

Uranium and thorium behavior in groundwater of the natural spa area “Choygan mineral water” (East Tuva)

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Abstract. The natural spa area “Choygan mineral waters”, a unique deposit of natural carbon dioxide mineral waters in Siberia, is located in the Eastern Sayan Mountains. There are 33 spring discharges in this area. Spring waters are mainly of HCO₃-Na-Ca type. TDS varies from 300 mg/L to 2600 mg/L, the temperature ranges from 7 °C (in spring 33) to 39 °C (in spring 12), pH varies from 5.9 to 8.3, and the value of the oxidation-reduction potential is from -170 mV to 236 mV. All studied waters were divided into two groups according to their temperature and geochemical conditions: cold fresh water in oxidizing environment and warm slightly brackish water in reducing environment. The uranium concentration varies from 0.7 to 14 µg/l and the thorium concentration varies from 0.001 to 0.33 µg/l in the studied waters. The predominant uranium complexes are (UO₂(CO₃)₃)⁴⁻, (UO₂(CO₃)₂)²⁻, UO₂CO₃, (UO₂(PO₄)₂)⁴⁻ in the waters in oxidizing and reducing environments. It was found that acid-alkaline and oxidizing-reducing conditions were the determining factors for uranium behavior and speciation in the studied waters. The pH conditions are determining factors for thorium behavior and speciation in the studied waters. In slightly acidic water the predominant thorium species is negatively charge complex (ThCO₃(OH)₃)⁻ (more than 95 %).

1. Introduction

The natural spa area “Choygan mineral waters”, a unique deposit of natural carbon dioxide mineral waters in Siberia, is located in the Eastern Sayan Mountains. Its formation is related to the latitudinal fault in the area with current and recently extinct volcanic activity in the East Sayan Mountains. The Choygan warm and cold springs are a potential deposit of natural carbon dioxide medicinal waters. The discharging cold and thermal natural carbon dioxide groundwaters have a unique set of bioactive components: Rn, SiO₂, CO₂, Fe, etc. This unique site is of abiding interest for researchers. The first studies of these groundwaters were performed by I.S. Kryzhin (1858), S.V. Obruchev (1945), V.G. Tkachuk (1955), E.V. Pinneker (1966–1967).

The attention focused on the study of these waters has contributed to the development and improvement of the research and getting new knowledge about chemical composition, processes and mechanisms of formation, balneology, etc [1, 2].

However, the abundance of most trace elements, including uranium and thorium, in groundwaters of the natural spa area Choygan has not been studied in detail. Therefore, the aim of this research is to



study the abundance and species of uranium and thorium in groundwaters of the natural spa area “Choygan mineral waters”.

Uranium can be found in nature both in geological and aqueous environment. The concentration of U in groundwater is less than 15 µg/L. The U concentration in groundwater and surface water can reach 1 mg/L [3]. Uranium exists as various chemical species in natural waters, including the free metal ions (UO_2^{2+}), and complexes with inorganic and organic ligands (both anion and cation) [4].

A lot of works are devoted to the study of the uranium behavior in the environment. A speciation of uranium depends on several factors, including pH, Eh, concentrations of organic matter, calcium carbonate or other ligands. Phosphate, carbonate, and humic substances are the most common ligands in natural waters. Hexavalent (U (VI)) and tetravalent (U (IV)) are the main oxidation states of U in nature waters.

In an open system, under oxidizing conditions, $\text{pH} < 5$, lack of natural organic matter and potential ligands, uranyl ion (UO_2^{2+}) dominates in waters with pH below 5 or hydroxy complexes in waters with pH below 6.5. Increase of pH (> 7) and the CO_3^{2-} and HCO_3^- ions contribute to the formation of the di- and tri-carbonate complexes [3]. Moreover, as referred to [5, 6] phosphorus with a relatively high concentration (6×10^{-4} mol/L) and low pH contribute to the sorption of U (VI).

