Origin of high $^{234}U/^{238}U$ ratio in post-permafrost aquifers

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Abstract. Isotope composition and concentration (δ^2H, $\delta^{18}O$, $^{234}U/^{238}U$, Ar, $^{40}Ar/^{36}Ar$, $^3He/^4He$ and $^{20}Ne/^4He$) were measured in the groundwaters (Tomsk-7). Water has a distinct cold climate isotope signature δ^2H = -127..-140, $\delta^{18}O$ = -17.0.. -18.2 in contrast of modern meteoric water δ^2H = -117, $\delta^{18}O$ = -15.9. Stable isotopes are in concord with noble gas temperature t_{NGT} = 0..+4 °C and helium model ages t = 7-14 ka. Disequilibrium uranium $^{234}U/^{238}U$ up to 16 (activity ratio) obtained and explained of ^{234}U leaching by the melt water during the permafrost degradation.

Introduction

During the last decades, the Earth sciences have become increasingly focused on U-series isotope geochemistry and its application in global climate exchange. In closed systems older than 10^6 yrs uranium-238 decay chain should be at equilibrium that is rightly applied to general volume of Earth's crust. Secular equilibrium is $^{234}U/^{238}U = \gamma \approx 1$ in activity ratio or $^{234}U/^{238}U \approx 5.47 \cdot 10^{-5}$ in atom ratio (Holden 1990; Ludwig et al. 1992; Cheng et al., 2000).

Uranium mass distribution between solid and liquid phases in water-saturated rocks is about $U_{SOLID}/U_{AQUA} \approx 1000:1$ as a rule, therefore it was to be expected $\gamma \approx 1$ in deluted uranium. However depletion of ^{238}U in natural objects is a well known phenomenon after (Chalov 1954, 1964, 1975), (Cherdyntsev 1955, 1971), (Rosholt 1959), (Thurber 1962), (Rosholt and Ferreira 1965), etc. They and follow workers demonstrated very wide scale of $^{234}U/^{238}U$ ratios in natural environmental which present in Table 1. The application of U-series geochemistry to the Earth Sciences was thoroughly summarized by (Ivanovich and Harmon 1982, 1992).

More significant result from Table 1 is $^{234U}/^{238}U$ ratio in ocean (big averaging reservoir on Earth's surface) which is $\gamma \approx 1.15$ that points to preferred transport of ^{234}U from continents in comparison with ^{238}U. Excluded very high γ in bones, the greatest depletions of ^{238}U are observed in groundwaters. For example (Yamamoto et al. 2003) showed $^{234}U/^{238}U$ activity ratios a wide range from 2.7 to 51 in Tatsunokuchi hot spring waters and (Polyakov 1991) obtained $^{234}U/^{238}U \approx 54$ in cold water on island Saaremaa (Estonia).

The range of $^{234}U/^{238}U$ is affected by combination of recoil and leaching processes which discussed in large quantity of works. Initially the recoil atom is displaced from the site where parent one was located. The displacement distance is approximately n*10 nm depending on the substrate (Harvey 1962). It can thus be ejected directly into an adjacent phase, for example in water or other mineral. On the other hand, the daughter ^{234}U (free radical) is more likely to be oxidized to hexavalent state (U^{6+}) and forming the more soluble $(^{234}UO_2)^{2+}$ ions or complex with carbonates $^{234}UO_2(CO_3)_2^{2-}$ than parent species ($^{238}U^{4+}$) included in mineral lattice (Chalov 1975, Sun and Semkow 1998, Cui and Eriksen 2000, Marcos et al. 2000). Lastly, the tracks are damaged by the α-particles, which sizes are about 2 µm (Fleisher et al. 1975, Farley et al. 1996). These three reasons make the daughter species more prone to subsequent mobilization from solid phase to water than parent one.

This article is an attempt to bring the advances in the explanation of high $^{234}U/^{238}U$ ratio in some groundwaters and examining the time scale of any dynamic processes induce fractionation.

Table 1. Ranges of $^{234}U/^{238}U$ activity ratio found in natural environments after (Chenery et al. 2002, data recalculated into activity ratio).

