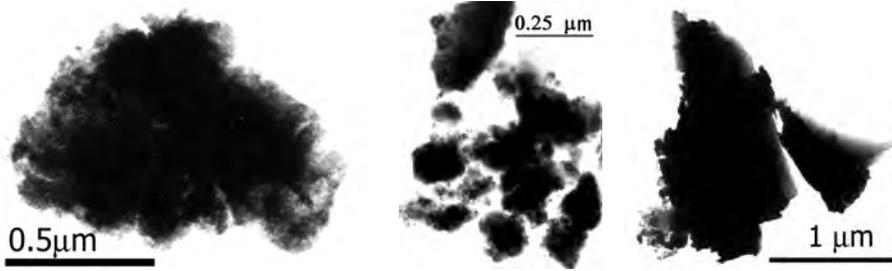
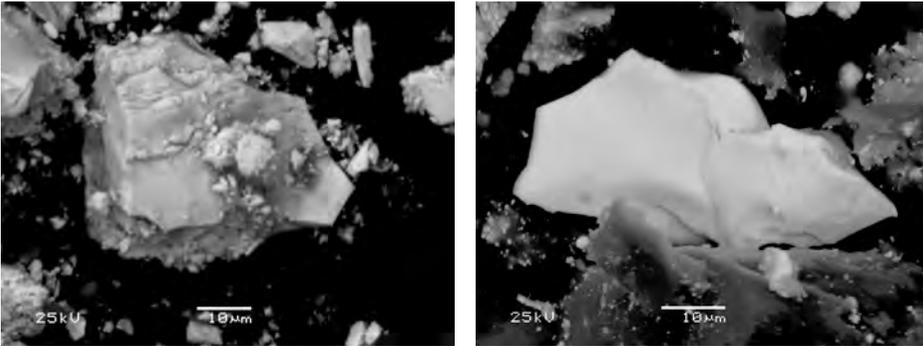


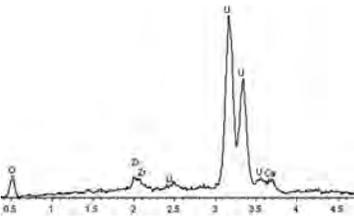
Fig. 1. Uraninite: a – the TEM-image of uraninite particles in suspension preparation; corresponding SAED pictures show fall of degree of crystallinity of particles (from left to right) up to electron-amorphous state;

a

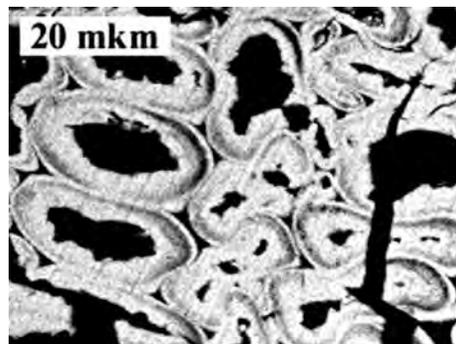
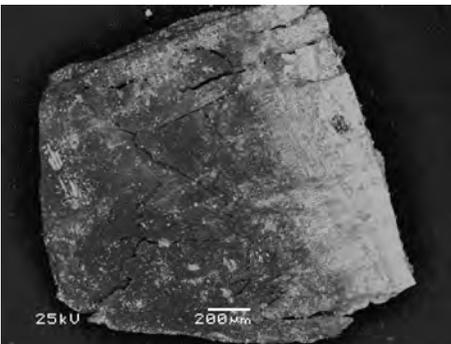


b

b – fragments of glassy (vitriform) uranium-oxide matter (with Ca, Zr impurity), the SEM (BSE)- image;



c – a coalificated fragment of lignite (black) with uranium-oxide impregnation (white), with a pyrite (light gray) and quartz (dark gray) – on the left; the uraninite phytomorphous – on the right.



c

hardened gel. As regarding their composition these glasses are close to uranium dioxide, but besides main mineral-forming component they contain admixtures of Zr, Ti, Si, Fe, S, P. Few finds of similar uranium-bearing glasses are considered in the work (Dymkov *et al.*, 2003); here are discussed possible conditions of their formation at the expense of transformation of nasturan, zircon and brannerite in the process of argillization of uranium ores. At the figure are displayed images of glass-like microfragments of uraninate, resembling hardened gel, with typical conchoidal fracture on a chip (Fig. 1b) and composition spectrum. This is a main ore phase at the hydrogene deposit of paleovalley type Khokhlovskoye, Southern Transuralian (Khalezov, 2009; Veichkin *et al.*, 2009). In the same ores uranium-oxide "gel" was found as phytomorphs and impregnation in carbonificated fragments of lignites (Fig. 1c).

In exogene ores uranium oxides are often related to carbonificated organic material, but more often dispersed nasturan is confined to cementic material or itself plays a role of cement. By present time, notwithstanding the proved many stage formation, polymineral composition of uranium black, its dominant component, according to statistics, is more often nasturan as oxide UO_{2+x} (Sidorenko, Doynikova, 2008).

Coffinite with ideal crystallochemical formula $USiO_4$ is considered to be a single silicate of U^{4+} , which is formed under natural conditions. Exogene coffinite, as a rule, is well crystallized (Fig. 2). Endogenic (hydrothermal) coffinite is usually metamict, X-ray amorphous. Practically up till the end of 80s coffinite was considered as endogenic uranium mineral, and his presence in composition of exogene ores was regarded as rare specific feature. Modern data show, that this U^{4+} -silicate is rather wide spread as significant component of friable black's ores (powder uraninite ores). In this case sizes of its needle or oval crystals make up 1–10 μm , but more often coffinite is represented by cloddy formations of several microns in size (Fig. 2a, b). Characteristic feature of exogene coffinite – high degree of its crystallinity, ability to preserve structure (dot patterns of microdiffraction) even at considerable loss of uranium. During coffinite study in suspension preparations most often are displayed microdiffraction patterns, corresponding to planes of inverse lattice $(010)^*$ and $(021)^*$, which testifies to predominant development in microcrystals corresponding faces (010) and (052) .

