

SIMPLE URANIUM OXIDES, HYDROXIDES $U^{4+} + U^{6+}$, SIMPLE AND COMPLEX URANYL HYDROXIDES IN ORES

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The review of published and new own data of simple uranium oxides revealed that the formation of five simple oxides is probable: nasturan, sooty pitchblende, uraninite, uranothorianite, and cerianite. Among simple oxides, nasturan, sooty pitchblende, and uraninite are the most abundant in ores varied in genesis and mineralogy. Uranothorianite or thorium uraninite (aldanite) is occasional in the ores, while cerianite is believed in U-P deposits of Northern Kazakhstan.

Hydrated nasturan is the most abundant among three uranium (IV + VI) hydroxides in uranium ores. Insignificant ianthinite was found in few deposits, whereas cleusonite was identified only in one deposit. Simple uranyl hydroxides, schoepite, metaschoepite, and paraschoepite, are widespread in the oxidized ores of the near-surface part of the Schinkolobwe deposit. They are less frequent at the deeper levels and other deposits. Studtite and metastudtite are of insignificant industrial importance, but are of great interest to establish genesis of mineral assemblages in which they are observed, because they are typical of strongly oxidized conditions of formation of mineral assemblages and ores.

The X-ray amorphous urhite associated with hydrated nasturan and the X-ray amorphous hydrated matter containing ferric iron and U^{6+} described for the first time at the Lastochka deposit, Khabarovsk krai, Russia are sufficiently abundant uranyl hydroxides in the oxidized uranium ores.

Significant complex uranyl hydroxides with interlayer K, Na, Ca, Ba, Cu, Pb, and Bi were found basically at a few deposits: Schinkolobwe, Margnac, Wölsendorf, Sernyi, and Tulukuevo, and are less frequent at the other deposits, where quite large monomineralic segregations of nasturan and crystals of uraninite were identified. In the other cases, uranium is leached from the oxidizing zone down to background, or richer oxidized ores are formed (Sernyi, Rössing, Shakoptar, and Pap deposits). These features of oxidized uranium ores are theoretically and economically important.

2 figures, 5 table, 50 references.

Keywords: uranium oxides (IV + VI), uranium hydroxides, simple and complex uranyl hydroxides, economic ores, X-ray amorphous matter, deposits.

Uranium (IV + VI) oxides are part of nearly all economic fresh uranium ores. Simple and complex uranium oxides are known. Complex oxides, brannerite, davidite, samarskite, and others are not discussed here and data of them are not given requiring the extensive additional material that causes increasing size of this article. Simple oxides identified in most economic ores and in the oxidizing zone are replaced by significant hydroxides; however, different versions of ore replacement are more frequent.

The aim of this study is review of published and new data to find out the importance of simple uranium (IV + VI) oxides in the formation of economic ores and alteration of these ores under oxidizing conditions as well as to establish the conditions of formation of varied uranium (IV + VI) hydroxides, simple and complex uranyl hydroxides, and

uranium leaching with oxidizing simple oxides and their natural assemblages at certain deposits. In addition to the formation of uranium hydroxides, the precipitation of uranyl arsenates or vanadates and X-ray amorphous of hexavalent uranium is important to discuss in the case of change of parameters of oxidizing zone in comparison with parameters of fresh ores; other theoretically and economically important features of oxidizing uranium ores are also discussed.

Simple uranium oxides

The features of five simple uranium oxides are given in Table 1. No vorlanite ($CaU^{6+}O_4$) (Galuskin *et al.*, 2011) is given here. Possibly, its formula is incorrect, because the X-ray data ($a = 5.3813\text{Å}$) correspond to uraninite, in which this dimension ranges from 5.38 to

Table 1. Simple uranium (IV+VI) oxides

Mineral, formula	Morphology of crystals, a_0 (Å)	Color and other characteristic features
Uraninite $UO_{2.0-2.9} \cdot nPbO, ThO_2, TR_2O_3$ и and less frequent CaO, where n ranges from 0 to few units	Octahedron and cube, a_0 5.38-5.65	Black, with semimetallic to resinous luster. Hardness 5.06-7.6; density 7.6-10.8
Nasturan $UO_{2.02-2.9} \cdot nPbO$ mCaO, where n and m range from 0 to few units	Sinter or kidney-shaped coloform dense seggregations, a_0 5.34-5.45	Black, with resinous luster. Hardness 4.7-5.9; density 4.9-7.7
Sooty pitchblende $UO_{2.08-2.96}$ and X-ray amorphous hydrated oxides and other uranium (IV + VI) minerals and phases	Loose films a_0 5.35-5.42 и and X-ray and poor-crystallized phases	Dark grey to light grey, dull. Hardness 1-3; density 3.8-4.8
Uranothorianite (Th,U) O_2 + UO_3 + PbO	Cubic crystals frequently with small octahedron faces, a_0 5.05-5.96	Dark grey. Translucent in thin chips. Hardness 6.5-7, density 8.7-9.9; n_{cr} 2.2. Isotropic
Cerianite-(Ce) (Ce,Th,U) O_2 + UO_3 + PbO	Small cubes and octahedra, powder seggregations, a_0 5.411-5.482	Dark greenish, amber yellow to brownish yellow with resinous luster, translucent, isotropic, $n > 2$

5.65Å (Table 1). The probable formula of the mineral studied by Galuskin *et al.* (2011) is $n(CaU^{4+}O_2) \cdot m(UO_3)$, where n is much less than m . Such formula corresponds to highly altered Ca-bearing uraninite.