Object	$^{234}U/^{238}U$		Object	$^{234}U/^{238}U$	
	min	max		min	max
Uderground waters	0.59	11.7	Igneous rocks	0.59	2.05
Terrestrial surface waters	0.78	2.44	Volcanic tuffs	0.49	1.56
Open-ocean water	1.07	1.15	Minerals and extract of minerals	0.78	7.80
Waters of uranium mineralisation	1.17	8.58	Sandstones	0.78	1.95
Various surfacial carbonates	0.88	2.93	Peat deposit	0.88	1.95
Fossil shells and bones	0.98	243.8			

Geological settings

Studied area is located to the north of Sewersk (Tomsk-7), when radioactive wastes of Siberian Chemical Combine (SCC) have been injected since 1963 in the deep terrigenous aquifers. Region is situated on south-east flank of Western Siberian artesian basin and on the north-west slope of Tomsk ledge of crystalline basement (see Figs. 1, 2 and Rybalchenko et al. 1998).

The geological groups of terrigenous marine and coastal sediments are distinguishes due to hydrogeological measurements and geological attributes. More sandy layers are identified as I, II, III, IVa, IVb, V and VI aquifers (bottom-up) and more clayey sediments are A-E aquitards. There are no carbonates in geological cross-section.

The groundwater recharge area is located to the north-east from the studied area on a watershed between rivers Tom' and Chulym at a distance about 40 km. The total regional water flow trends from the north-east to south-west towards the Tom' river valley. Groundwaters are fresh M = 0.2-0.4 g/l and sodium-calcium hydrocarbonate by chemistry.

Radioactive wastes are injected into I and II aquifers at the depth of about 270-390 m below surface. Filtration front of radioactive wastes is perfectly marked by

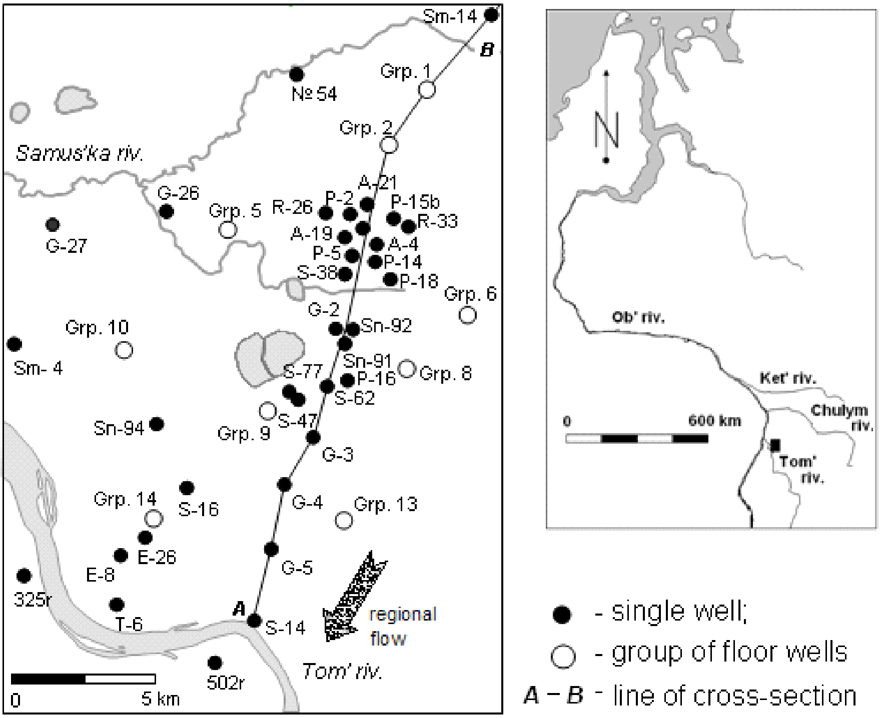

Fig. 1. Field plan of Sewersk region.

tritium, so its concentration in natural waters of IV aquifer and below is zero. In contrary the tritium contents in wastes are ranged up to $n*10^4$ Bq/l. Here will be analysed only data for natural water without considerable tritium to avoid of artificial effects.

