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FORM OF OCCURRENCE OF URANIUM IN GROUND WATERS AND CONDITIONS OF ITS PRECIPITATION AS UO_2

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(ABSTRACT)

Ionization constants of uranium compounds in aqueous solution were used to estimate the forms in which uranium occurs in ground water, and the conditions necessary for its precipitation. It is shown that in normal weakly acid, neutral, and weakly alkaline ground waters of different mineralization characteristics uranium occurs predominantly as uranyl di- and tri-carbonate anions. The Eh values calculated for various theoretical compositions in equilibrium with solid UO_2 are in good agreement with appropriate hydrogeochemical data. The Eh value at the beginning of the precipitation of U^{4+} from ground waters ranges from approximately 0.0 to -0.2v depending on the concentration of uranium in the solution, the magnitude and character of the salts in the water, its pH, and the concentration of the HCO_3^- ion.

The composition, temperature, Eh, pH, and total uranium content are given for 11 ground waters.

The role played by ground water in the deposition of uranium ore is clearly seen in deposits localized in water-bearing sedimentary rocks. The relation between chemical composition of ground water, localization of ore, and alteration of the wall rock has been established for a number of deposits of this type [1]. To determine the conditions of deposition of such ores, it is necessary to know the mode of occurrence of uranium in ground water. Direct determination of uranium compounds dissolved in water is a complicated problem [2], and in the case of ground water it

becomes even more difficult between the dissolved and physicochemical data, the proportions in which water. The problem is hundred meters the ion and therefore equilibrium 25°C can be used with

A method is presented uranium compounds in conditions of equilibrium compounds and a solid UO_2 with the data of details

It is definitely known valent uranium are still exist in the form of ur In the presence of other ion will form cation or U^{4+} ion.

It may be expected water will contain not complexes formed by it

Physicochemical
Uranium (I)

	Equation
	$UO_2(OH)_2 = UO_2OH^+ + OH^-$
	$UO_2OH^+ = UO_2^{2+} + OH^-$
	$UO_2(CO_3)_2(H_2O)_2^{2-} = UO_2^{2+} + 2CO_3^{2-}$
	$UO_2(CO_3)_3^{4-} = UO_2^{2+} + 3CO_3^{2-}$
	$UO_2Cl^+ = UO_2^{2+} + Cl^-$
	$UO_2SO_4 = UO_2^{2+} + SO_4^{2-}$
	$UO_2(SO_4)_2^{2-} = UO_2^{2+} + 2SO_4^{2-}$
	$UO_2(SO_4)_3^{4-} = UO_2^{2+} + 3SO_4^{2-}$
	U^{4+}
	$U(OH)_4 = U^{4+} + 4OH^-$
	$U^{4+} + H_2O = UOH^{3+} + H^+$
	$U^{4+} + 2H_2O = U(OH)_2^{2+} + 2H^+$
	$UCl^{3+} = U^{4+} + Cl^-$
	$UCl_2^{2+} = U^{4+} + 2Cl^-$
	$USO_4^{2+} = U^{4+} + SO_4^{2-}$
	$U(SO_4)_2 = U^{4+} + 2SO_4^{2-}$

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becomes even more difficult, for it is necessary to prevent reaction between the dissolved uranium compounds and air. However, the available physicochemical data on uranium solutions make it possible to calculate the proportions in which various uranium compounds may be present in water. The problem is simplified by the fact that down to a depth of a few hundred meters the temperature of ground water is usually from 20 to 30°C, and therefore equilibrium constants usually given for temperatures of 20-25°C can be used without correction.

A method is presented here for calculating the proportions of different uranium compounds dissolved in ground water, and for determining the conditions of equilibrium between definite concentrations of these compounds and a solid UO₂ phase. The results of calculations are compared with the data of detailed hydrochemical investigations.

It is definitely known that only the compounds of quadrivalent and hexivalent uranium are stable in natural waters. In pure water, uranium may exist in the form of uranyl (UO₂²⁺) and uranium (U⁴⁺) ions and their hydrates. In the presence of other salts (except in perchlorate solutions) the uranyl ion will form cation or anion complexes, and so will the less well known U⁴⁺ ion.

It may be expected that a complex multicomponent system such as ground water will contain not only the simple U⁴⁺ and U⁶⁺ ions but also various complexes formed by these ions with all the free complex-forming ions

Table 1
Physicochemical Constants Used in Calculation of Equilibria of Uranium Compounds Occurring in Ground Waters.