Among other simple oxides, the first three (uraninite, nasturan, and sooty pitchblende) are the most abundant in uranium ores. Up to now, mineralogists consider them as morphological varieties of uraninite although as seen from the table, they have individual morphology and are slightly different in composition. In addition, these minerals are different in origin. Uraninite is the highest-temperature uranium oxide (400–260°C), coloform nasturan is characteristic of medium to low-temperature assemblages (250°C and less), and friable sooty pitchblende is typical of supergene product. Four varieties of uraninite different in composition are distinguished: (1) uraninite containing global clarkite of concentration Th and REE; (2) aldanite (uranothorianite) (up to 46–69 wt.% ThO_2 and 0.7–13 wt.% REE_2O_3); (3) broggerite (up to 15 wt.% ThO_2 and 1–6 wt.% REE_2O_3); and (4) cleveite (nivenite) enriched in REE up to 15 wt.%. Aldanite, broggerite, and cleveite, compositional varieties of uraninite, are accessory minerals of granitic and syenitic pegmatites and some igneous rocks. The Th- and REE-free uraninite economic ores are

formed in varied geological environments. Economic deposits of uraninite are reported from granitic pegmatites (Namibia, Norway, Canada, Madagascar, Alaska), skarn (Bancroft, Ontario, Canada; Mary Cathline, Australia), Proterozoic basal conglomerates (Witwatersrand, South Africa; Eliot Lake, Canada; Jacobino, Brazil), and occasional hydrothermal deposits (Schinkolobwe, Democratic Republic of Congo). Heinrich (1962), Formation... (1974), Laverov *et al.* (1983), Typomorphic features... (1989), Frondel (1958), and Chernikov (2006–2007) described in detail these uranium deposits.

To obtain new concepts of the formation of uraninite ores, the mineralogy of the Rössing large deposit, Namibia, Southwestern Africa related to granitic pegmatites, where uraninite is the major mineral of the fresh ores (Berning *et al.*, 1976) should be discussed. The oxidizing zone of this deposit is similar to that of the Sernyi uranium deposit, Turkmenistan in both mineralogy and uranium grade. The major minerals of fresh ores at these deposits are different. At the Rössing deposit, this is crystalline uraninite, whereas at Sernyi, coloform nasturan. In the oxidizing zone of both deposits, insignificant uranyl and uranium hydroxides were found; at the Sernyi deposit, these are becquerelite, schoepite, and hydrated nasturan; at Rössing, this

is gummite, mixture of uranyl hydroxides and silicates (Fig. 1). Later uranyl silicates, beta-uranophane and uranophane are abundant in the oxidizing zone of these deposits. Carnotite is widespread at both deposits. In addition, at the Sernyi deposit, strelkinite and tyuyamunite were found. Other uranyl minerals are less frequent in the oxidizing zone of the both deposits. It is possible that the character of vertical distribution of uranium content at these deposits is similar too. At the Sernyi deposit, the oxidized ores are three times richer and mixed ores containing relict nasturan and sooty pitchblende are 2.8 times richer in uranium down to 1 m deep than fresh ores, i.e., like the Tomas Range uranium-fluorite deposit, Utah, USA, at Sernyi, supergene processes were important to form orebodies. Probably, at the Rössing deposit, these processes have an effect on the concentration of uranium in ores.

Nasturan characteristic mineral of economic hydrothermal and supergene deposits was found at certain Sn-W deposits, for example Butygychag, Northeastern Russia, occurrences and deposits in Khabarovsk krai, Northern Transbaikalian Region, and Cornwall, Great Britain. According to new unpublished data of Russia deposits and literature of Cornwall, at all objects, nasturan is associated with arsenopyrite, nickeline, galena, and chalcopyrite to form veinlets cutting earlier Sn-W ore veins.

The largest bodies of nasturan with uraninite and coffinite are formed in the discordance-type deposits with rich uranium, gold-uranium, copper-uranium, and base metal-uranium ores. The deposits located in the Aligator River district (North Territory, Australia) and Athabasca, western Canadian Shield (Northwest Territory, Canada) are the most typical and are reported in (Uranium..., 1980; Laverov *et al.*, 1983; Kulish, Mikhailov, 2004). No large this type deposits are found in Russia.

Hydrothermal uranium deposits with nasturan are known in Russia and abroad. According to the new data of ore samples, certain deposits described during exploitation as proper uranium are complex, gold-uranium. For example, in the oxidizing and cementation zones enriched in U at the Sernyi deposit (Chernikov, 2001, 2006–2007,



Fig. 1. Gummite (orange) and beta-uranophane (yellow) fill cavities in pegmatite at the Rössing deposit, Namibia.

2010), a high grade of Au (up to 15 g/t) was determined in carbonate veinlets superimposed on nasturan. Among other proper hydrothermal uranium deposits with nasturan, the following subtypes are distinguished: nasturan-carbonate, nasturan-fluorite, nasturan-quartz, nasturan-bituminous, and nasturan-hydromica. Complex ores are distinguished: U-Zr, U-As-Pb-Zn, U-Cu, and U-Mo, in which nasturan-bearing veins cut earlier mineral assemblages (Typomorphic features... 1989). In addition, at many deposits, especially at deep levels, for example Tulu-kuevo, Southeastern Transbaikalian Region, there are nanoscaled and X-ray amorphous segregations corresponding to hydrated nasturan in composition.

The great concentration of nasturan is known from hydrothermal deposits of so called five-element association, where the mineral is associated with Co, Ni, and Fe arsenides, and native silver and bismuth, and occasionally native As (Canada; Ore Mountains, Germany and Czech Republic). The Aktepe deposit (Uzbekistan) attributed to this type is small and probably, is rather poor explored.

At the Witwatersrand largest Au-U deposit, nasturan and uraninite associated with native gold and pyrite were deposited in the cement of conglomerate composed of quartz pebble. At U-P, U-V, U-coal, and infiltration

uranium deposits, nasturan and sooty pitchblende precipitate in siltstone, sandstone, limestone, and coal beds. They are associated with Mo, Cu, and Zn sulfides, V minerals, and native arsenic, selenium, and rhenium.

Sooty pitchblende (residual and regenerated) occurred below the oxidizing zone (in the cementation zone) of endogenic deposits or zone of strata oxidation of supergene ores are frequently polymineralic; in addition to nasturan, uranium silicates, phosphates, and titanates and the X-ray amorphous and nano-scaled U-bearing phases economically important and nearly not mentioned in literature are established in these ores. At many strata oxidation deposits and cementation zones of endogenic deposits (Chernikov, 1981), X-ray amorphous and nanoscaled phases are uranium (IV + VI) oxides or silicates or phosphates, which are easily leached by the any mode of recovery. At the other deposits, for example, Dariuot group, Mongolia, these phases consist of U-bearing oxides of Ti, U-bearing alteration products of anatase and probably ilmenite (Chernikov, Kostikov, 2006), from which uranium is difficultly recovered by in situ well leaching of uranium. According to new data, the same phases are characteristic of certain potential areas in the Vitim, South Vitim, and Eravnoe districts discussed by Khomentovsky *et al.* (2000).