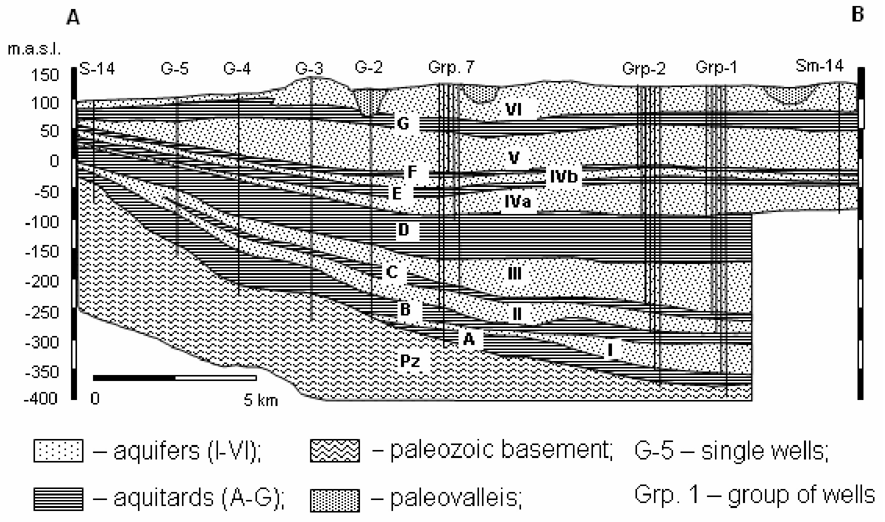

Fig. 2. Geological cross-section of Sewersk region.

Results and discussion

Isotope measurements were performed in period from 1995 to 2003 (δ^2H, $\delta^{18}O$, ^3H, $^{234}U/^{238}U$, Ar, $^{40}Ar/^{36}Ar$, $^3He/^4He$ and $^{20}Ne/^4He$). Stable isotopes were measured by standard procedure on pair of two-inlet MI-1201 mass-spectrometers, with accuracy 0.5 and 0.1 ‰ for hydrogen and oxygen respectively (Poljakov et al. 1988). Uranium isotope composition was measured on self-reconstructed alpha-spectrometer (Kuznetsov et al. 2000). Low tritium concentrations were measured after electrolytic concentration on TRICARB and MARC-2 apparatus by scintillation techinque with lower limit about 2 Bq/l (Poljakov et al. 1988). Extraction, purification and mass-spectrometric measurements of noble gases were carried out after (Kamensky et al. 1991). Standard deviations of reproducibility of volumertic argon analysis were 3-5 %, and isotope compositions 1, 1.5 and 3 % for $^{40}Ar/^{36}Ar$, $^{20}Ne/^4He$ and $^3He/^4He$, respectively.

Stable isotope composition of water taken from II-V aquifers is shown in Fig. 3 and Table 2. Majority of samples are shifted to the right of world meteoric water line (W.M.W.L., Craig's line on Fig. 3) and they have strong more negative delta values than the modern waters (Tom' river and meteoric water).

Table 2. Stable isotope data for groundwater of Sewersk region.

Borehole	Aquifer	$\delta^{18}O$, ‰ SMOW	$\delta^{2}H$, ‰ SMOW
E-8	V	-17.2	-128
Sn-92	V	-17.0	-127
Sn-91	IV	-17.7	-135
A-21	III	-17.6	-133
G-2	III	-18.0	-139
P-2	III	-17.8	-140
A-4	II	-17.4	-128
A-19	II	-17.8	-135
P-5	II	-17.6	-135
P15b	II	-18.2	-138
P-16	II	-18.1	-134
P-18	II	-17.2	-134
S-38	II	-17.5	-130
S-47	II	-18.0	-132
S-77	II	-17.9	-132
Tom' river		-15.7	-117
Meteoric water [a]		-15.96	-117.4

[a] Novosibirsk is the nearest point (Vienna, ISOHIS-GNIP http://isohis.iaea.org/).

It seems heaving of isotope values caused by frozen of water after recharging (Polyakov 1995). There are no permafrost in this region now, but isle permafrost obtained on about 250 km to north in Ket' river valley, maximum of ice cement is located on the deep 120-280 m (Evseeva 1998). This interval approximately likes to the average altitude of II-IV aquifers, in addition III aquifer contains water with the lightest isotope composition and more shifts from W.M.W.L. If the shift was produced by the frozen mechanism then initial delta was below then δ^2H = -

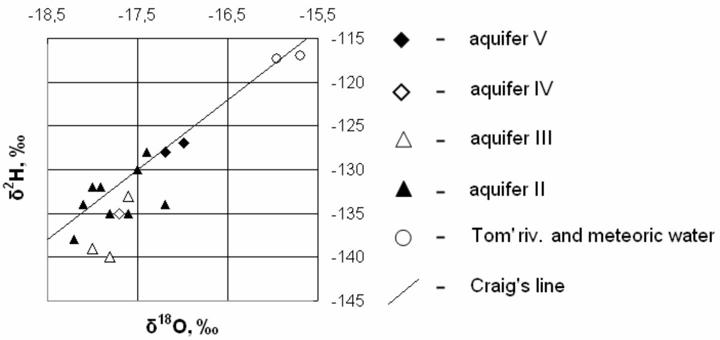

Fig. 3. Stable isotope composition. The isotope data shifts to the right of Craig's line (W.M.W.L.) and possibly to heavier values are caused by frozen of water after recharging.