Equation	K	Refer- ence
U ⁶⁺		
UO ₂ (OH) ₂ = UO ₂ OH ⁺ + OH ⁻	10 ⁻¹²	3
UO ₂ OH ⁺ = UO ₂ ²⁺ + OH ⁻	10 ^{-9.8}	4
UO ₂ (CO ₃) ₂ (H ₂ O) ₂ ²⁻ = UO ₂ ²⁺ + 2CO ₃ ²⁻ + 2N ₂ O	10 ^{-14.7}	5
UO ₂ (CO ₃) ₃ ⁴⁻ = UO ₂ ²⁺ + 3CO ₃ ²⁻	10 ^{-18.9}	5
UO ₂ Cl ⁺ = UO ₂ ²⁺ + Cl ⁻	10 ^{-6.88}	6
UO ₂ SO ₄ = UO ₂ ²⁺ + SO ₄ ²⁻	10 ^{-1.10} for ionic strength μ=1	7
UO ₂ (SO ₄) ₂ ²⁻ = UO ₂ ²⁺ + 2SO ₄ ²⁻	10 ^{-2.55} for μ=1	7
UO ₂ (SO ₄) ₃ ⁴⁻ = UO ₂ ²⁺ + 3SO ₄ ²⁻	10 ^{-8.40} for μ=1	7
U ⁴⁺		
U(OH) ₄ = U ⁴⁺ + 4OH ⁻	10 ^{-51.96}	8
U ⁴⁺ + H ₂ O = UOH ³⁺ + H ⁺	10 ^{-1.14}	8
U ⁴⁺ + 2H ₂ O = U(OH) ₂ ²⁺ + 2H ⁺	10 ^{-2.28}	8
UCl ³⁺ = U ⁴⁺ + Cl ⁻	10 ^{-6.10}	8
UCl ₂ ²⁺ = U ⁴⁺ + 2Cl ⁻	10 ^{-6.11}	8
USO ₄ ²⁺ = U ⁴⁺ + SO ₄ ²⁻	10 ^{-2.24} for μ=3.5	7
U(SO ₄) ₂ = U ⁴⁺ + 2SO ₄ ²⁻	10 ^{-3.42} for μ=3.5	7

present in the water. Under equilibrium conditions the proportion of these ions will be determined by their ionization constants, and their maximum concentration will be determined by the character of the medium determining the activity coefficients and the oxidation-reduction equilibria of the components present in the system.

The most common ions present in ground waters are Cl^- , SO_4^{2-} and CO_3^{2-} , and it is these ions that will combine with the uranium ions to form complexes. The equilibrium relations of the uranium compounds most likely to occur in ground waters, the activity coefficients of uranium oxides, and the principal components of uranium ores deposited by ground waters are given in Table 1.

It can be seen from the values of the activity coefficients of $\text{UO}_2(\text{OH})_2$ and $\text{U}(\text{OH})_4$, that the UO_2^{2+} and U^{4+} ions may become concentrated only in waters with low OH^- content, i. e., in acid waters, and that uranyl ions will predominate. Among the complex uranium ions the uranyl carbonate ions are most stable. Their ionization constants are many times higher than those of the uranyl sulfate and uranyl chloride complexes. Evidently the uranyl carbonate ions will predominate, not only in the bicarbonate, but also in the neutral sulfate and chloride or weakly alkaline ground waters which usually contain a certain amount of bicarbonate ion.

The calculation of the proportions in which various uranium compounds occur in ground water requires simultaneous solution of all equations listed in the tables. However, the ions formed by dissociation of salts with low activity coefficients and the ions with low ionization constants may be neglected without affecting the accuracy of the calculations. This is illustrated below by a calculation in which all uranium ions likely to occur in ground water are taken into account.