Cerianite [cerianite-(Ce)] was described for the first time in lenses hosted in altered carbonate rock from wall rock of nepheline syenite of the Sudbury uranium district (Ontario, Canada) (Graham, 1955). These lenses up to 0.3 m in length contain cerianite-(Ce), carbonate, nepheline, feldspar, tremolite, magnetite, ilmenite, and apatite. The mineral contains admixture of other *REE* and Th. Complete relative substitution of CeO_2 , UO_2 , ThO_2 , La_2O_3 and partial substitution of Y_2O_3 , In_2O_3 and ZrO_2 was identified (Duwez, Odell, 1950; Rüdorff, Valet, 1952; Padurow, Schusterius, 1953). Uranium was not measured in cerianite by chemical methods. According to the X-ray data of strongly radioactive metamictic cerianite-Ce ignited at 1000°C from microcline pegmatite Nesöya, East Antarctica (Matsumoto, Sakomoto, 1982) and Aktass, Kazakhstan (Kudaibergenova, Zubov, 2007), U content in this mineral is possibly higher than Th. Most d-spacings of

ignited cerianite-(Ce) from Nesöya and Aktass (Table 2) are closer to those of synthetic uraninite, rather than thorianite. The unit-cell dimension of ignited cerianite-(Ce) (5.451 Å) is remarkably different from that of standard cerianite-(Ce) (5.411 Å) and synthetic thorianite (5.6 Å). According to these data, it is closer to synthetic uraninite (5.46 Å). Hence, high radioactivity of cerianite-(Ce) from East Antarctica and Kazakhstan is caused by uranium, rather than thorium.

Like Ce, cerianite in most types of uranium ore is insignificant, it may be very important to form complex uraniferous carbonatite and U-P deposits. At least, predominant Ce among *REE* was established in certain U-bearing apatites of U-P deposits in Northern Kazakhstan. Korolev *et al.* (1983) noted 35.5% Ce with 27.6% La, 15.6% Nd, and less content of the other *REE* in apatite from gneiss. The author of this article revealed the similar *REE* content in apatite from the Tastykol deposit, Northern Kazakhstan. The presence of Ce as cerianite is well allowable.

Thorianite and uranothorite (U^{4+}Th) O_2 or Th-bearing uraninite (aldanite) are basically found in placers worldwide. Pegmatites are considered to be a source of these minerals (Sri Lanka; India; Siberia, Russia). In the placers, thorianite is associated with zircon, ilmenite, and thorite, while in pegmatites, with zircon, monazite, and beryl.

Th-bearing uraninite along with uranothorite is the major ore mineral in peralkaline granitic complexes of the Bokan Mountain located south of town Alaska, USA. Coffinite and brannerite were also identified in these ores. At the Ross Adams mine in this district, in 1957–1977, 1000 t of U_3O_8 was recovered with the grade of this oxide in the ore about 1% (Boze *et al.*, 1974; Yang, 1985). In the other cases, thorium uraninite is insignificant in non-economic ores and is accessory minerals in granite and granitic pegmatites.

Uranium (IV+VI) hydroxides

This group consists of hydrated nasturan, ianthinite, and cleusonite (Table 3). First of them, described as hydronasturan (Getseva, 1956) is frequent in ores. It is resulted from both hydration of nasturan in supergene zone and precipitation from uraniferous under-

Table 2. Interplanar-spaces and unit-cell dimension of cerianite, thorianite, and uraninite

Cerianite-(Ce), Nesöya, 1000°C, 7 hours			Cerenianite-(Ce) (ASTM)		Thorianite synthetic (ASTM)		Uraninite synthetic (ASTM)		Cerianite-(Ce), Aktass, Kazakhstan	
<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₁
	3.193	49	—	—	—	—	—	—	—	—
	3.182	45	—	—	—	—	—	—	—	—
111	3.51	100	3.124	100	3.234	100	3.14	100	3.14	100
200	2.723	40	2.706	29	2.800	35	2.73	50	2.71	10
220	1.929	48	1.913	51	1.980	58	1.926	80	1.90	20
			1.926	46	—	—	1.926	80	—	—
311	1.643	45	1.632	44	1.689	64	1.645	90	1.63	5
222	—	—	1.562	5	1.611	20	1.574	40	1.57	5
400	—	—	1.353	5	1.396	20	1.365	30	1.35	5
<i>a</i> ₀ = 5.451			<i>a</i> ₀ = 5.411		<i>a</i> ₀ = 5.600		<i>a</i> ₀ = 5.46		—	

Table 3. Uranium (IV+VI) hydroxides

Mineral, formula	Symmetry, unit- cell dimensions (Å)	Morphology of crystals. Color, luster, density (D), hardness (H)	Optical parameters	Strong reflections in X-ray diffraction pattern (intensity)	Other characteristic features
Hydrated nasturan (hydronasturan) UO _{2.3-2.9} •3-9H ₂ O	X-ray amorphous or poor-crystallized cubic phases	Dense aggregates. Dark grey;; vitreous; D 4.3-4.7; H 2-4.5	<i>n</i> 1.715-1.781 decreases as O ₂ and H ₂ O increase	X-ray amorphous, occasional weak diffuse reflections	Reflectance 6.4-11.4%.
Ianthinite U ₂ ⁴⁺ (UO ₂) ₄ O ₆ (OH) ₄ •9H ₂ O	Orthorhombic, <i>a</i> ₀ 11.52; <i>b</i> ₀ 7.15; <i>c</i> ₀ 30.3.	Tabular. Violet; vitreous; D 5.16 (calc. 5.03); H 2-3	<i>γ</i> 1.92; <i>β</i> 1.9; <i>α</i> 1.674, perfect cleavage parallel to (001), clear cleavage parallel to (100)	7.61 (10); 3.81 (6); 3.59 (6); 3.35 (6); 3.22 (9); 1.68 (5)	Pleochroic: violet — <i>γ</i> , colorless — <i>α</i>
Cleusonite (Pb,Sr)(U ⁴⁺ ,U ⁶⁺) (Fe ²⁺ ,Zn) ₂ (Ti,Fe ²⁺ , Fe ³⁺) ₁₈ (O,OH) ₃₈	Trigonal, <i>a</i> ₀ 10.576; <i>c</i> ₀ 21.325.	Tabular.	—	—	—