In contrast to uraninite in samples of exogene ores electron-amorphous coffinite was never found. As a result appears methodical note important for mineralogical diagnostics. At analysis of finely dispersed black's ores it is possible erroneous diagnostics using only traditional X-ray diffraction method: on the background of X-ray amorphous uranium oxides mineral composition of such ores will be determined as monocoffinitic.

Crystal structure of coffinite relates to zircon type. Thus, coffinite is a member of group of isostructural minerals: zircon – coffinite – thorite – xenotime ($ZrSiO_4 - USiO_4 - ThSiO_4 - YPO_4$), which gives way to isomorphous substitutions of uranium for Th и TR_Y . Under natural conditions isomorphism of U^{4+} and Th in coffinite is limited (although in synthetic specimens one could observe continuous row of solid solutions coffinite – thorite). At substitution of U^{4+} for TR preference has yttrium group of REE. Entrance of phosphorus in composition of coffinite is supported by many finds of P-bearing coffinites in exogene ores (Belova *et al.*, 1980), which is explained by possible pseudomorphous formation of coffinite after ningyoite.

Investigation of different and numerous samples showed, that coffinite in ores of infiltration deposits is exclusively close related to carbonificated organic material. For example, in microfragment from the ore of the above mentioned Khokhlovskoye deposit were observed alternated accumulations of microcrystals of coffinite between coaly layers.

Coffinite in polished sections might be erroneously diagnosed as ningyoite, while carrying out optic diagnostics (by color, reflecting ability and inner reflexes). Therefore for diagnostics of X-ray amorphous coffinite it is necessary to use AEM methods besides usual optic methods.

Brannerite – practically single mineral species among titanates, in which U^{4+} is mineral-forming element. *Davidite*, often mentioned by geologists as uranium titanate is not properly uranium mineral. It is proved, that practically, from crystallochemical point of view, davidite is rare earth TR-titanate, which conventionally is related to ilmenite group; in its composition uranium is not mineral-forming element, but isomorphous admixture (Sidorenko, 1978).

Usually in mineralogical practice for investigation of structural characteristics of metamict brannerite is applied previous ignition of the sample. Using possibility of electron diffraction during study of X-ray amor-

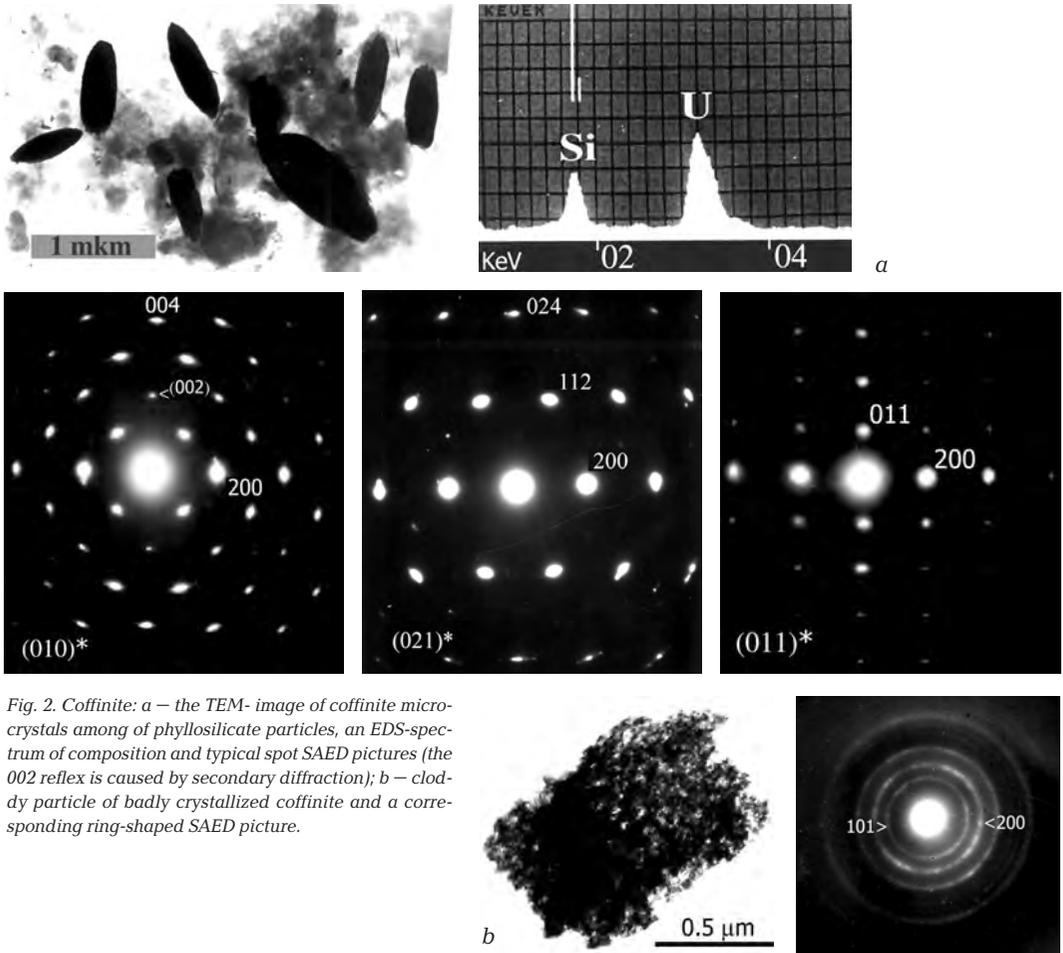


Fig. 2. Coffinite: a – the TEM- image of coffinite microcrystals among of phyllosilicate particles, an EDS-spectrum of composition and typical spot SAED pictures (the 002 reflex is caused by secondary diffraction); b – cloddy particle of badly crystallized coffinite and a corresponding ring-shaped SAED picture.