Analysis of Water from Black Uranium Ore in Carbonate Rocks

	Dissolved ions							Physico-chemical characteristic Eh, V; pH; t °C
	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺ +K	Ca ²⁺	Mg ²⁺	U	
g/l	1.028	0.106	1.391	0.749	0.311	0.071	4 · 10 ⁻⁶	-0.425; 6.6; 20
g-ion(at)/l	0.029	0.002	0.023	0.032	0.015	0.006	1.7 · 10 ⁻⁸	

In this case the ionic strength of the solution, i. e., half the sum of the products of molar concentration of the ions by the square of their valences, is 0.065. In a solution with this ionic strength the activity coefficients used to change from the stoichiometric to the active (thermodynamic) concentrations of ions with valences of 1, 2 and 4 are: $f(1) = 10^{-0.1}$, $f(2) = 10^{-0.38}$ and $f(4) = 10^{-1.52}$, respectively [9].

a) RELATION AMONG THE U^{4+} COMPOUNDS (Highest possible concentrations)

Using the activity coefficient of $\text{U}(\text{OH})_4$, we calculate the active concentration of uranium ions in the water under consideration:

Substituting using the

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$$a_{U^{4+}} = \frac{10^{-21.96}}{(10^{-7.4})^4} = 10^{-11.31}$$

Substituting this value in the equations of the ionization constants of U^{4+} and using data from the chemical analysis of water, we have:

$$a_{U(OH)_3^{+}} = 10^{-16.66}$$

$$a_{U(OH)_2^{2+}} = 10^{-11.33}$$

$$a_{UCl_3^{+}} = 10^{-23.67}$$

$$a_{UCl_2^{2+}} = 10^{-28.44}$$

$$[USO_4^{2+}] = 10^{-22.07}$$

$$[U(SO_4)_2] = 10^{-21.89}$$

Thus, the maximum concentrations of these forms of U^{4+} are vanishingly small as compared with the analytically determined concentration ($1.7 \cdot 10^{-8}$ g-at/l). Even the highest active concentration of U^{4+} in the form of $U(OH)_2^{2+}$ is lower than the actual concentration by a factor of 10^4 . It is evident that practically all uranium in the solution is present in a higher oxidation state.

b) RELATIONS AMONG THE U^{6+} COMPOUNDS

The quantitative relations among the U^{6+} ions are determined by their ionization coefficients, and the sum of these ions equals the total concentration of uranium as determined by chemical analysis. Solving the system of equations simultaneously for the conditions determined by analyses of water, and neglecting as negligibly small the concentrations of ionic forms lower than $[UO_2^{2+}]$, we get:

$$[UO_2^{2+}] = 10^{-11.8}$$

$$[UO_2OH^{+}] = 10^{-9.46} = 2 \cdot 10^{-10}$$

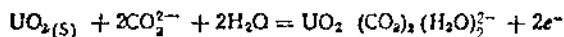
$$[UO_2(CO_3)_2(H_2O)_2^{2-}] = 10^{-7.68} \cdot 1.4 \cdot 10^{-8} = 82\%$$

$$[UO_2(CO_3)_3^{4-}] = \frac{10^{-6.50} \cdot 3 \cdot 10^{-9}}{\Sigma U = 1.7 \cdot 10^{-8}} = 15\%$$

Therefore, almost all uranium is present in this water in the anionic form, predominantly as uranyl dicarbonate dihydrate and partly as uranyl tricarbonate.

The correctness of the calculations of the dominant uranium compounds present in water which is assumed to be saturated may be checked by calculating the Eh of the equilibrium between water and ore, and then comparing the calculated values with those measured at the sampling locality.

For example, the equilibrium between $UO_2(CO_3)_2(H_2O)_2^{2-}$ and $UO_2(s)$ is determined by the equation:



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a) Carbonate Rocks

U	Physico-chemical characteristic Eh, V; pH; t °C
$4 \cdot 10^{-6}$	-0.125; 6.6; 20
$1.7 \cdot 10^{-8}$	

half the sum of the
square of their valences,
activity coefficients
(thermodynamic) con-
(1) = $10^{-0.1}$, f(2) = $10^{-0.33}$

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to the active concen-
on;

The oxidation-reduction potential of this reaction at 25°C and a total pressure of one atmosphere is:

$$Eh = -0.207 + 0.03 \log \frac{a_{\text{UO}_2(\text{CO}_3)_2 \cdot (\text{H}_2\text{O})_2^{2-}}}{a_{\text{CO}_3^{2-}}} \quad [11].$$

Substituting numerical data for the sample in this equation, we get:

$$Eh = -0.207 + 0.03 \log \frac{10^{-0.32} \cdot 10^{-7.66}}{(10^{-3.32})^2} = -0.13 \text{v.}$$