ground waters penetrated in the ore zone at depth. In the oxidizing zone, nasturan is gradually replaced through hydrated nasturan to urhite, which in turn is replaced by the X-ray amorphous hydroxides described for the first time, containing ferric iron, and enriched in Nb₂O₅ and SiO₂. Chemical analyses are below. In turn, uranium hydroxides with ferric iron are replaced by uranyl silicates.

Cleusonite found in two localities in the western Swiss Alps near Cleuson (Switzerland) in greenschist facies gneiss is Pb-Sr

hydrous oxides of tetra- and hexavalent uranium, ferrous and ferric iron, and zinc and titanium. It is associated with uraninite, tennantite, and hematite. Its economic importance is unclear.

Ianthinite, the only uranyl hydroxide mineral containing tetravalent uranium is found in small amount at the Schinkolobwe deposit (Thoreau, R. du Trieu de Terdonck, 1933; Gerasimovsky, 1956), in fluorite veins with nasturan in Wölensdorf, Bavaria, Germany, and at the Bigai, La Crusel, and Boi Noir

deposits, France (Branche *et al.*, 1951; Guillemin, Protas, 1959). At the Tulukuevo deposit, L.N. Belova identified ianthinite in hydroxide subzone at the depth of 90–120 m (Ishchukova *et al.*, 2005). It is economically insignificant.

Simple uranyl hydroxides

Holfertite, $U_{1.75}^{6+}Ti^{4+}Ca_{0.25}O_{7.17}(OH)_{0.67}(H_2O)_3$, found in fractures and cavities in rhyolite of the Searale Canyon, Thomas Range, Utah, USA (Sokolova *et al.*, 2005) is not discussed in this article. This mineral was not established in uranium ores. In addition, it is described as uranyl mineral with U^{6+} in its formula, whereas uranyl compounds contain linear group UO_2^{2+} , triatomic doubly charged cation presents independent structural unit in the mineral and affects its properties. The formula suggested by the authors of the cited paper does not correspond to uranyl minerals and given data do not allowing it reliable establishment.

Schoepite, metaschoepite, and paraschoepite (Crist, Clark, 1960) are simple hydrous uranyl hydroxides with variable content of free water. In this case, the formula of paraschoepite is not exactly determined. Well-shaped tabular crystals of schoepite and paraschoepite were observed in samples from the Schinkolobwe deposit (Democratic Republic of Congo). There, these minerals are abundant near surface as alteration product of uraninite or ianthinite. Under near-surface conditions, the minerals are intimately associated with curite and soddyite; they are less frequent at the deeper level of the oxidizing zone of the Schinkolobwe deposit. At this level, these minerals associated with becquerelite precipitate on the crusts of ianthinite (Vaes, Guillemin, 1959). At the deposits Wölensdorf, Bavaria, Germany and Great Bear Lake, Canada, these minerals precipitate on nasturan or occur as pseudomorphs after ianthinite adjacent to nasturan.

The formation of schoepite and paraschoepite in near-surface environment by replacing autunite and phosphuranylite is reported (Gritsaenko *et al.*, 1959; Chernikov, 1963; Belova, 1975). The author of this paper has studied in detail the similar phases considered as paraschoepite and schoepite from

the certain occurrences in the Kyzylsai deposit, Kirgizia and Taboshary deposit, Tajikistan. In the both cases, they are mixture of boltwoodite or uranophane, clay minerals, and varieties of mineral described as phosphurancalcite (Chernikov, Sidorenko, 1978). In the other cases, the opinion that schoepite and paraschoepite are resulted from replacing autunite and phosphuranylite under near-surface conditions, is appeared to be wrong.

Studtite, $UO_4 \cdot 4H_2O$, and metastudtite, $UO_4 \cdot 2H_2O$ (structural formulae are given in Table 4) are extremely unusual minerals, in which uranyl peroxide indicates high oxidized conditions during the formation of these minerals. They are described from Schinkolobwe and Menzenschwand, South Black Forest, Germany (Walenta, 1974; Deliens, Piret, 1983; Smith, 1988). Despite their insignificant economic importance, these minerals are of great interest to establish origin of mineral assemblages.

Complex uranyl hydroxides

Numerous uranyl hydroxides containing interlayer free H_2O and cations K, Na, Ca, Ba, Cu, Pb, and Bi are identified. Previously, some of them were suggested to be uranates, but crystallochemical study shows that these minerals belong to uranyl hydroxides (Crist, Clark, 1960; Protas, 1959, 1964). Among these minerals, very rare compreignacite from the Margnac deposit, Haute-Vienne, France (Protas, 1964) was found in the oxidation products of nasturan to be associated with bilietite and becquerelite. Rameauite (Cesbron *et al.*, 1972) is Ca-bearing variety and agrinierite is Ca-Sr variety of compreignacite. These minerals were described from the same deposits in the same alteration products of nasturan.

The Margnac deposit comprises a series of silicified NW and NE-trending fractures in granite. Occasionally, these fractures contain barite and fluorite with disseminated nasturan. Rare minerals accompanying nasturan are micrograins of iron sulfides, galena, sphalerite, chalcopyrite, and extremely rare bismuthinite. In some places, these fractures are cut by albitized and chloritized granite containing red calcite and hematite. In granite, cavities with leached quartz are found. Ura-

niium mineralization that is nasturan and coffinite completely replacing albite, in these places is maximal. In the oxidation zone, zoning of fractures is exhibited (outward):

- a – dark nodules of "gummite" with ianthinite, schoepite, and relict nasturan;
- b – red and orange "gummite" with becquerelite, billietite, schoepite, compreignacite, agrinierite, and rameauite; rameauite is the most abundant minerals among them;
- c – yellow to pale yellow massive to powder-like uranophane; calcite crystals in fractures in "gummite" are occasional;
- d – highly altered limonitized granite (Cesbron *et al.*, 1972).