The subsurface uranium environment could be strongly adsorbed on iron hydroxides, clay minerals and dissolved organic matter, although desorption may occur due to competition between mineral surface and ligands for binding of uranyl [3]. The last data show that complexes with dissolved organic matter (DOM) and uranyl complexes of calcium (Ca-uranyl carbonate complexes) play an important role in water chemistry of uranium. These complexes are still omitted from many speciation calculations and have minor importance in the alkaline pH range. However, Gustafsson et al. (2009) included dissolved organic C (DOC) in their simulation of U species and showed that the dominance of DOM- UO_2 complexes at $\text{pH} < 7.2$ under atmospheric CO_2 pressure. When partial CO_2 pressure (P_{CO_2}) in that study was increased 10-fold, the pH threshold, at which DOM- UO_2 complexes dominated decreased to 6.6, illustrating that carbonate species are predominantly complex-forming ligands [7].

2. Materials and methods

The natural spa area “Choygan mineral waters” is located between $52^\circ 34' 45.98''\text{N}$ and $52^\circ 34' 59.95''\text{N}$, and between $098^\circ 45' 17.12''\text{E}$ and $098^\circ 45' 25.27''\text{E}$ in the absolute height of 1550 m in the north-eastern part of the Tuva region on the western slope of the Eastern Sayan Mountains. The groundwaters discharge in 33 springs within a relatively small area of the Arzhaan-Khem river valley.

These mineral springs are confined to a large E–W striking fault in Precambrian rocks (gneisse, marble, schist) intruded by Paleozoic granites and diorites. The Upper Proterozoic Sailygskaya water-bearing sequence embraces marble, schist and marbled limestone interbedded with shale, quartzite, conglomerate and intruded by Devonian granite intrusions of Brensky sequence. Discharge of hot and cold springs are accompanied by the deposition of recent travertine. The travertine dome has a brown color due to Fe oxides and hydroxides.

The study of Choygan groundwater was performed in the summer of 2013. 33 water samples were collected. Electrical conductivity, temperature and pH were measured *in situ* using a portable device Water Test. Water chemical composition analysis was performed in Fundamental Research Laboratory of Hydrogeochemistry, Education and Research Centre “Water” (Tomsk Polytechnic University, Tomsk, Russia). Water samples were investigated by the following methods: titrimetric (HCO_3^- , CO_2 , CO_3^{2-}), ion chromatography (SO_4^{2-} , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Na^+ , K^+). The concentrations of trace elements, including uranium and thorium, were measured by ICP-MS (NexION 300D, Perkin Elmer, USA).

The geochemical modeling program HydroGeo (author M. Bukaty) was used to predict uranium and thorium speciation in the studied waters. For the calculations, the following variables were used: pH, Eh, temperature, 17 based ions: H^+ , OH^- , H_2O , e^- , Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^- , $(\text{SO}_4)^{2-}$, $(\text{HCO}_3)^-$, Fe^{3+} ,