The Eh for the equilibrium between $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{s})$ is given by the equation:

$$Eh = -0.32 + 0.03 \log \frac{a_{\text{UO}_2(\text{CO}_3)_2^{2-}}}{a_{\text{CO}_3^{2-}}} \quad [11].$$

And in our example:

$$Eh = -0.32 + 0.03 \log \frac{10^{-1.32} \cdot 10^{-8.56}}{(10^{-3.32})^2} = -0.13 \text{v.}$$

Under the conditions of chemical equilibrium the oxidation-reduction potential of a solution determines the proportions of all oxidized and reduced compounds capable of reversible oxidation-reduction reaction present in it. Therefore, the calculated values of Eh for the above reactions when $\text{UO}_2(\text{s})$ is in equilibrium with ground water must correspond to the Eh of a water solution saturated with uranium.

In our example the value of Eh of water measured at the sampling locality is -0.125 v, or practically the same as the calculated value (Eh = 0.13 v).

The results of calculations of the uranium compounds present in ground waters, the Eh values computed for definite concentrations of these compounds in equilibrium with $\text{UO}_2(\text{s})$, and hydrogeochemical data measured in the field are given in Table 2.

It can be seen from the table that the uranyl carbonate complexes always predominate, whatever the composition and total alkalinity of ground water. The concentration of the sulfate and chloride complex ions in common neutral and weakly alkaline ground waters has little significance and may be neglected in calculating uranium compounds present in the waters.

The first two examples are of waters taken directly from deposits of black uranium ore. The Eh values for these waters agree well with the measurements of the oxidation-reduction potential made in the field, indicating that the waters are saturated with uranium. It is evident also that waters with different uranium concentrations are saturated with this element.

The oxidation-reduction potential at the beginning of precipitation of UO_2 from ground waters bears a complex relationship to the character and magnitude of total mineralization of water, its pH, the concentration of the complex-forming substances, and the total uranium concentration. All these factors must be considered in calculating the Eh of the beginning of precipitation of uranium from ground waters.

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Table 2. Results of Calculations of Uranium Compounds Present in Ground Waters of Different Compositions, and of the Eh at the Beginning of the Precipitation of Uranium as UO_2 .

No. in seq.	Water-bearing rock	Composition of ground water	Physicochemical characteristics			Uranium in water, E-ion(at)/l		Ehequill with UO_2 , v
			t°C	Eh, v	pH	[$\text{UO}_2(\text{OH})^+$]	[$\text{UO}_2(\text{CO}_3)_2^{2-}$]	
1	Fine-grained sand	$\text{SO}_4 \text{Cl}_{30}$ $\text{M}_{2.4} \text{Na}_2 \text{Ca}_2 \text{Mg}_{17}$	22	-0.093	7.2	$\frac{2 \cdot 10^{-8}}{16}$	$\frac{1 \cdot 10^{-8}}{8}$	-0.10
								$\frac{1.2 \cdot 10^{-7}}{100}$
								$\frac{1.7 \cdot 10^{-6}}{1.7 \cdot 10^{-6}}$

Table 2. Results of Calculations of Uranium Compounds Present in Ground Waters of Different Compositions, and of the Eh at the Beginning of the Precipitation of Uranium as UO_2 .

