Noble gases isotopes and tritium as tracers in environmental hydrogeology

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Introduction

The noble gases isotopes and tritium enable us very effective tools for investigation of a groundwater flow and a mass-transport of pollutants. For these aims are realized both the special tracer experiments and using isotopes which were put into environmental spontaneously due to artificial or natural processes before study. Using of these last artificial and natural isotopes is preferably for most practical problems regarding of environmental engineering, because of:

- it deflates a common cost of study;
- area and time circulation scale of these isotopes is lot more than any special tracer experiment;
- this method enables straight away to study the reaction of hydrogeological systems on large scale and long isotope impact.

Early in the XX century it was formulate a conception of the active and slow water circulation zones of Earth crust. This conception was based on comparison of the geochemical characteristics of shallow and deep waters. Though the conception had not any quantitative age criterions but it was meant there are young and old waters in an underground hydrosphere. The time scales for young and old waters was appeared when the isotope dating methods were developed. In this study are examined two methods:

- tritium/helium-3 – $^3H/^3He$;
- uranium/helium – $(U+Th)/^4He$.

Both ages and also the isotope geochemical data, which should be found for dating procedure, perfectly were used for the environmental protection aims. There are estimation of actual speed of a groundwater filtration and a retardation factor of pollutants in young waters, which subject to negative anthropogenic impact, a drinking water supply, a radioactive and high-toxic waste disposal. Farther some theoretical principles of the groundwater dating and the practical ages will be show.

Groundwater dating

A scale of any method is determined proportion between some of the technical and physical parameters. In our case the lower limit of dating depend on sensitivity of helium-3 and helium-4 measurements. It averages several months for $^3H/^3He$ and several thousands of years for $(U+Th)/^4He$, respectively. Now the upper limit of $^3H/^3He$ is about 50 years, backup to 1952 when thermonuclear bomb was tested firstly. The upper limit of $^3H/^3He$ for future time maybe estimate as $t = 7*\tau_{1/2} \cong 80$ years (where $\tau_{1/2}$ is half-life of tritium), i.e. terminus when about 1% of the present-day tritium will keep in system. The $(U+Th)/^4He$ method essentially has not the upper limit and the uranium/helium ages more than several tens of millions years are known.

Basic formulas and definitions

Young waters of active circulation zone of underground hydrosphere

After LIBBY and KAUFMAN (1954) was popular the tritium method, because of tritium is only the radioactive isotope which the water molecules include, but this method has the strict limitations as operated with the simple radioactive decay equation:

$$[^3H] = [^3H_0]*\exp(-\lambda*t) \quad (1)$$

So, the input function of tritium $[^3H_0]$ and the dilution of young water by the tritium dead old water must be set for the correct groundwater age obtain. These two limitations result in the tritium method gives only the semi-quantitative estimations.

TOLSTIKHIN & KAMENSKY (1969) took into account the accumulation of helium-3 due to the tritium decay:

$$^3H \rightarrow {}^3He_{TRI} + \beta$$

and suggested to calculate the input concentration of tritium as:

$$[^3H_0] = [^3H] + 4.021*10^{14}*[^3He_{TRI}] \quad (2)$$

after substitutions (2) in (1) and transformation:

$$t = 17.69*\ln(1 + 4.021*10^{14}*[^3He_{TRI}]/ [^3H]) \text{ years} \quad (3)$$

where $[^3H]$ – tritium and $[^3He_{TRI}]$ – the tritiogenic helium-3 concentrations, which are measured present-day in water, TU and ccSTP/cc H_2O, respectively.

Old waters and fluids of slow circulation zone

The uranium/helium-4 method was developed for the natural gas exploring (SAVCHENKO, 1935; BARNES & CLARCE, 1987):

$$[^4He_R] = (12.1*[U] + 2.9*[Th])*T*(1-L) *(D_R/D_W)*(1-p)/p \quad \text{ccSTP/g } H_2O \quad (4)$$

where [U] and [Th] – the concentrations of uranium and thorium, ppm; T – the continuance of water-rock contact, years; L – the helium conservation coefficient for water-bearing rocks, D_R and D_W – the density of rocks and water, g/g; p – porosity.

Uranium-helium method was popular among the hydrogeologists until 60-70th, but it fairly often gave false ages, which discordance with the hydrogeological conditions. Many specialists tried to correct calculation formula by some coefficients that had not the realistic positive effect.

Mixing of young and old waters

Mixing of helium from active and helium from the slow water circulation zones is main process, which causes the worst faults of a dating procedure both in the tritium/helium-3 and in the uranium/helium methods. So, briefly view the basic principles of the helium isotope evolution in the underground hydrosphere (see Fig.1).