Al^{3+} , $(\text{UO}_2)^{2+}$, $(\text{PO}_4)^{3-}$, SiO_2 and 72 species, including 49 uranium species and 12 thorium species: UO^+ , U^{2+} , $(\text{UO}_3)^-$, $(\text{UOH})^{2+}$, UO_3 , $(\text{UO}_4)^{2-}$, $(\text{HUO}_4)^-$, $(\text{HUO}_3)^-$, UO_2OH , $((\text{UO}_2)_4(\text{OH})_7)^+$, UO_2OH^+ , $\text{UO}_2(\text{OH})_2$, $((\text{UO}_2)_2(\text{OH})_2)^{2+}$, $((\text{UO}_2)_3(\text{OH})_4)^{2+}$, $((\text{UO}_2)_3(\text{OH})_5)^+$, $((\text{UO}_2)_2(\text{OH})_7)^-$, $(\text{UO}_2(\text{OH})_3)^-$, $((\text{UO}_2)_2(\text{OH})_3)^{3+}$, $(\text{UO}_2(\text{OH})_4)^{2-}$, $(\text{U}(\text{OH})_3)^+$, $\text{U}(\text{OH})_4$, $(\text{U}(\text{OH})_2)^{2+}$, HUO_2 , $(\text{HUO}_2)^+$, U^{4+} , U^{3+} , $(\text{UOH})^{3+}$, UO_2 , $(\text{UO}_2)^+$, $(\text{USO}_4)^{2+}$, $\text{U}(\text{SO}_4)_2$, $\text{UO}_2\text{S}_2\text{O}_3$, $(\text{U}(\text{CO}_3)_5)^{6-}$, $(\text{U}(\text{CO}_3)_4)^{4-}$, $((\text{UO}_2)_2\text{CO}_3(\text{OH})_3)^-$, $(\text{UO}_2(\text{CO}_3)_3)^{5-}$, $(\text{UO}_2(\text{CO}_3)_3)^{4-}$, $(\text{UO}_2(\text{CO}_3)_2)^{2-}$, UO_2CO_3 , $\text{UO}_2(\text{HCO}_3)_2$, $(\text{UO}_2\text{HCO}_3)^-$, $((\text{UO}_2)_3(\text{CO}_3)_6)^{6-}$, $(\text{UO}_2(\text{PO}_4)_2)^{4-}$, $(\text{UO}_2)_3(\text{PO}_4)_2$, $(\text{UO}_2\text{H}_2\text{PO}_4\text{H}_3\text{PO}_4)^+$, $(\text{UO}_2\text{H}_3\text{PO}_4)^{2+}$, $(\text{UO}_2\text{H}_2\text{PO}_4)^+$, $(\text{UHPO}_4)^{2+}$, $\text{U}(\text{HPO}_4)_2$, $(\text{Th}(\text{OH})_5)^-$, $(\text{Th}(\text{OH})_3)^+$, $(\text{Th}(\text{OH})_2)^{2+}$, $(\text{ThOH})^{3+}$, $(\text{Th}(\text{OH})_6)^{2-}$, $\text{Th}(\text{OH})_4$, $(\text{ThCl})^{3+}$, $(\text{ThSO}_4)^{2+}$, $\text{Th}(\text{SO}_4)_2$, $(\text{Th}(\text{SO}_4)_3)^{2-}$, $(\text{ThCO}_3(\text{OH})_3)^-$, $(\text{Th}(\text{CO}_3)_3)^{6-}$.

3. Results and Discussion

According to the hydrogeological and hydrogeochemical features, the studied groundwaters are divided into several types: natural carbon dioxide fissure-vein waters in reducing and oxidizing environments and groundwater of the regional-jointing zone (background waters) (table 1). The natural carbon dioxide fissure-vein waters in reducing environment are the water of springs № 1, 6–13, 15–17, 19–20, 22, 31–32. The natural carbon dioxide fissure-vein waters in oxidizing environment discharge in springs № 2–5, 21 and 23–28, 30. The groundwaters of the regional-jointing zone discharge in springs 33, 29, 29a [1, 2].

Within the studied area, the warm natural carbon dioxide fissure-vein waters in reducing environment are located in the central part of the Argens-Khem river valley, including the left bank. The temperature varies from 24 °C to 40 °C. This type of waters is characterized by slightly acidic conditions (mean value of pH 6.4). The mean value of Eh is 21 mV. TDS values are up to 1969 mg/L. Warm waters belong to the HCO_3 -Ca-Na type. The TDS values and the concentrations of such major ions as HCO_3 , Cl, Ca, Na, Mg, K and Si increase to the water temperature.

Table 1. Chemical composition of Choygan mineral waters, mg/L.

Parameter	Mean content		
	Natural carbon dioxide fissure-vein waters		Groundwaters of the regional-jointing zone
	Reducing environment	Oxidizing environment	
T, °C	30	18	9
Eh, mV	21	196	203
pH	6.4	6.3	7.6
CO_2	759.5	880.3	22.8
HCO_3^-	1619.4	959.6	229.5
SO_4^{2-}	14.2	28.4	10.1
Cl^-	23.8	11.0	3.3
Ca^{2+}	221.6	185.4	66
Na^+	290.4	109.2	2.3
Mg^{2+}	32.5	20.3	6.1
K^+	44.6	16.8	2.7
PO_4^{3-}	0.11	0.03	0.04
Th	0.00003	0.000004	0.000003
U	0.003	0.005	0.001
Th/U	0.008	0.002	0.014
TDS	1969	1212	320
Chemical type	HCO_3 -Ca-Na	HCO_3 -Na-Ca	HCO_3 -Ca
Number of points	18	12	3

The natural carbon dioxide fissure-vein waters with oxidizing conditions are cold where the temperature ranges from 11 to 20 °C. The waters are fresh and slightly acidic with the mean value of TDS of 1212 mg/L and the pH value of 5.9–6.7. The free carbonic acid concentration reaches 1488 mg/L (spring 4). The values of Eh vary from 170 to 236 mV. The mean value is 196 mV. Besides, the concentrations of sulfate ions in the waters from 5 to 59 mg/L underline the oxidizing conditions in the studied waters (table 1). According to the ratio of major ions the studied waters refer to the HCO_3 -Na-Ca type.