phous substance, were obtained structural characteristics of brannerite in its natural not heated-up state (Ivanova *et al.*, 1982). Endo- gene uranium titanate was studied from the Antei deposit of the ore field Strel'tsovskoye, developing as impregnation and nests in metasomatically altered granites (Fig. 3). Determined by SAED (microdiffraction) parameters of the mineral ($a = 9.8$, $b = 3.8$, $c = 6.7$ Å; $\beta \approx 119^\circ$) correspond to monoclinic cell of synthetic brannerite and cell of the thorium titanate isostructural to it. Structural similarity of natural brannerite and synthetic ThTi_2O_6 was proved by coincidence of a number of diffraction characteristics (syngony, angle of monoclinic structure, parameter b , intensity of $00l$ reflexes). On this basis in the work (Ivanova *et al.*, 1982) is exposed, that brannerite is uranium titanate $\text{U}(\text{TiO}_3)_2$, but not a complex oxide of U and Ti, as was considered before. Notion "complex oxide" of U и Ti, widely used in literature at describing of bran-

nerites, is not crystallochemically based and is erroneous.

Here it is worthwhile to make some deviation. Recent discovery of holfertite (Belakovskiy *et al.*, 2006) testifies to existence in nature of Ca-uranyl-titanate. Uranyl (U^{6+}) minerals are not the object of this article. However this fact of appearance of not known previously U-Ti-minerals should attract special attention of geologists. At revealing of positive correlation between uranium and titanium in mineral formations it is necessary to make more thorough, than previously, and detailed diagnostics of mineral with determination of uranium valence.

About phosphates of tetravalent uranium

By the present time at uranium mineralogy are known trustworthily four U^{4+} -phosphates (Belova *et al.*, 1998), related to different mi-

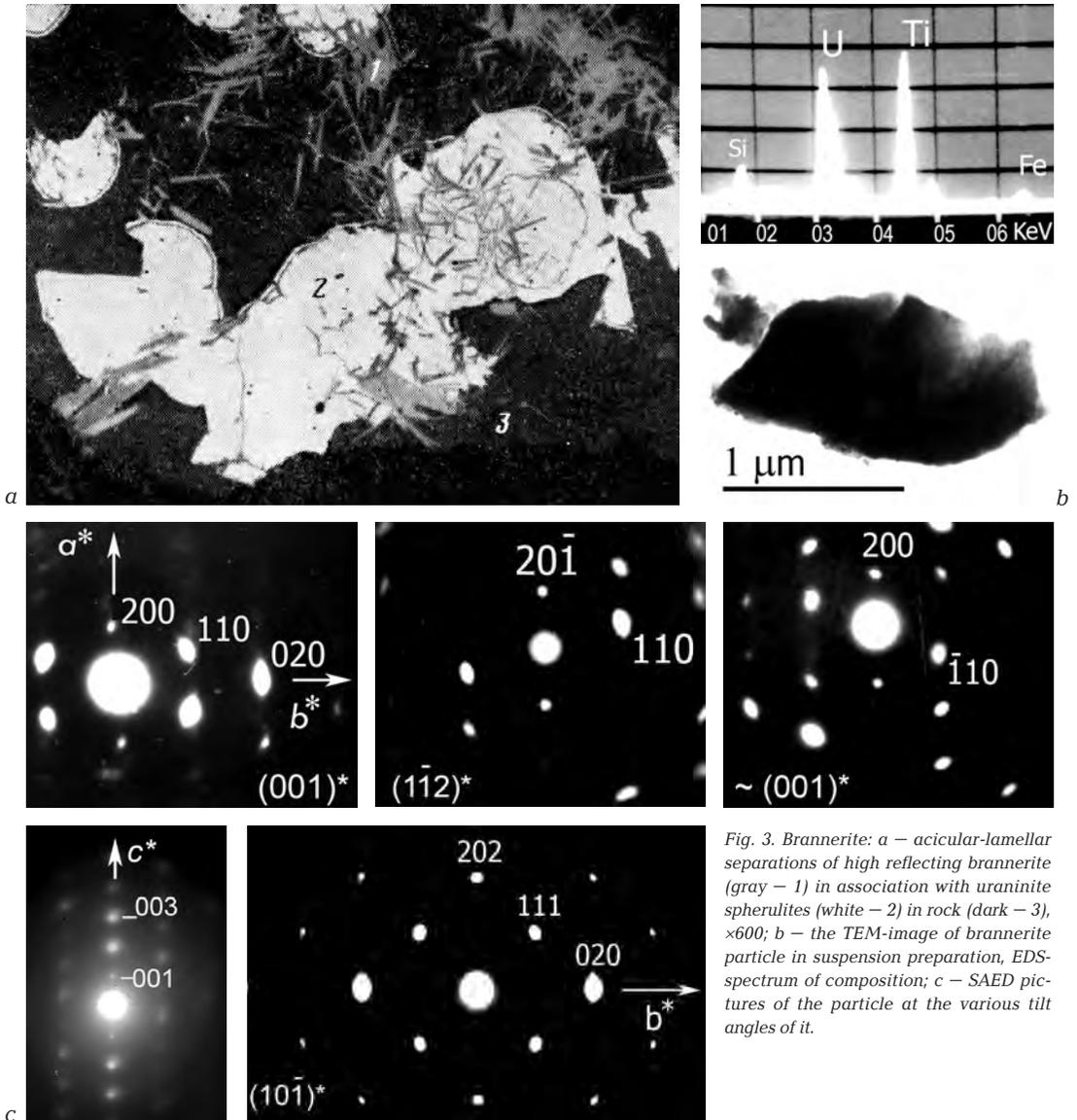


Fig. 3. Brannerite: a – acicular-lamellar separations of high reflecting brannerite (gray – 1) in association with uraninite spherulites (white – 2) in rock (dark – 3), $\times 600$; b – the TEM-image of brannerite particle in suspension preparation, EDS-spectrum of composition; c – SAED pictures of the particle at the various tilt angles of it.