Becquerelite, calcium uranyl hydroxide, previously assigned to simple uranyl hydroxide (Getseva, Savel'eva, 1956; Soboleva, Pudovkina, 1957; Frondel, 1958) is sufficiently widespread in the oxidized zone of the Schinkolobwe deposit. It occurs adjacent to uraninite, but after ianthinite; the latter is frequently replaced by schoepite (Thoreau, du Trieu de Terdonck, 1933; Vaes, Guillemin, 1959). Ianthinite exhibiting the initial stage of uraninite alteration is replaced by schoepite under oxidized conditions. The oxidized rim around crystals of uraninite reaching 15–20 cm across is largely composed of becquerelite and curite. Both other uranyl hydroxides and uranyl silicates are less frequent in this zone. An orange zone next to the zone of becquerelite-curite consists of curite and uranyl silicates. Becquerelite in the orange zone is nearly absent. In addition to curite and becquerelite, numerous uranyl hydroxides were found in the oxidized zone: billietite, fourmarierite, vandendriesscheite, wölsendorfit, masuyite, studtite, richetite, and protasite. However, all listed minerals are minor.

Becquerelite as alteration product of nasturan is reliably determined also in the ores of the Wölsendorf deposit in fluorite veins. At the Margnac deposit, becquerelite associated with compreignacite (see above) occurs in the zone of orange "gummite". Frondel (1958) reported insignificant becquerelite as alteration product of nasturan at the sandstone-type deposits of the Colorado Plateau, USA. The formation of the mineral associated with schoepite and fourmarierite predates the precipitation of uranyl vanadates (carnotite and

tyuyamunite) in the oxidizing zone of these deposits. Frondel (1958) noted the mineral in the oxidizing zone of the other uranium deposits in the USA and Canada. In the former Soviet Union, becquerelite was found in the oxidizing zone of the Sernyi, Turkmenistan and Botta Burum, Kirgizia.

The X-ray amorphous urhite first described by Getseva (1956) is quite abundant among simple hydrated oxides of hexavalent uranium. It was studied in detail at the Lastochka deposit, Khabarovsk krai. Figure 2 shows hydrated nasturan replaced by the secondary uranium minerals. The chemical composition of hydrated nasturan, urhite, and alteration products is given in Table 5. Initial alteration products of urhite and hydrated nasturan are replaced by Fe-rich U-bearing X-ray amorphous matter. As a result, isometric clusters are formed around nasturan or uranyl hydroxides (Fig. 2). The mechanism of formation of this matter is unclear. The chemical composition is characterized by high Si, H_2O , and Fe^{3+} and U^{6+} oxides (Table 5). The comparison of given compositions clearly indicates strong release of uranium during oxidation of nasturan and supergene alteration of residual products of its transformation. Simultaneously with release of uranium, Si, Al, H_2O , and Fe are introduced in the residual products replacing nasturan.

Residual oxidized products of nasturan of all stages of supergene alteration are enriched in Zr, Nb, Ti, and occasional Mo in comparison with primary mineral exceptional crusts of uranophane opened by trenches, in which only 0.0n % were measured. Uranium leached from oxidized nasturan and residual products of its alteration precipitates partially in fractures in the wall rocks at the same level and partially below, in the cementation zone.

Kopchenova *et al.* (1975), who reported the stage alteration of fine nasturan in albitite, revealed the gradual replacement of nasturan by the X-ray amorphous uranium hydroxides, hydronasturan and urhite, which replaced uranium, calcium, and lead silicates. Ishchukova *et al.* (2005) gave the following structure of the oxidizing zone of the Tulukuevo deposit (after Belova). Below 120 m from the surface, primary ores with nasturan in U ore and nasturan, coffinite, and molybdenite in U-Mo ore were