No. in seq.	Water-bearing rock	Composition of ground water	Physicochemical characteristics			Uranium in water, $\frac{g-ion(at)/l}{\%}$		Z U	Eh _{equil} with UO_2 , v
			t, °C	Eh, v	pH	[$UO_2(OH)_2$]	[$UO_2(CO_3)_2 \cdot 2H_2O$]		
1	Fine-grained sand	$M_{1.4} \frac{SO_4^2 Cl_{1.9}}{Na_{2.1} Ca_{3.2} Mg_{1.7}}$	22	-0.093	7.2	2.10 ⁻⁶	9.10 ⁻⁶	1.2.10 ⁻⁷	-0.10
2	Limestone	$M_{3.7} \frac{Cl_{1.3} HCO_3^2}{Na_{2.0} Ca_{2.7} Mg_{1.1}}$	20	-0.125	6.6	~0	1.4.10 ⁻⁶	1.7.10 ⁻⁶	-0.13
3	Granite	$CO_{2.2} M_{2.8} \frac{HCO_3^2 SO_4^2}{Ca_{1.1} Mg_{3.2} Na_{2.7}}$	0	+0.16	5.8	1.9.10 ⁻⁸	1.9.10 ⁻⁷	2.1.10 ⁻⁷	-0.03 (for 25°C)
4	Limestone	$M_{2.1} \frac{SO_4^2 Cl_{1.5} HCO_3^2}{Na_{2.4} Mg_{2.2} Ca_{2.2}}$	20	+0.24	7.0	5.10 ⁻⁶	8.3.10 ⁻⁷	1.10 ⁻⁶	-0.07
5	Same	$O_{0.0005} M_{0.5} \frac{HCO_3^2 SO_4^2}{Ca_{1.0} Mg_{1.0} Na_{2.1}}$	19	+0.5	7.4	8.10 ⁻⁹	1.5.10 ⁻⁷	1.7.10 ⁻⁷	-0.095
6	"	$H_2S_{0.007} CO_{0.16} M_{3.5} \frac{Cl_{1.8} HCO_3^2 SO_4^2}{Na_{3.0} Ca_{2.2} Mg_{1.8}}$	23	n. det.	6.8	2.10 ⁻⁸	3.2.10 ⁻⁷	4.2.10 ⁻⁷	-0.10
7	Granite	$M_{2.1} \frac{Cl_{1.0} SO_4^2}{Na_{2.1} Ca_{2.7} Mg_{1.0}}$	30.5	+0.20	8.1	2.5.10 ⁻⁸	5.5.10 ⁻⁷	1.25.10 ⁻⁶	-0.11
8	Same	$C_{0.0005} M_{0.9} \frac{HCO_3^2 SO_4^2 Cl_{1.50}}{Na_{1.9} Ca_{1.2}}$	20	+0.28	7.8	1.5	1.6.10 ⁻⁷	1.26.10 ⁻⁶	-0.12
9	Consolidated gravel	$M_{0.7} \frac{Cl_{1.7} HCO_3^2 SO_4^2}{Na_{2.0} Ca_{2.4} Mg_{1.6}}$	25	+0.07	7.6	2.5.10 ⁻⁹	3.5.10 ⁻⁶	4.2.10 ⁻⁶	-0.13
10	Limestone	$H_2S_{0.014} M_{0.7} \frac{HCO_3^2 SO_4^2}{Ca_{2.1} Mg_{5.1} Na_{2.8}}$	19	-0.08	8.36	—	3.6.10 ⁻⁸	7.1.10 ⁻⁶	-0.18
11	Limestone and sandstone	$M_{0.6} \frac{HCO_3^2 SO_4^2}{Na_{2.0} Ca_{3.3} Mg_{2.1}}$	17	n. det.	7.7	—	1.5.10 ⁻⁸	8.4.10 ⁻⁶	-0.2

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[11].

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$$E = -0.13v.$$

and $UO_2(s)$ is given by

[11].

$$E = -0.13v.$$

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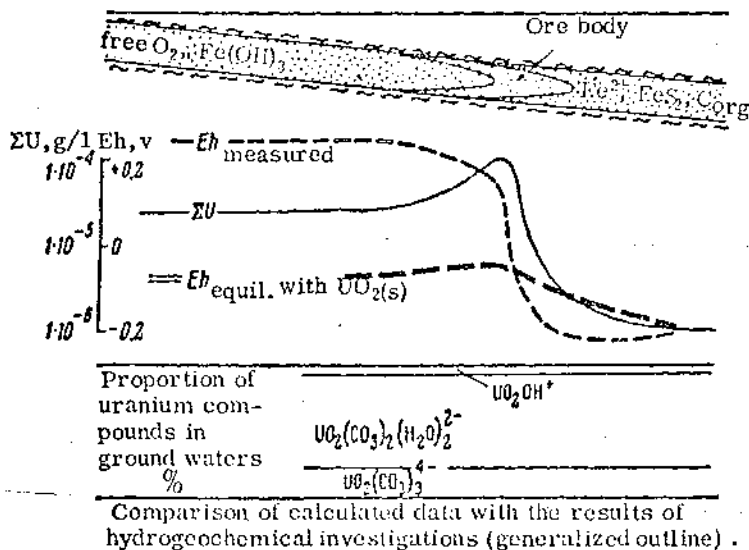
ic zonation determined

by variations in hydrogeochemical conditions. In such cases the presence of dissolved oxygen in ground water is indicated by limonitization of the country rock. In the oxidized zones wedging out from the ore there is a sharp decrease in the Eh of the ground water from high positive values to negative values, accompanied by a decrease in the concentration of uranium in the water. This indicates that uranium is still being deposited. Before passing through the ore body, ground water has a higher uranium concentration than afterwards, and this indicates that it is contributing uranium to the deposit [12, 13].