neral groups (Table). Thus, it is evident existence in mineral world of higher, than mineral group, taxon – phosphates of tetravalent uranium (U^{4+} -phosphates). This taxon is lesser than mineral class, which unites all phosphates. For association of U^{4+} -phosphates was selected taxon *family*, which has wide application in mineralogical classification. According to definition of G.B. Bokiy “*this taxon unites mineral species by similarity of their composition, ...independently of mineral structure*” (Bokiy, 1997). This new mineral family (super-group) of tetravalent uranium was opened as a result of detailed crystallochemical investiga-

tions by the method of electron microdiffraction (SAED) in transmission AEM (Doynikova, 2005). The minerals of U^{4+} -phosphate family are united by common conditions of their formation in zone of reduction in hypergene environment.

Lermontovite – one of minerals of this family. Discovery of this new mineral in our country (Melkov, Pukhal'skiy, 1957) gave rise to study of tetravalent uranium phosphates. Its name was given to designation of mineral group, including also two other minerals – **vyacheslavite** and **urfoite** (Doynikova, 2005). Minerals of lermontovite group are formed in

Table 1. Crystallochemical characteristics of the tetravalent uranium

| Minerals | Chemical formula | Structural parameters (Å) symmetry, space group | Colour, density, (g/cm ³) | Optical constants | Reference |
|--|---|---|---------------------------------------|-----------------------------------|-----------------------------|
| Rhabdophane group CePO ₄ ·H ₂ O | | | | | |
| Ningyoite | (U,Ca,Ce) ₂ (PO ₄) ₂ ·1–2H ₂ O | rhombic, pseudohexagonal | brown, | $n_{cp} \approx 1.64$ | Muto <i>et al.</i> , 1959 |
| | CaU(PO ₄) ₂ ·nH ₂ O | n = 1–2 | green | | Belova <i>et al.</i> , 1985 |
| | | hexagonal, P6 ₂ 22 | (in slices) | | |
| | | a 6.86, c 6.38, | 4.74 (calc.) | | |
| | | Z 3 | | | |
| "Tristramite" | (CaU ⁴⁺ Fe ³⁺)[(PO ₄)(SO ₄)(CO ₃)]·1.5H ₂ O | hexagonal, P6 ₂ 22 | greenish- | $n_o = 1.644$ | Atkin <i>et al.</i> , 1983 |
| | Ca>>U>>Fe; PO ₄ >>SO ₄ | a 6.913, c 6.422, | yellow | $n_e = 1.664$ | Belova <i>et al.</i> , 1987 |
| | | Z 3 | 3.8–4.2; 4.18 (calc.) | | |
| Lermontovite group, generalised formula: UPO ₄ OH·nH ₂ O | | | | | |
| Vyacheslavite | (U _{1.061} Ca _{0.041})(PO ₄)(OH) _{1.3} ·2.7H ₂ O | rhombic, Cmc ₂ , C2cm; | dark-green, | $n_g = 1.731–1.729$ | Belova <i>et al.</i> , 1984 |
| | | a 6.96, b 9.10, | 4.6–5.2; | $n_m = 1.729–1.726$ | |
| | | c 12.38, Z 8 | 5.02 (calc.) | $n_p = 1.700$ | |
| Lermontovite | (U _{0.94} Tl _{0.4} Ca _{0.02}) _{1.0} (PO ₄)(OH) _{1.2} ·0.4H ₂ O | rhombic, Ccca-?, | green, | $n_g = 1.724–1.726$ | Melkov <i>et al.</i> , |
| | | a 9.74, b 19.0, | 4–4.5; | $n_m = 1.707$ | 1983 |
| | | c 10.1; Z 8 | 4.37 (calc.) | $n_p = 1.686–1.690$ | |
| | (U _{0.73} Ca _{0.005}) _{0.74} (PO ₄) | monoclinic, | " " | " " | Sidorenko <i>et al.</i> , |
| | | a 10.00, b 19.40, | | | 1986 |
| | | c 8.55; γ 96° | | | |
| Urfoite | U _{0.85} Ca _{0.004} (PO ₄) _{1.0} (OH) _{0.48} ·0.3H ₂ O | rhombic, Ibca, | emerald- | $n'_g \approx n'_m \approx 1.734$ | Belova <i>et al.</i> , 1996 |
| | | a 14.06, b 13.22, | green | $n'_p \approx 1.707–1.708$ | |
| | | c 14.4; Z 24 | 4.29 (calc.) | | |

Note. * – electron microdiffraction data (SAED).

reduction zone in hypergenese environment, it is characteristic their association with black uranium ore generations.

All minerals of the group are represented yet by single finds. These minerals are close by composition, have general idealized formula U(PO₄)(OH)·nH₂O, but are different by structural parameters. Their unification into the group (Table) at present time is rather conventional. It is not excluded, that in the future, at refinement of crystallochemical data using new finds, each of the minerals might appear representative of independent group.