The groundwaters of the regional-jointing zone are characterized by oxidizing conditions. The mean value of the redox potential is 203 mV. These waters are cold with the mean temperature of 11 °C. Acid-alkaline properties of the water are slightly alkaline. The studied waters belong to the HCO_3 -Ca chemical type. The TDS values vary from 290 to 350 mg/L.

The studied water types differ from each other by the concentration of uranium and thorium. The uranium concentrations vary from 0.7 to 12 $\mu\text{g/L}$ in the natural carbon dioxide fissure-vein waters in reducing environment. The highest concentrations of uranium are observed in springs 16, 17, 19 and 31. From reducing to oxidizing conditions, the uranium concentration changes and increases with an increase of the TDS values. High uranium content varying from 0.16 to 14 $\mu\text{g/L}$ is observed in the natural carbon dioxide fissure-vein waters in oxidizing environment. The high concentration of uranium is typical for the waters with positive values of Eh. This is caused by the high solubility of U^{6+} in comparison to U^{4+} [8, 9].

Thorium accumulates mainly in the natural carbon dioxide fissure-vein waters in reducing environment. The mean concentration of thorium is 0.00003 mg/L in this type of waters. Its concentration is 8 times higher than those in the waters in oxidizing environment, where the mean concentration of thorium is 0.000004 mg/L.

The world average concentration of uranium in the rocks is 1–4 mg/kg while the content of thorium is three times higher and reaches 13 mg/kg. The concentrations of U in groundwater are usually low, typically in the range of 0.1–1 $\mu\text{g/L}$, although they can reach up to several tens or hundreds of $\mu\text{g/L}$ as a result of reactions with minerals in aquifers. The concentration of thorium is quite low and reaches up to 0.24 mg/L, which can be explained by the weak migration capacity of thorium in groundwater [3]. Uranium and thorium tend to occur together in the geological unit formation, due to the similarity in their ionic radius. The U^{4+} is easily oxidized and migrates during crustal evolution, whereas Th is stable in the oxidation zone. Therefore, Th is considered as a reference concentration and can be used to study the state of the original uranium concentration [10].

According to the abundance of uranium and thorium in granitic rocks, where the investigated waters occur, the thorium-uranium ratio is not less than 4. In the studied waters, the thorium-uranium ratio decreases from 0.0027 (an average) in the natural carbon dioxide fissure-vein waters in reducing environment to 0.0003 in natural carbon dioxide fissure-vein waters in oxidizing environment. This tendency is caused by uranium and thorium behavior in natural waters. The concentration of thorium in the natural carbon dioxide fissure-vein waters in reducing environment exceeds those in the natural carbon dioxide fissure-vein waters in oxidizing environment. At the same time, reverse behavior is characteristic for uranium: the concentration of uranium in the waters in the oxidizing environment is two times higher than those in the waters in the reducing environment. This is the main difference between the abundance of these elements in waters and rocks, which is determined by the peculiarities of the uranium and thorium speciation in natural waters [8, 9].

According to the results of physicochemical modeling of uranium speciation, bicarbonate complexes $(\text{UO}_2(\text{CO}_3)_2)^{2-}$ (up to 67 %), $(\text{UO}_2(\text{CO}_3)_3)^{4-}$ (up to 65 %), and UO_2CO_3 (up to 2 %) are the most abundant uranium species in the natural carbon dioxide fissure-vein waters with the Eh values varying from 0 to 142 mV and pH 6,4–6,9 (figure 1A). In the waters with Eh <0 and pH 6,1–6,4, the proportion of UO_2 and $\text{U}(\text{OH})_4$ complexes increases up to 48% and $(\text{U}(\text{OH})_3)^+$ (up to 5 %) and $((\text{UO}_2)_3(\text{CO}_3)_6)^{6-}$ (up to 5%). With the decrease of Eh value up to -90 – -170 mV and the pH value up to 6, the proportion of UO_2^0 complex increases up to 48 % and becomes predominant, whereas the proportion of $(\text{U}(\text{OH})_3)^+$ complex reaches 5 %.