140 ‰ and $\delta^{18}O$ = -18 ‰ and consequently temperature of the recharging water was closed to zero.

Radiogenic argon was subtracted by using $^{40}Ar/^{36}Ar$ ratio and the concentrations of atmospheric argon were interpreted as under controlled conditions of the atmospheric noble gases dissolution in the recharge water. It is possible to neglect altitude of the Earth' surface, because of it is varied in the narrow range 40-200 m above sea level (m.a.s.l.), so a temperature is a main parameter (Aeschbach-Hertig et al. 1999). The temperatures of the argon dissolution were calculated and listed in Table 4 as NGT, a precision of this estimation is not better 1 °C. Minimum of the temperature is in III aquifer that is adjusted with the stable isotope data.

Using $^{3}He/^{4}He$ vs $^{20}Ne/^{4}He$ systematics (Kamensky et al. 1991) we calculated an amount of the radiogenic helium in waters (see Table 3). Concentration of uranium and thorium in the water-bearing rocks was analysed by ICP MS and was compared with the large quantity of the gamma-logging data. Limits of [U] and [Th] variation are not wide (see Table 4).

For (U-Th)/4He age calculation is used mathematical model, which based on the follow equations (Rumynin and Karachevtsev 1992, scheme see on Fig. 4):

$$v_i m_i \frac{\partial C_i}{\partial x} - m_i n_i P_i' - J_{i-1} + J_i = 0 \text{ , where } J_i = \frac{D_M}{m_{0i}} (C_i - C_{i+1})$$

Table 3. Calculated data for groundwater of Sewersk region.

Aquifer	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰	NGT , °C	Radiogenic helium, [^{4}He], cm^3SPT/cm^3H_2O
V	-17.1 (2) [a]	-128 (2)	+4.2 (8)	$6.81 \cdot 10^{-8}$ (8)
IV	-17.7 (1)	-135 (1)	+2.6 (8)	$3.92 \cdot 10^{-7}$ (8)
III	-17.8 (3)	-137 (3)	–0.2 (8)	$3.34 \cdot 10^{-6}$ (8)
II	-17.7 (9)	-133 (9)	+1.4 (8)	$5.28 \cdot 10^{-6}$ (8)
I			+2.0 (4)	$4.78 \cdot 10^{-6}$ (4)
Pz basement				$1.37 \cdot 10^{-5}$ (1)

[a] here and after number of measurements is in the brackets.

Table 4. Uranium and thorium in rocks of Sewersk region.

Horizon	U, ppm	Th, ppm	Th/U
V, *F*, **IVb**, *E*, **IVa**	2.27 (14)	7.42 (14)	3.3
D, **III**, *C*, **II**, *B*	1.26 (29)	5.34 (29)	4.2

Table 5. Uranium isotope data for groundwater of Sewersk region.

Borehole	Aquifer	^{234}U/^{238}U ±2σ	Borehole	Aquifer	^{234}U/^{238}U ±2σ
325r	V	1.74 ±0.63	G-26	III	1.94 ±0.63
502r	V	1.74 ±0.63	R-33	III	4.73 ±0.31
S-14	IV	6.47 ±0.79	Sn-94	III	14.7 ±2.6
Sm-4	IV	3.9 ±1.1	R-26	II	16.1 ±3.9
T-10	IV	9.9 ±1.2	S-16	II	2.46 ±0.22

and ν_i –filtering velocity, LT^{-1}; m_i, m_{0i} – thickness of aquifer and aquitard, respectively, L; n_i – porosity; D_M – molecular diffusion, L^{2}T^{-1} , C_i – helium concentration, molL^{-3}; P'_i – production rate of ^{4}He in solid, molL^{-3}T^{-1}; x – lateral coordinate, L.