The diagram compares the data of hydrogeochemical investigations in the field with the results of calculations of the Eh of the equilibria between water and $UO_2(s)$ based on theoretical determination of the uranium compounds present in water. The predominant uranium complexes in ground water are the uranyl carbonate anions. Before passing through the ore body ground water is undersaturated with uranium with respect to $UO_2(s)$, in the ore body itself it is saturated, and at the wedging out end of the deposit and beyond it is oversaturated although its concentration of uranium is strongly decreased. The hypothesis that the precipitation of uranium from ground water at the wedging out end of the oxidized zone is caused by oxidation-reduction reactions is confirmed by calculation.

Thermodynamic calculations are applicable to equilibrium conditions. It is very probable that the observed oversaturation of water in uranium for a given Eh and pH at the wedging out ends of ore bodies and beyond them in the direction of water flow reflects the slow rate of formation of minerals containing UO_2 . It is possible also that metastable forms including complexed U^{4+} ions form in the water.

Ground waters are undersaturated in uranium when the rocks through which they circulate are deficient in uranium. Mixed waters composed of waters from uranium deposits and from uranium-poor rocks belong to this category. In areas with oxidized uranium ores, waters with high Eh contain



uranium in concentrations of order of magnitude corresponding to the solubility of UO_2 . It is to be expected when there is a sharp decrease in the Eh of the ground water from high positive values to negative values, accompanied by a decrease in the concentration of uranium in the water. This indicates that uranium is still being deposited. Before passing through the ore body, ground water has a higher uranium concentration than afterwards, and this indicates that it is contributing uranium to the deposit [12, 13].

Thus, the data of physical and chemical forms in which uranium occurs in the ground water and its precipitation. The results of calculations are in agreement with the data of hydrogeochemical investigations. It is understood that these calculations are applicable to conditions of ionic strength less than 0.1.

The calculations show that in weakly alkaline ground water uranium is precipitated predominantly as uranyl carbonate. The complexes are destroyed by the precipitation of uranium at the beginning of precipitation. At about -0.2 v, depending on the Eh of the solution, the magnitude and character of the precipitation, the concentration of the HCO_3^- ions.

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uranium in concentrations of the order of $n \cdot 10^{-2}$ g/l, approximately corresponding to the solubility of the U^{6+} hydroxide in such waters. This is to be expected when there is a scarcity of anions capable of fixing the cationic uranium in solution in the form of difficultly soluble secondary minerals.

Thus, the data of physical chemistry can be used to calculate the principal forms in which uranium occurs in ground waters and the conditions of its precipitation. The results of such calculations are in good agreement with the data of hydrogeochemical investigations. Of course, it must be understood that these calculations are applicable only to solutions with ionic strength less than 0.1, which corresponds to a total salinity of 4-6 g/l.

The calculations show that in the common weakly acid, neutral and weakly alkaline ground waters of different compositions uranium occurs predominantly as uranyl di- and tricarbonato anions. Uranium is precipitated from such waters in the quadrivalent form when the uranyl carbonate complexes are destroyed by oxidation-reduction reactions. The Eh value at the beginning of precipitation of uranium from ground waters varies from 0 to about -0.2 v, depending on the concentration of uranium in the solution, the magnitude and character of the salts in the water, its pH, and the concentration of the HCO_3^- ion.

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URANIUM AND THORIUM IN ROCKS

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The distribution of U and Th in rocks from the Urals and Southern Mugodzhars was investigated. The thorium content in these rocks is more abundant than in granitic rocks. The Th/U ratio in these rocks is entirely different from that in granitic rocks. A direct correlation of the content of rare earth elements and thorium in rare earth minerals and the sum of the U and Th content in these rocks was observed.

It was believed until now that the content of U and Th in nepheline syenites and in granitic rocks [1, 2] and in alkalic rocks of the Lovozero complex is approximately four times higher than in general [3, 4]. Our investigations in the Southern Mugodzhars have shown that these rocks have higher U and Th content than supposed that other nepheline syenites have relatively high uranium content.

In the Urals, nepheline syenites occur in length and up to 3-5 km in diameter.