In the spring waters with PO_4^{3-} content is more than 0.05 mg/L, uranyl phosphate $(\text{UO}_2(\text{PO}_4)_2)^{4-}$ emerges. The content of this complex reaches 10 %. In the water with the concentration of PO_4^{3-} is 0.46 mg/L this complex prevails, its content reaches up to 76%.

The predominant uranium complexes are $(\text{UO}_2(\text{CO}_3)_2)^{2-}$ (up to 80 %), $(\text{UO}_2(\text{CO}_3)_3)^{4-}$ (up to 54 %), and UO_2CO_3 (up to 3 %) in the slightly acidic natural carbon dioxide fissure-vein waters in oxidizing environment. With the values of pH up to 5.9–6.2, the proportion of $(\text{UO}_2(\text{CO}_3)_2)^{2-}$ complex increases, whereas the percent of $(\text{UO}_2(\text{CO}_3)_3)^{4-}$ complex decreases, and the UO_2CO_3 and $((\text{UO}_2)_3(\text{CO}_3)_6)^{6-}$ complexes emerge. The proportions of $(\text{UO}_2(\text{CO}_3)_2)^{2-}$ and $(\text{UO}_2(\text{CO}_3)_3)^{4-}$ complexes are equal under neutral conditions. Such behavior of uranium complexes is typical for the investigated type of waters [7, 11–13].

The formation of uranyl-carbonate complexes is caused by the occurrence of HCO_3^- and CO_3^{2-} in the groundwaters and pH 4.5–6.5. In this case a sufficient concentration of the ligand (CO_3^{2-}), and, consequently, the displacement of equilibrium toward the formation of carbonate complexes are provided [7, 9, 11–13].

The migration of uranium with carbonate compounds reduces, whereas the migration of uranyl ion with phosphate complexes increases in the waters with low pH. The percent of migration ($\text{UO}_2(\text{PO}_4)_2^{4+}$ is 30 %, ($\text{UO}_2\text{H}_2\text{PO}_4^+$ – 10 %, ($\text{UO}_2\text{H}_2\text{PO}_4\text{H}_3\text{PO}_4^+$ – 35 % at pH 5.9.