Ningyoite CaU(PO₄)₂·2H₂O, discovered at Japan calcium-uranium phosphate (Muto *et al.*, 1959), is related to the group of rhabdophane; later was discovered at various world regions. Till the end of 20th century ningyoite was not related to economic uranium minerals, as far as his presence in composition of uranium blacks "was lost" due to insufficient level of study of the latter. At present ningyoite is considered to be rather common mineral in ores of the infiltration deposits (Doynikova, 2007).

It is worthwhile to underline, that characteristic feature of ningyoite is micron size of its crystals: usually 1–2 μm, rarely more than 10 μm (Fig. 4), as well as its specific confinement to areas enriched in organic material. Thus, in samples of uranium ores of one of deposits at Bulgaria was practically absent another mineralization, a sample represented friable mixture of organic matter with ningyoite (Doynikova *et al.*, 2003).

Tristramite (Atkin *et al.*, 1983), mineral of rhabdophane group, is not individual mineral species, its identity with ningyoite was proved earlier (Belova *et al.*, 1987). As far as tristramite is not annulled by the International Commission on New Minerals, Nomenclature and Classification, it is displayed in the Table in inverted commas (which reflects doubt in its individuality).

As a result of crystallochemical investigations it is established, that all three phosphates of the lermontovite group, as well as previously studied ningyoite, represent independent mineral species of the family of phosphates of tetravalent uranium. Vyacheslavite

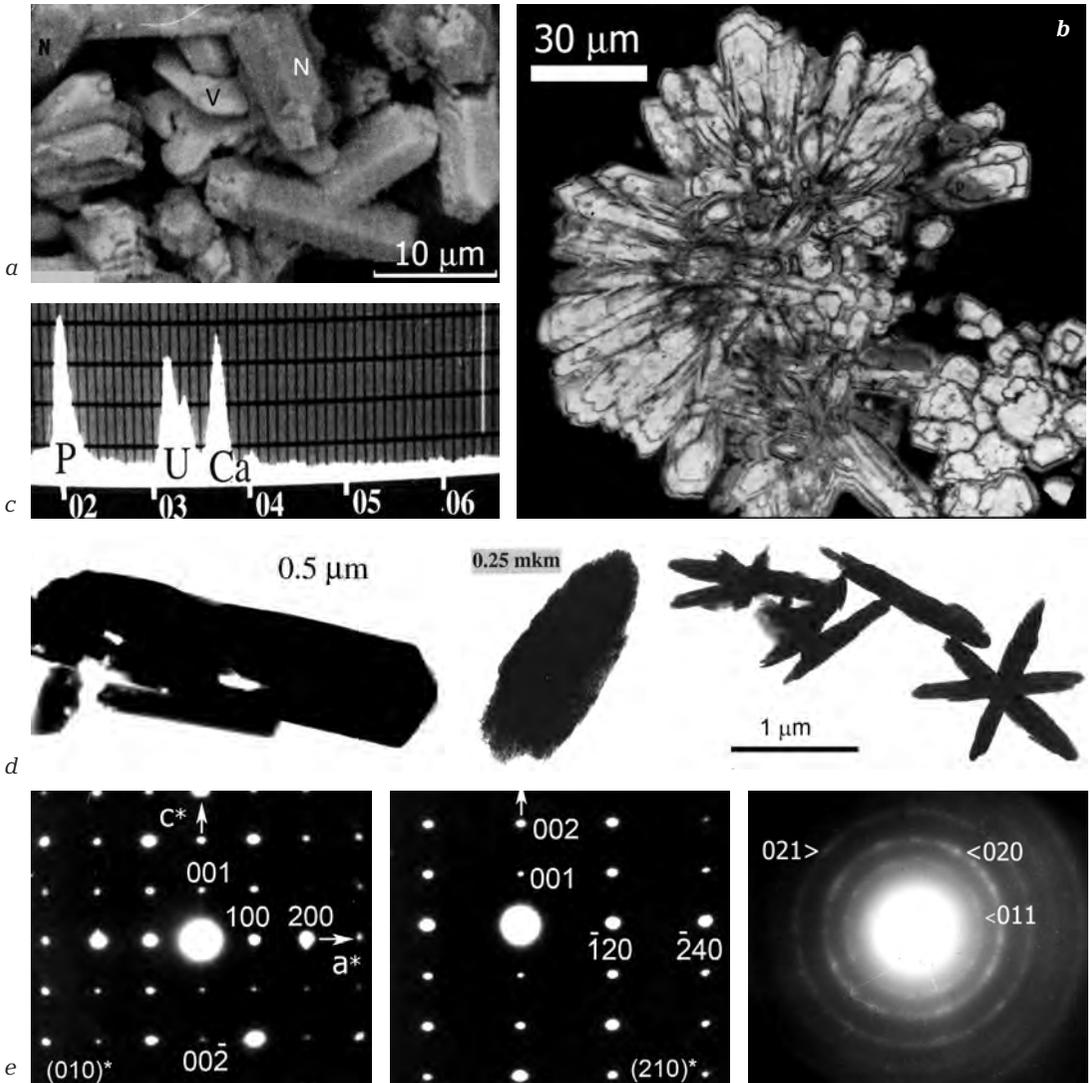


Fig. 4. Ningyoite: a, b. SEM (BSE) image (Scharmova, Scharm, 1994), Stráž-deposit, northern Bohemia, Czech Republic; a – columnar crystals of ningyoite (N) intergrown with plates of vyacheslavite (V); b – rosette-like aggregate of euhedral ningyoite crystals, with thin dark interbeds of a pyrite (P) in growth zones; c – EDS-spectrum of pure ningyoite composition; d – forms of microcrystals, TEM-image; e – typical SAED pictures.

is almost pure uranium phosphate with insignificant quantity of calcium; the ratio U:P = 1:1, but negligible predominance of uranium is always fixed. Lermontovite contains yet less calcium, but about 10% of thallium is present. In urfoite composition is observed deviation towards decreasing of uranium in ratio U:P = 1:1. But in ningyoite quantity of calcium is equal to that of uranium or somewhat predominates it. One might with sufficient confidence suggest, that each from uranium U^{4+} phosphates could afterwards form independent subgroup, which should be ad-

ded by new, structurally close mineral species. In particular we are sure, that such one will be the lermontovite subgroup with minerals, containing in cation part also alkaline element (thallium) alongside with uranium.