Table 4. Hydroxides of hexavalent uranium

Mineral, formula	Symmetry, unit-cell dimensions (Å)	Morphology of crystals. Color, luster, density (D); hardness (H)	Optical parameters	Strong reflections in X-ray diffraction pattern (intensity)	Other characteristic features
Urhite $\text{UO}_3 \cdot 1.7\text{-}3.1\text{H}_2\text{O}$	X-ray amorphous	Brown, amber yellow; vitreous; D 3.8-4.17; H 2-3	n 1.647-1.680	X-ray amorphous	—
Studtite $[(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$	Monoclinic; a_0 11.85; b_0 6.80; c_0 4.25; β 93°51' ($C2/m$)	Fibers. Yellow.	γ 1.68; β 1.555; α 1.545 (1.537)	5.93 (10) 3.40 (8) 2.96 (6) 2.23 (6)	—
Metastudtite $(\text{UO}_2)\text{O}_2(\text{H}_2\text{O})_2$	Orthorhombic; a_0 6.51; b_0 8.78; c_0 4.21 ($Immm$)	-/-	—	5.24 (10) 4.41 (7) 3.80 (7) 3.54 (8)	—
Schoepite $[(\text{UO}_2)_6\text{O}_2(\text{OH})_{12}] \cdot 12\text{H}_2\text{O}$ and Metaschoepite $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}] \cdot 10\text{H}_2\text{O}$	Orthorhombic; a_0 14.74 and 14.73; b_0 16.66 and 16.72; c_0 14.36 and 13.99 ($Pbca$) and ($Pbna$)	Prismatic. Yellow; vitreous; D 2-2.7; H 2-3	γ 1.735; α 1.685-1.705	7.34 (vs) 3.57 (ms) 3.22 (s) 2.01 (ms)	Pleochroic: yellow — γ , β ; colorless — α
Paraschoepite $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 2\text{H}_2\text{O}(\text{?})$	Orthorhombic; a_0 15.22; b_0 16.83; c_0 14.12 ($Pbca$)	Columnar. Yellow; vitreous	γ 1.74; α 1.785	7.88 (7) 3.38 (9) 3.09 (10) 2.89 (10) 2.08 (9) 1.82 (8) 1.59 (8)	-/-
Compreignacite $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2 \cdot 7\text{H}_2\text{O}$	Orthorhombic; a_0 14.85; b_0 7.175; c_0 12.187; ($Pnmm$)	Prismatic. Yellow; D 5.03; H 3	γ 1.802; α 1.798	7.40 (vs) 3.70 (s) 3.58 (s) 3.53 (ms) 3.34 (s) 3.19 (ms)	Pleochroic: yellow — γ ; colorless — α
Rameauite $\text{K}_2\text{Ca}(\text{UO}_2)_6\text{O}_6(\text{OH})_4 \cdot 9\text{H}_2\text{O}$	Monoclinic; a_0 14.22; b_0 14.26; c_0 13.97 ($C2/c$)	Prismatic. Orange; D 5.6	2V 32°	7.12 (vs) 3.57 (s) 3.495 (vs) 3.14 (vs) 3.12 (vs)	Perfect cleavage parallel to {010}
Agrinierite $(\text{K}_2\text{Ca,Sr})(\text{UO}_2)_3\text{O}_4 \cdot 4\text{H}_2\text{O}$	Orthorhombic; a_0 14.04; b_0 24.07; c_0 14.13 ($Cmmm$)	Tabular. Orange; D 5.7	2V 55°	7.08 (vs) 6.05 (s) 3.52 (s) 3.49 (s) 3.13 (vs)	Perfect cleavage parallel to {001}
Vandenbrandeite $\text{Cu}^{2+}(\text{UO}_2)(\text{OH})_4$	Triclinic; a_0 7.86; b_0 5.44; c_0 6.10 ($P1$)	Tabular. Dark green; D 5.03; H 4	γ 1.80; β 1.78; α 1.76; 2V great	5.25 (6) 3.87 (7) 3.47 (6) 3.16 (10) 1.83 (8)	Perfect cleavage parallel to {110}
Becquerelite $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}$	Orthorhombic; a_0 13.84; b_0 12.38 c_0 14.92 ($Pnma$)	Prismatic. Yellow; adamantine; D 5.9; H 2-3	γ 1.820-1.835; β 1.805-1.25; α 1.725-1.750; 2V 32°	7.50 (10) 3.75 (8) 3.56 (8) 3.22 (9) 2.58 (7)	Pleochroic: yellow — β , α ; colorless — γ
Protasite $\text{Ba}(\text{UO}_2)_3\text{O}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	Monoclinic; a_0 12.29; b_0 7.22; c_0 6.96 (Pn)	Tabular. Orange; metallic	γ 1.83; α 1.79; 2V 60-65°	7.06 (50) 3.14 (100) 3.11 (35) 2.496 (35)	Good cleavage parallel to {010}

Table 4.

Billietite $Ba(UO_2)_6O_4(OH)_6 \cdot 8H_2O$	Orthorhombic; a_0 7.15; b_0 12.07; c_0 15.08 (<i>Pnma</i>)	Tabular. Yellow; adamantine; D 5.18-5.36; H 2-3	γ 1.839-1.79; β 1.832-1.78 α 1.733-1.725; 2V 35-47°	7.53 (10) 3.77 (9) 3.17 (8) 2.03 (6) 1.654 (4)	Pleochroic: yellow – γ ; colorless – α
Vandriesscheite $Pb_3(UO_2)_{20}O_{12}(OH)_{22} \cdot 22H_2O$	Orthorhombic; a_0 13.96-14.12; b_0 14.36-16.80; c_0 14.30-14.72. (<i>Pmma</i>)	Prismatic. Orange; adamantine; D 4.5-5.5; H 3	γ 1.820-1.89; β 1.81-1.882; α 1.76-1.79; 2V up to -50°	7.41 (8) 3.61 (9) 3.22 (10) 2.55 (4) 2.01 (4)	Pleochroic: yellow – γ ; colorless – α
Fourmarierite $Pb(UO_2)_4O_3(OH)_4 \cdot 4H_2O$	Orthorhombic; a_0 14.00-14.1; b_0 16.47-16.75; c_0 14.39-14.55 (<i>Pbnm</i>)	Tabular. Red; adamantine; D 5.74; H 3-4	γ 1.04-1.94; β 1.9-1.92; α 1.85-1.865; 2V up to 55°	3.45 (9) 3.09 (10) 2.44 (6) 1.996 (6) 1.07 (8)	Pleochroic: yellow – γ ; colorless – β, α
Masuyite $Pb(UO_2)_3O_3(OH)_2 \cdot 3H_2O$	Orthorhombic; a_0 14.09-13.9; b_0 12.08-12.31; c_0 14.27-14.98 (<i>Pbnm</i>)	Tabular. Orange-red; D 5.08	γ 1.917; β 1.906; α 1.785; 2V -50°	7.10 (10) 3.54 (8) 3.15 (9) 2.51 (5) 1.984 (6)	Pleochroic: yellow – γ, β ; colorless – α
Curite $Pb_2(UO_2)_5O_7 \cdot 4H_2O$	Orthorhombic; a_0 12.50-12.55; b_0 13.01; c_0 8.37-8.40 (<i>Pna2</i>)	Prismatic. Orange; adamantine; D 7.19-7.4; H 4-5.	γ 2.12-2.15; β 2.07-2.11; α 2.05-2.06; 2V great	6.28 (10) 3.97 (9) 3.14 (8) 2.55 (6) 1.74 (5)	Pleochroic: dark red – γ ; orange – β ; yellow – α
Wölsendorfite $Pb_7(UO_2)_{14}O_{19}(OH)_4 \cdot 12H_2O$	Orthorhombic; a_0 11.92-11.95; b_0 13.96-13.99; c_0 6.90-7.02	Prismatic. Orange; D 6.8	γ 2.09 α 2.05	3.45 (9) 3.09 (10) 2.44 (6) 1.97 (8)	Good cleavage along {001}
Spriggite $Pb_3[(UO_2)_6O_8(OH)_2] \cdot 3H_2O$	Monoclinic. a_0 28.36; b_0 11.99; c_0 13.998 (<i>C2/c</i>)	Prismatic. Orange; vitreous; D 7.0; H - 4	γ 1.891 α 1.807	6.92 (60) 3.46 (80) 3.10 (100) 1.918 (60)	Strongly pleochroic from light yellow to dark orange
Richetite $Pb_9(UO_2)_{36}(OH)_{24}O_{36}$	Triclinic.	Dark green. Adamantine	γ 1.99 β 1.98	–	Pleochroic: green – γ ; pale yellow – β
Bauranoite $Ba(UO_2)_2O_3 \cdot 5H_2O$ and metabauranoite $Ba(UO_2)_2O_3 \cdot 2H_2O$	Orthorhombic.	Dense aggregates. Brown; adamantine; D 5.39-5.42	γ 1.932-1.960; β 1.94; α 1.911-1.925	–	–
Kalkuranit $Ca(UO_2)_2O_3 \cdot 5H_2O$ and metakalkuranit $Ca(UO_2)_2O_3 \cdot 2H_2O$	Unknown.	Orange; waxy; D 4.62-4.9	–	–	–
Uranosphenite $Bi(UO_2)O_2(OH)$	Monoclinic.	Long. Orange; D 6.12-6.89; H 2-3.	γ 2.05-2.06; β 1.981-1.985; α 1.955-1.959; 2V great	5.25 (6) 3.87 (7) 3.47 (6) 3.16 (10) 1.83 (8)	Non pleochroic
Clarkeite (Na,K, Ca,Pb)(UO ₂)O(OH) $\cdot 0-1H_2O$	Trigonal.	Reddish brown; waxy; D 6.39; H 4-5.	γ 2.11; β 2.098; α 1.997; 2V 30-50°	5.77 (8) 3.34 (9) 3.17 (10) 1.968 (7)	–