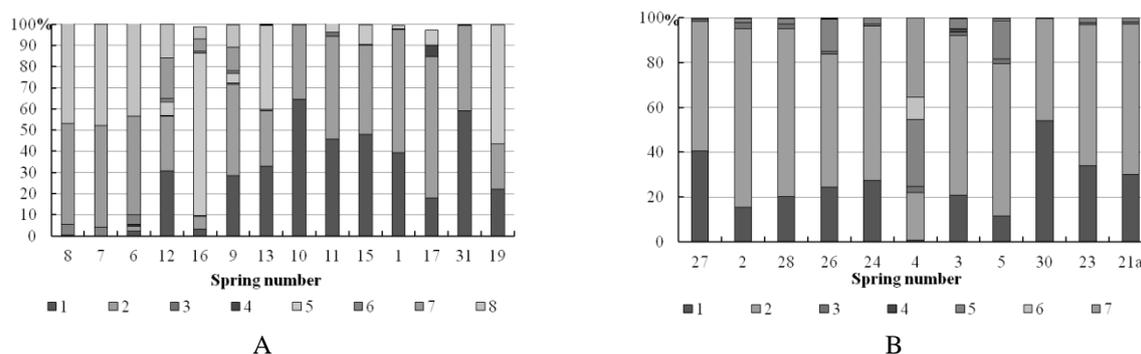


Figure 1. Proportions of uranium complexes as a function of Eh: (A) in the natural carbon dioxide fissure-vein waters with reducing conditions (1 – $(\text{UO}_2(\text{CO}_3)_3)^{4+}$, 2 – $(\text{UO}_2(\text{CO}_3)_2)^{2+}$, 3 – UO_2CO_3 , 4 – $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, 5 – $(\text{UO}_2(\text{PO}_4)_2)^{4+}$, 6 – $(\text{U}(\text{OH})_3)^+$, 7 – UO_2 , 8 – $\text{U}(\text{OH})_4$); (B) in the natural carbon dioxide fissure-vein waters with oxidizing conditions (1 – $(\text{UO}_2(\text{CO}_3)_3)^{4+}$, 2 – $(\text{UO}_2(\text{CO}_3)_2)^{2+}$, 3 – UO_2CO_3 , 4 – $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, 5 – $(\text{UO}_2(\text{PO}_4)_2)^{4+}$, 6 – $(\text{UO}_2\text{H}_2\text{PO}_4)^+$, 7 – $(\text{UO}_2\text{H}_2\text{PO}_4\text{H}_3\text{PO}_4)^+$).

The acid-alkaline conditions in the waters have a great influence on thorium migration as element-hydrolyzate. The negatively charge ($\text{ThCO}_3(\text{OH})_3^-$) is predominant thorium complex (more than 95 %) in slightly acidic waters of all studied types. The percent of this complex increases up to 100 % under neutral conditions. The proportion of the ($\text{ThCO}_3(\text{OH})_3^-$) complex decreases due to the formation of the positively charge thorium hydroxocomplexes ($(\text{Th}(\text{OH})_3)^+$ and $(\text{Th}(\text{OH})_2)^{2+}$) if pH-value decreases to 5.9–6.2.

4. Summary and Conclusions

The features of the water chemical composition in the natural spa area “Choygan mineral waters” were studied. The following water types were identified: warm natural carbon dioxide waters in reducing environment, cold natural carbon dioxide waters in oxidizing environment and groundwaters of the regional-jointing zone (background water).

The natural carbon dioxide waters in reducing environment belong to the $\text{HCO}_3\text{-Ca-Na}$ chemical type. The mean value of TDS is 1916 mg/L. The uranium concentrations vary from 0.7 to 12 $\mu\text{g/L}$. The thorium concentrations vary from 0.001 to 0.33 $\mu\text{g/L}$.

The second group of the waters is cold natural carbon dioxide waters in oxidizing environment. They are fresh with the average value of TDS is 1212 mg/L. Their chemical type is $\text{HCO}_3\text{-Na-Ca}$. The free carbonic acid concentrations vary from 200 to 1488 mg/L. The geochemical conditions of this water type are favorable for the uranium accumulation, the concentration of which is from 0.93 to 14 $\mu\text{g/L}$. The uranium concentration is higher in this type of water than that in the natural carbon dioxide waters in reducing environment. This is caused by the high concentration of free carbonic acid in the waters and the high positive values of Eh. The thorium concentrations in these waters range from 0.001 to 0.03 $\mu\text{g/L}$.

The predominant uranium complexes are $(\text{UO}_2(\text{CO}_3)_3)^{4+}$, $(\text{UO}_2(\text{CO}_3)_2)^{2+}$, UO_2CO_3 , $(\text{UO}_2(\text{PO}_4)_2)^{4+}$ in the waters in oxidizing and reducing environments. However, in the waters in oxidizing environment there are also such uranium complexes as $(\text{UO}_2\text{H}_2\text{PO}_4)^+$ and $(\text{UO}_2\text{H}_2\text{PO}_4\text{H}_3\text{PO}_4)^+$, the total percent of which is less than 2 %. In the waters in reducing environment the total proportion of these complexes increases up to 10 % and 35 %, respectively. In addition to the carbonate and phosphate complexes

the UO_2 , $\text{U}(\text{OH})_4$ and $(\text{U}(\text{OH})_3)^+$ compounds occur in the water in reduction environment. It was proved that acid-alkaline and oxidizing-reducing conditions are the determining factors for uranium behavior and speciation in the studied waters.

The acid-alkaline conditions are determining factors for thorium behavior and speciation in the studied waters. In the slightly acidic water the predominant thorium species is a negatively charge complex $(\text{ThCO}_3(\text{OH})_3)^-$ (more than 95 %). The proportion of the $(\text{ThCO}_3(\text{OH})_3)^-$ complex decreases due to the formation of positively charge thorium hydroxocomplexes $(\text{Th}(\text{OH})_3)^+$ and $(\text{Th}(\text{OH})_2)^{2+}$ when pH-value decreases up to 5.9–6.2.

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