Phospho-silicate phase of uranium U^{4+} . Not known previously uranium silicate was established in association with disperse uranium oxide during study of friable hydrogenic ores of the Dalmatovskoye uranium deposit of paleovalley type (Doynikova *et al.*, 2009) by the methods of scanning AEM. This mineral phase of U^{4+} is predominant in ore intervals of

one of studied boreholes, it is confined, as a rule, to altered feldspar and is represented by microcrystals of slightly elongated lenticular form, with unclear side faces. Microcrystal sizes are about of several microns. Aggregates of microcrystals are often found (Fig. 5), colloform segregations occur more seldom. Idealized formula of the studied phase is $(U,Ca)[(Si,P)O_4]_2$, where $U:Ca \approx 3:1$ and $Si:P \approx 3:1$. Relation between cation and anion components is $(U,Ca):(Si,P) = 1:2$, that is twice as less than in coffinite, where $U:Si = 1:1$. As far as relief objects were studied but not polished ones, results of analyses were normalized, the problem was not solved concerning presence of OH-group or water in composition of this phase. Since quantitative EDS-analysis showed (in atomic units) considerable predominance of silicon over phosphorus (three times), the phase might be characterized as uranium silicate, containing phosphorus, or more exactly – uranium phospho-silicate.

Morphology of segregations of found uranium phase is close to forms of hypergene U^{4+} -minerals: coffinite and ningyosite. In contrast to ningyosite, in composition of this U-phospho-silicate is observed constant predominance of U over Ca. The phase under consideration differs from P-bearing coffinite first of all by constant presence of calcium, as well as by consistent ratio Si/P. Thus, one could probably add one more mineral – phospho-silicate of uranium to already known minerals of tetravalent uranium.

At present this uranium phase is studied only as regarding composition. Data of scanning AEM revealed specific features of composition, which allow us to say about individuality of this mineral phase, but its structure parameters are yet absent. For receiving diffraction characteristics of this U^{4+} -phase, taking into consideration its micron sizes and occurring into polymineral mixture, it is more preferable method SAED, realized in transmissive AEM.

About place of calcium in minerals of tetravalent uranium

The problem of mode of occurrence of Ca in composition of U^{4+} -minerals attracts attention for a long time and remains a subject of discussion. It is interesting the fact, that both phosphates and phospho-silicate described above contain Ca alongside with U^{4+} . Is it possible to say here about isomorphous substitution?

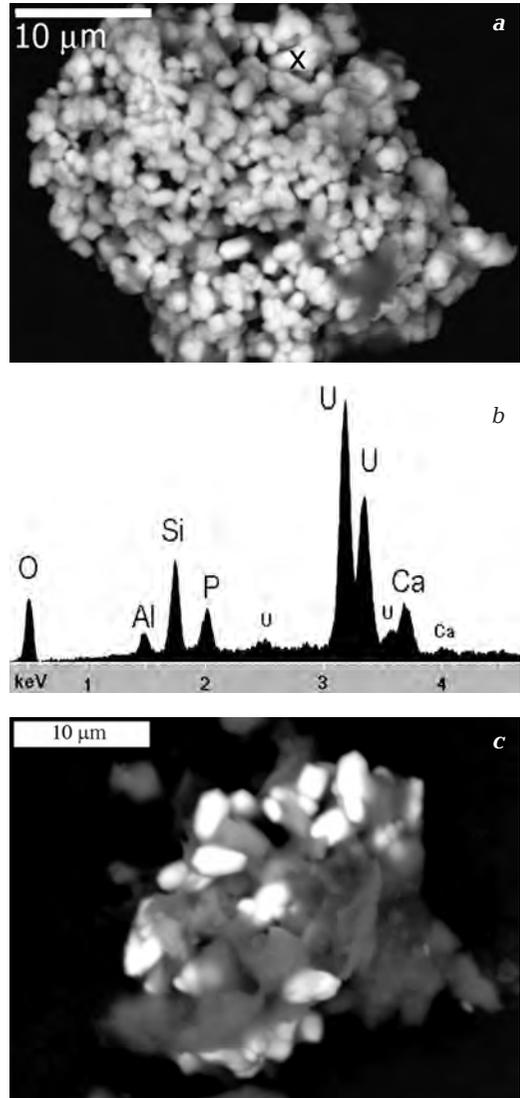


Fig. 5. Ca-phosphosilicate of U^{4+} (white): a – the aggregation of microcrystals; b – EDS-spectrum of composition in marked point (x); c – separations among aluminosilicates.

Isomorphous substitution of U^{4+} for Ca^{2+} at equality of their ionic radii always invoked doubt due to crystallochemical individuality of each of them. For a long time there is a discussion about place of calcium in uranium minerals. At first equality of ionic radii and isostructurness of uraninite and fluorite were taken as foundation of isomorphous substitution of U^{4+} and Ca^{2+} . It was accepted without doubt, that in apatite structure U^{4+} substitutes for Ca^{2+} . Denial of this version came from technologists of treatment of ores, in which U^{4+} is related to apatite. Having extracted

pure apatite they did not receive expected concentration of uranium. Therefore, uranium is not structural admixture of apatite.