Notes. Reflections in X-ray diffraction pattern (s) strong, (ms) medium strong, and (vs) very strong.

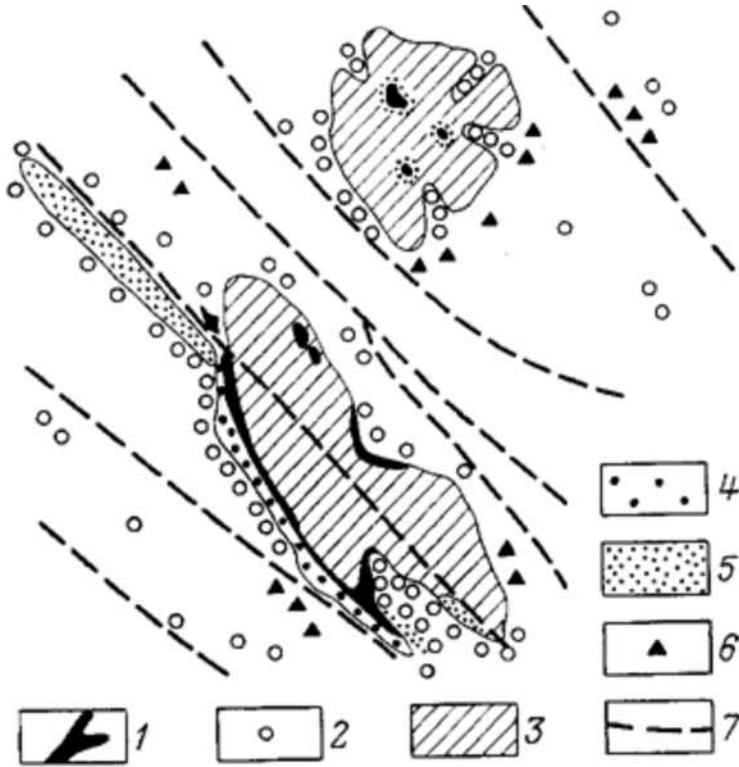


Fig. 2. Replacement of nasturan by oxidized minerals, Lastochka deposit, Khabarovsk krai.

(1) Relicts of nasturan; (2) beta-uranophane; (3) brown Fe- and U-bearing mineral; (4) curite-furmarierite-type hydroxides; (5) urhite; (6) limonite; (7) fractures.

identified at the deposit. At the depth of 120–90 m, there is the hydroxide subzone with ianthinite, schoepite, and paraschoepite after U ore and umohoite, mourite, and molybdenite after U-Mo ore, silicate-hydroxide subzone with protasite, wölsendorfite, bauranoite, uranospinite, novö ekite, chernikovite, and other uranium micas developed after U ore, and calcurmolite, iriginite, moluranite, and umohoite replacing Mo-U ore are traced upward from the level 60–90 m. Uranophane and beta-uranophane are found in the both ore types. According to our data, minor kalkuranit with metamorphic variety reported from the occurrences at the Murun massif (Rogova *et al.*, 1973) was observable in the silicate-hydroxide subzone. Down to 60 m from the surface, silicate subzone with uranophane and beta-uranophane in U ore and iriginite and calcurmolite in Mo-U ore follows. Down to 30 m, subzone of uranium leaching with Fe-Mn hydroxides, occasional uranophane and powellite after U-Mo ore is observed.

At the other Russia's and abroad deposits, the stage replacement of nasturan by uranyl minerals is less clear; subsequence of minerals is frequently disturbed. Commonly, the stage formation of minerals with oxidation of dense U ore is caused by sulfides, arsenides, and coffinite in the nasturan and uraninite veins. For example, the oxidation of coffinite associated with nasturan at the beginning of the process results in the precipitation of uranyl silicates rather than hydroxides, while arsenides cause the formation of uranyl arsenates. In the gallery at the Lastochka, a block of nasturan ore with small inclusions of As-bearing pyrite was found. The supergene alteration of this block resulted in the precipitation of trögerite and uranospinite after fresh nasturan.