Combined equations for $i = 4$ (A+I+B+II), (C+III), (D+IVa+E+IVb), (F+V) (see Fig. 2); [U], [Th], x_i from this work; D_M, n, and m_i from (Alexandrova et al. 2003) were calculated numerically by fit on C_i, due to iteration of ν_i. Constant boundary conditions were on upper limit $C_{UPP} = 0$ and lower one C_{LOW} equal to the helium concentration in water of Paleozoic basement. Obtained ν_i and measured x_i were used for the age calculations, results of simulation are listed on Fig. 5.

The isotope ages for I, II, III aquifers lie in the range of 7-14 ka and look like to the end of the last glacial period in this region (see Fig.6). The measured uranium contents in groundwater are low or about ICP MS limit (0.01 µg/l) only in S-14 is [U] ~ 0.02 µg/l, so 1300 l samples were collected and prepared by co-precipitation with charcoal on the isotope analysis. The measured isotope composition of uranium varies from 1.74 to 16.1 (Table 5) and show very disequilibrium uranium in the deep interval 150-300 m below Earth' surface, which likes on the isle permafrost location in Ket' river valley.

What is a reason(s) of the soluted uranium disequilibrium? The hydrothermal activity is absent in region at least after start of Cretaceous, the dilution of rocks in water can be ignore completely take into consideration the chemistry of water is fresh and the concentration of uranium is very low. The distinct cold climate isotope signature (δ^2H, δ^{18}O) of water is adjusted with NGT of groundwater (t_{NGT} =0..4 °C) and with isotope ages about $t \approx 10$ ka for I, II and III aquifers, therefore the disequilibrium is most likely stimulated by the permafrost degradation.

Possibly follow process led to forming of isotope effect on the soluted uranium. During the Pleistocene ice cycle ^{234}U is accumulated in the rock, but could not leave the lattice, because the water was frozen. After start of the ultimate deglaciation the melt water extracted whole of ^{234}U which was born in 120 ka time interval. Excess of ^{234}U is very low in that part of II aquifer (see S-16 in Table 5) which was located below the permafrost bottom, i.e. deeper 350 m from the Earth' surface. In addition excess of ^{234}U absents in the upper aquifers (V and VI) where the old melt water replaced to modern meteoric water due to high rate of the water cycle.

Conclusion

Isotope data (δ2H, δ18O, 234U/238U, Ar, 40Ar/36Ar, 3He/4He and 20Ne/4He) were measured in the groundwaters (Tomsk-7). Water has a distinct cold climate isotope signature δ2H = -127..-140, δ18O = -17.0.. -18.2 in contrast of modern meteoric water δ2H = -117, δ18O = -15.9. Stale isotope data are in concord with

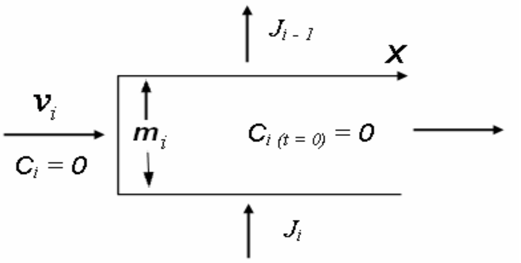

Fig. 4. Mathematical model of radiogenic helium migration.

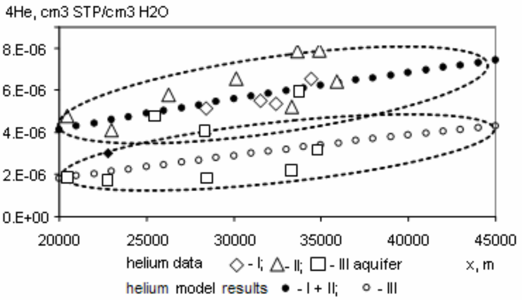

Fig. 5. Comparison of measured helium data and model one for I, II, III aquifers.

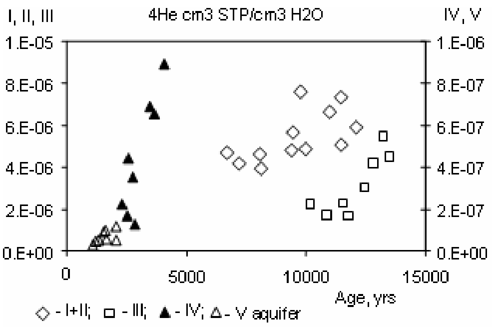

Fig. 6. The helium model ages of groundwater.

noble gas temperature tNGT = 0..+4 oC and the model helium ages 7-14 ka. Disequilibrium in the uranium serie (234U/238U up to 16) is explained of 234U leaching by the melt water during the last permafrost degradation.

Acknowledgments

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