However, it is known entrance of uranium into pyrochlore structure with formation of uranpyrochlore $(Ca,Na,U)(Ti,Nb,Ta)O_6(F,OH)$, in which uranium U^{4+} statistically occupies in the structure sites of Ca^{2+} . By X-raying method are revealed also consequences of this event: disordering of the pyrochlore structure, up till destruction (possibly through metamictization), breach of stoichiometry. For preservation of the charge balance at increase of uranium content in structural motive $AB_2O_6(OH,F)$ there is enrichment of the mineral in Ti in site B (Ta,Nb). As a result breach of stoichiometry in structural motive takes place. Besides, own crystal structure of the mineral breaks up. Taking into consideration widening of bands of diffraction spectra, alongside with enrichment of structure in uranium at first occurs decreasing of elementary cell sizes (twofold), then breach of three-dimensional order, further – complete metamictization.

At ordered setting of U^{4+} and Ca^{2+} in structural positions mineral obtains individual crystalline structure, that, probably takes place in the structure of ningyoite. The second example, as we suggest, will be the structure of the new found U^{4+} -phase of phospho-silicate composition.

The phase under consideration (Ca- U^{4+} -phospho-silicate) is interesting due not only to mixed anion composition, but also by high content of Ca, which alongside with uranium becomes mineral-forming element.

We should note that rather clearly fixed relation of uranium and calcium in idealized composition of ningyoite $(CaU)PO_4$ (U:Ca = 1:1) and in composition of phospho-silicate $(U,Ca)[(Si,P)O_4]_2$ (U:Ca = 3:1) testifies to ordering of setting of U^{4+} and Ca^{2+} in structural sites of cations.

Isomorphism $SiO_4 - PO_4$ was shown at study of P-bearing coffinites: Si and P coexisted in single structure, responsible for electron diffraction (Belova *et al.*, 1980).

From crystallochemical point of view, change of chemical composition from coffinite $USiO_4$ to ningyoite $(Ca,U)PO_4$, that is complete replacement of Si for P, is accompanied by appearance of calcium in cation part. Crystal structure is cardinaly changed from tetragonal to hexagonal one. Therefore, here takes place not isomorphism $U^{4+} - Ca$, but formation of cation part of composition by two elements. Characteristic for ningyoite some predominance of Ca over U (variable value,

max 2:1), might be considered as one of variants of filling of Ca in the structure. However, as a whole a general regularity of ningyoite composition U:Ca = 1:1 is preserved (Doynikova, 2003).

Then we shall consider change of composition from silicate coffinite $USiO_4$ to the found U^{4+} -phospho-silicate $(U,Ca)[(Si,P)O_4]_2$. In comparison with ningyoite relative further predominance of U over Ca in cation part, where U:Ca = 3:1, is accompanied by isomorphism (Si–P) also in anion part of composition. Thus, combination of silicate SiO_4 and phosphate PO_4 groups in structure of U^{4+} -mineral results in obligatory appearance here of Ca ion. In composition of the phospho-silicate balance of valency is achieved by equivalent, with the same ratio 3:1, replacement of U for Ca and Si for P.

According to existing at present data, we have in view predominantly structural, individual, but not isomorphous position of Ca in minerals of tetravalent uranium. "Pair" substitution of such kind practically takes place into crystallochemical group apatite – britholite (apatite – typical phosphate, and britholite – its silicate structural analogue). It is worthwhile to underline, that exactly silicate analogue with constant presence of phosphorous has U^{4+} in its composition.

Thus one could see development of U^{4+} -phosphate family at the expense of appearance of phospho-silicate branch. Transformation of anion part of compositions takes place, while in this case in cation part U^{4+} obligatorily "cooperates" with Ca.

We suggest, that calcium (up to 3.3% CaO), which according to data of A.B. Khalezov (2009), instrumentally is fixed in composition of uraninites simultaneously with phosphorus (up to 2% P_2O_5), is not related to uraninite structure. Its presence is probably related to origin of phase heterogeneity (formation of new microphase?).

And nonstructural Ca? Evidently, it is present as admixture in composition of unstructural hardened gels of uranium-oxide composition, so called uranium-bearing glasses (~ 2% Ca).

Conclusion

Already available experimental data testify to increasing of number of U-minerals, in which mineral-forming element is represented by tetravalent uranium. Considerable progress in cognition of U^{4+} -minerals is provided by transition of mineralogical investiga-

tions to local levels of "electron" micromineralogy. Utilization of AEM did not only expand spectrum of natural U^{4+} phosphates, but allowed us, at last, to say more definitely about structural relation of Ca to U^{4+} , it also opened a new page in mineralogy of tetravalent uranium, showing possibility of existence of U^{4+} -phospho-silicates.

The work was carried out with partial finance support of the Programme of leading scientific schools (supervisor – academician of RAS N.P. Laverov).