The high permeability of orebodies causes the dissolution of nasturan rather than its hydration. For example, at the Uchkuduk-type deposits, Tajikistan, the oxidation of uranium ores hosted in sand was not accom-

Table 5. Chemical composition (wt.%) of hydrated nasturan and alteration products, Lastochka (Tumannyi) deposit, Khabarovsk krai, Russia

Oxides	Hydrated	Urhite	Urhite	U-Fe phases		Brownish	Uranophane	Uranophane
	nasturan					yellow veinlet		
UO ₂	31.76	—	—	—	—	—	—	—
UO ₃	51.65	66.02	61.30	26.14	18.72	49.0	46.33	52.75
SiO ₂	2.25	5.24	5.84	12.12	21.25	9.48	11.51	21.57
Al ₂ O ₃	2.15	0.17	1.35	4.82	5.67	2.41	3.06	5.92
Fe ₂ O ₃	—	2.06	7.06	36.95	36.87	2.58	3.70	0.64
CaO	2.54	2.03	2.50	1.12	1.58	2.40	2.30	5.28
MgO	—	0.71	0.27	0.58	0.48	0.41	0.36	0.35
PbO	1.80	1.90	2.43	—	1.00	0.91	1.00	—
ZrO ₂	0.55	0.62	1.28	1.22	0.30	2.10	3.35	—
Nb ₂ O ₅	4.86	3.70	3.15	2.11	1.40	9.00	8.00	—
As ₂ O ₅	0.15	3.33	0.12	—	0.73	—	0.02	—
K ₂ O(Na ₂ O)	—	—	—	—	0.23	1.23	1.22	0.32
MoO ₃	0.06	0.04	0.03	0.05	0.01	4.86	4.65	0.04
TiO ₂	—	0.30	0.70	0.67	0.19	1.93	2.55	show
H ₂ O	2.44	13.33	14.03	11.89	11.9	11.9	11.69	12.85
Cl	—	—	—	—	—	1.72	—	—
Total	100.21	99.45	100.06	97.67	100.33	99.93	99.74	99.72

panied by the formation of uranyl minerals and orebodies are separated from the oxidized brown sand colored by Fe³⁺ hydroxides by light band from which U and Fe are completely leached. The similar phenomenon is observable at the roll deposits of the South Kazakhstan, Siberia, Transbaikal Region, and sedimentary basins in Bulgaria. When the permeability of orebodies is irregular, nasturan is replaced by uranophane and shrökingerite rather than by uranyl hydroxides. For example, at the Rizak deposit, Kurama Ridge, Uzbekistan, located in mountainous district, modern oxidized zone begins its formation and veinlets of gummite with curite, becquerelite and billietite were observed at the surface. At few cm below surface, pockets of nasturan and hydrated nasturan retain in the gummite veinlets. Aside the gummite veinlets, uranophane occurring as thin crusts and earthy films fills fractures in wall rocks. In addition to uranium minerals, only Mn oxides, calcite, and kaolinite were observable in

this place. Downward, content of nasturan and hydrated nasturan increases in the veinlets and at a few meters below surface, these minerals are predominant. In this place, the ore-bearing fracture joins with a post-ore fracture zone. Content of nasturan in the orebody below junction of ore-bearing fracture and post-ore fracture zone sharply decreases, whereas concentration of uranophane significantly increases. No uranyl hydroxides were found in these places, although the oxidized zone is traced deeper. Sooty pitchblende is occasional in the oxidized ores.

Conclusions

Thus, according to new and literature data, simple oxides in uranium ores are nasturan, sooty pitchblende, and less frequent Th- and REE-free uraninite. Uranium-bearing cerianite is probable at complex carbonatite and U-P deposits and Th-bearing uraninite is the major ore mineral of peralkaline granite

of the Bokan Mountains, Alaska. Uraninite and nasturan are established to be transformed in different way in relation to permeability. Dense monomineralic segregations of uraninite and nasturan are oxidized to form hydroxide minerals. Currently, numerous simple and complex uranyl oxides, three uranium (IV + VI) oxides, and a few X-ray amorphous phases of hexavalent uranium are reported. Overwhelming majority of uranyl hydroxides occur in a few deposits: Schinkolobwe, Wölsendorf, Margnac, Tulukuevo, and Lastochka, where quite large monomineralic segregations of nasturan or uraninite crystals. Uranyl hydroxides are also formed as a result of oxidation of uraninite in pegmatite.

In the water-permeable areas, simple oxides are replaced by uranyl silicates omitting hydroxide stage or uranium is leached from the oxidized ore without formation any uranyl minerals. The oxidation of ore with sooty pitchblende in sand results in nearly complete removal of uranium. Gritsaenko *et al.* (1959) reported the leached oxidation zones. Highly leached oxidized zone is characteristic of most deposits in the Streltsovka structure, Southeastern Transbaikal Region and other deposit in Russia and abroad. Here-with, in the most cases, significant part is carried out of the orebody. In the other deposits, basically located in arid areas, a richer oxidized ore is formed: Sernyi, Turkmenistan; Rössing, Southwestern Africa, U-V deposits Shakoptar and Maili Sai, Kirgizia, and Pap, Uzbekistan (Chernikov *et al.*, 2010).

In addition, oxidation of nasturan associated with arsenides, As-bearing pyrite or native arsenic results in the formation of trögerite and other uranyl arsenates at the initial stage of nasturan transformation (Aktepe, Uzbekistan; Lastochka, Khabarovsk krai), rather than uranyl hydroxides. Hence, the stages of the formation of the oxidizing zone at the uranium deposits suggested by Belova (1975) are a rare particular instance with minor uranium hydroxides in uranium ores. During formation, the oxidizing zone both increases and decreases in size in comparison with size of primary orebody. In the humid areas, uranium is leached down to a significant depth in the oxidizing zone; in the other cases, content of uranium does not change substantially with oxidation of nasturan and uraninite ore

or significantly increases in comparison with fresh ore.

These features of uranium ore oxidizing are important for both theory and economics. In particular, they should be into account to elaborate exploration criteria for uranium deposits prospected by outcrops of orebodies as it was noted previously (Chernikov, 2010). Poor-crystallized nanoscaled X-ray amorphous matter is important because it reflects on technological properties of the ores especially when uranium is leached in situ by well.

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