References

- Atkin D., Bashatn I. R., Bowles J.W. Tristramite, a new calcium uranium phosphate of the rhabdophane group // *Mineral. Mag.* **1983**. V. 47. P. 393–396.
- Belokobskiy D.I., Pautov L.A., Sokolova E., Hawthorne F.C. Holferite, a new hydroxyl-hydrated uranium titanate from Starvation Canyon, Thomas Range, Utah, USA // *Mineral. Rec.* **2006**. V. 37. P. 311–317.
- Belova L.N., Gorshkov A.I., Doynikova O.A., Sivtsov A.V. About analogy of tristramite and ningyoite // *Izv. of the USSR Academy of Sciences.* **1987**. Ser. geol. No 11. P. 136–137. (in Russian).
- Belova L.N., Gorshkov A.I., Doynikova O.A., Sivtsov A.V. A new group of minerals – phosphates of U (IV) // *DAN.* **1998**. V. 358. No 2. P. 215–217. (in Russian).
- Belova L.N., Gorshkov A.I., Doynikova O.A., Sivtsov A.V., Trubkin N.V. One more phosphate of tetravalent uranium // *DAN.* **1996**. V. 349. No 3. P. 361–363. (in Russian).
- Belova L.N., Gorshkov A.I., Ivanova O.A., Dikov Yu.P., Sivtsov A.V. Ningyoite in the light of new experimental data // *Izv. of the USSR Academy of Sciences.* **1985**. Ser. geol. No 3. P. 101–109. (in Russian).
- Belova L.N., Gorshkov A.I., Ivanova O.A., Sivtsov A.V. About nature of so called P-bearing coffinite // *DAN SSSR.* **1980**. V. 255. No 2. P. 428–430. (in Russian).
- Belova L.N., Gorshkov A.I., Ivanova O.A., Dikov Yu.P., Sivtsov A.V., Boronikhin V.A. Vyacheslavite $U^{4+}(PO_4)(OH) \cdot nH_2O$ – new phosphate of uranium // *Zap. VMO.* **1984**. Part 113. Vyp. 3. P. 360–365. (in Russian).
- Bokiy G.B. Systematics of nature silicates // *Results of science and technics. Series crystallochemistry.* V. 31. M.: VINITI. **1997**. 292 p. (in Russian).
- Burns P.C., Finch R.J. Wiartite: Crystallographic evidence for the first pentavalent-uranium mineral // *Amer. Miner.* **1999**. Vol. 84. № 9. P. 1456–1460.
- Doynikova O.A. Dispersion minerals of uranium of reduction zone of hypergenesis: mineralogy and crystallochemistry. Doctoral thesis. **2005**. M.: IGEM RAS. 277 p. (in Russian).
- Doynikova O.A. Genetic crystallochemistry of mineral components of uranium blacks // *Geochemistry.* **2003**. No 12. P. 148–151. (in Russian).
- Doynikova O.A. Uranium deposits with a new type of black mineralization: the phosphate one // *Geology of ore deposits.* **2007**. V. 49. No 1. P. 60–78. (in Russian).
- Doynikova O.A., Belova L.N., Gorshkov A.I., Sivtsov A.B. Uranium black: problems of genesis and mineral composition // *Geology of ore deposits.* **2003**. V. 45. No 6. P. 514–530. (in Russian).
- Doynikova O.A., Solodov I.N., Chertok M.B. Mineral composition of uranium ores of the Dalmatovskoye deposit // *Geology of ore deposits.* **2009**. V. 51. No 6. P. 540–549. (in Russian).
- Dymkov Yu.M., Doynikova O.A., Volkov N.I. Find of U-Fe-Zr-Ti-S-P-gel at the exogenous-epigenetic uranium deposit Khokhlovskoye (Southern Transurals) // *Geochemistry.* **2003**. P. 62–67. (in Russian).
- Ivanova O.A., Mel'nikov I.V., Gorshkov A.I., Vampilov M.V. Brannerite in light of data of analytical electronic microscopy // *Izv. of the USSR Academy of Sciences.* **1982**. Ser. Geol. No 2. P. 63–71. (in Russian).
- Khalezov A.B. Uranium deposits in river paleovalleys of the Urals region. M.: VIMS. **2009**. 145 p. (in Russian).
- Melkov V.G., Pukhal'skiy L.Ch. Prospecting of uranium deposits. M.: Gosgeoltekhizdat. **1957**. 220 p. (in Russian).
- Melkov V.G., Belova L.N., Gorshkov A.I., Ivanova O.A., Sivtsov A.V. New data on lermontovite // *Mineralogical Journal.* **1983**. V. 5. No 1. P. 82–87. (in Russian).
- Muto T., Meyrowits R., Pommer A.M., Mura-no T. Ningyoite – a new uranous phosphate mineral from Japan // *Amer. Mineral.* **1959**. V. 44. № 5–6. P. 633–639.
- Scharmova M., Scharm B. Rhabdophane group minerals in the uranium ore district of northern Bohemia (Czech Republic) // *J. Czech Geol. Soc.* **1994**. V. 39. № 4. P. 267–280.
- Sidorenko G.A. Crystallochemistry of uranium minerals. M.: Atomizdat. **1978**. 216 p. (in Russian).
- Sidorenko G.A., Gorobets B.S., Dubinchuk V.T. Modern methods of mineralogical analysis

- of uranium ores. M.: Energoatomizdat. **1986**. 184 p. (in Russian).
- Sidorenko G.A., Doynikova O.A.* What is it uranium black // Materials on geology of deposits of uranium, rare and rare-earth metals. Informats. sborn. KNTS. **2008**. V. 152. P. 212–231. (in Russian).
- Sidorenko G.A., Doynikova O.A.* Uranyl minerals – indicators of formation conditions of uranium deposits // Exploration and protection of Earth interior. **2009**. No 2. P. 14–22. (in Russian).
- Teterin Yu.A., Kulakov V.M., Baev A.S., Nevzov N.B., Melnikov I.V., Streltsov V.A., Mashirov L.G., Suglobov D.N., Zelenkov A.G.* A study of synthetic and natural uranium oxides by X-ray photoelectron spectroscopy // Physics and Chemistry of Minerals. **1981**. T. 7. № 4. P. 151–158.
- Velichkin V.I., Solodov I.N., Doynikova O.A., Nesterova M.V., Chertok M.B., Shugina G.A., Shulik L.S., Ganina N.I., Rekun M.L.* Study of geochemical and mineralogical features of uranium ores of the Khokhlovskoye deposit // Materials on geology of deposits of uranium, rare and rare-earth metals. Informats.sborn. KNTS. **2009**. Vyp. 154. P. 69–93. (in Russian).