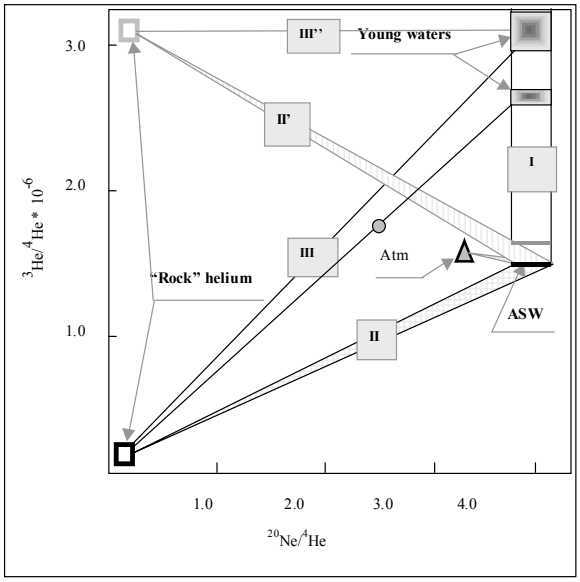

Fig. 1: $^3He/^4He$ versus $^{20}Ne/^4He$ systematic of the helium isotopes evolution in underground hydrosphere.

ASW – air saturated water; **Atm** – atmospheric noble gases.

Lines: **I** – isotope evolu-tion of young water due to tritium decay;
II, **II'** – accumu-lation of rock-forming helium in water;
III, **III'** – mixing of young and old waters
○ – single sample

The isotope composition of the air-saturated water is the starting-point of all helium systematic. The atmospheric rare gases are dissolved in the fresh meteoric water, which has follow isotope characteristics $^3He/^4He = (1.382 \pm 0.006)*10^{-6}$ (MAMYRIN et al., 1970; WEISS 1970; TOP et al., 1989) and $^{20}Ne/^4He = (4.26 – 3.81)$ (TOP et al., 1989) for the temperature range from 0 to 20°C (black line on Fig. 1). The meteoric water seepage through Earth surface and turn in the unsaturated zone, where sometimes the infiltration water can absorb “excess” air (AESCHBACH-HERTIG et al., 1998; STUTE et al., 1997). Then isotope characteristics of the infiltration water are shifted from **ASW** position to the atmosphere composition. The isotope coordinates of the infiltration water with an “excess” air belong to small light-grey triangle, which joins **ASW** line (0% of “excess” air) to **Atm** point (100% of air) on Figure 1.

When the infiltration water crosses a water table and come into the saturated zone then gas exchange between the underground water and atmosphere is stopped and accumulation of the

radiogenic products are started. For the young water, i.e. water of the active circulation zone (subscript **Y**), only accumulation of tritiogenic helium-3 is the considerable process (now age scale less than 50 years), so $(^3He/^4He)_Y$ ratio increases along the streak **I**, but $^{20}Ne/^4He$ ratio is constant. Left and right borders of the streak **I** equal to $^{20}Ne/^4He$ ratio for 20 and 0°C, respectively. A current value of $(^3He/^4He)_Y$ ratio depends on the initial tritium concentration and interval of time which elapsed after isolation of water in the saturated zone. This residence time of the tritiogenic helium-3 atoms in the underground hydrosphere is tritium/helium-3 age (t) of the young water.

More considerable process for the isotopes of the rare gases in the old waters and fluids from the zone of slow circulation (subscript **O**) is the accumulation of ^3He and ^4He, which are emanated from the water-bearing rocks due to dispersed U, Th, and ^6Li (scale more than 1000 years, see accumulation lines **II** and **II'**). Therefore an evolution trend of $^3He/^4He$ isotope ratio completely depends on $(^3He/^4He)_R$ ratio in the water-bearing rocks (subscript **R** means the rock-product helium), in contrast $(^{20}Ne/^4He)_O$ ratio always is decreased:

$$(^3He/^4He)_O = \{[^3He_{ASW}] + [^4He_R]^* (^3He/^4He)_R)\} / \{[^4He_{ASW}] + [^4He_R]\}, \quad (5)$$

$$(^{20}Ne/^4He)_O = [^{20}Ne]_{ASW} / \{[^4He_{ASW}] + [^4He_R]\} \quad (6)$$

where $[^3He_{ASW}]$, $[^4He_{ASW}]$ and $[^{20}Ne]_{ASW}$ are the concentrations of the atmogenic component in the infiltrogenic water; $[^4He_R]$ is estimated from (4) and $(^3He/^4He)_R$ is calculated or measured in the water-bearing rocks.

Figure 1 shows as the general case of the helium accumulation (see evolution lines **II** from $(^3He/^4He)_{ASW}$ to $(^3He/^4He)_R \approx 2*10^{-8}$), and also the rare case (see lines **II'** from $(^3He/^4He)_{ASW}$ to $(^3He/^4He)_R \geq 3*10^{-6}$) (MAMYRIN & TOLSTIKHIN, 1984). A current value of the helium concentration, and correspondingly $(^{20}Ne/^4He)_O$ ratio, is depended from equation (3). The uranium/helium age (T) is the time of the water-rock interaction after isolation of water in the saturated zone.

For the old water it can be supposes all natural tritium straight away turned in helium-3. Then $^3He/^4He$ ratio for **ASW** amounted $\approx 1.7*10^{-6}$, if the concentration of the initial tritium was about 1TU (see the grey line inside streak **I** slightly higher of **ASW**), but this shift from **ASW** is the negligible quantity for the isotope evolution of the old water with age more than 10^4 years.

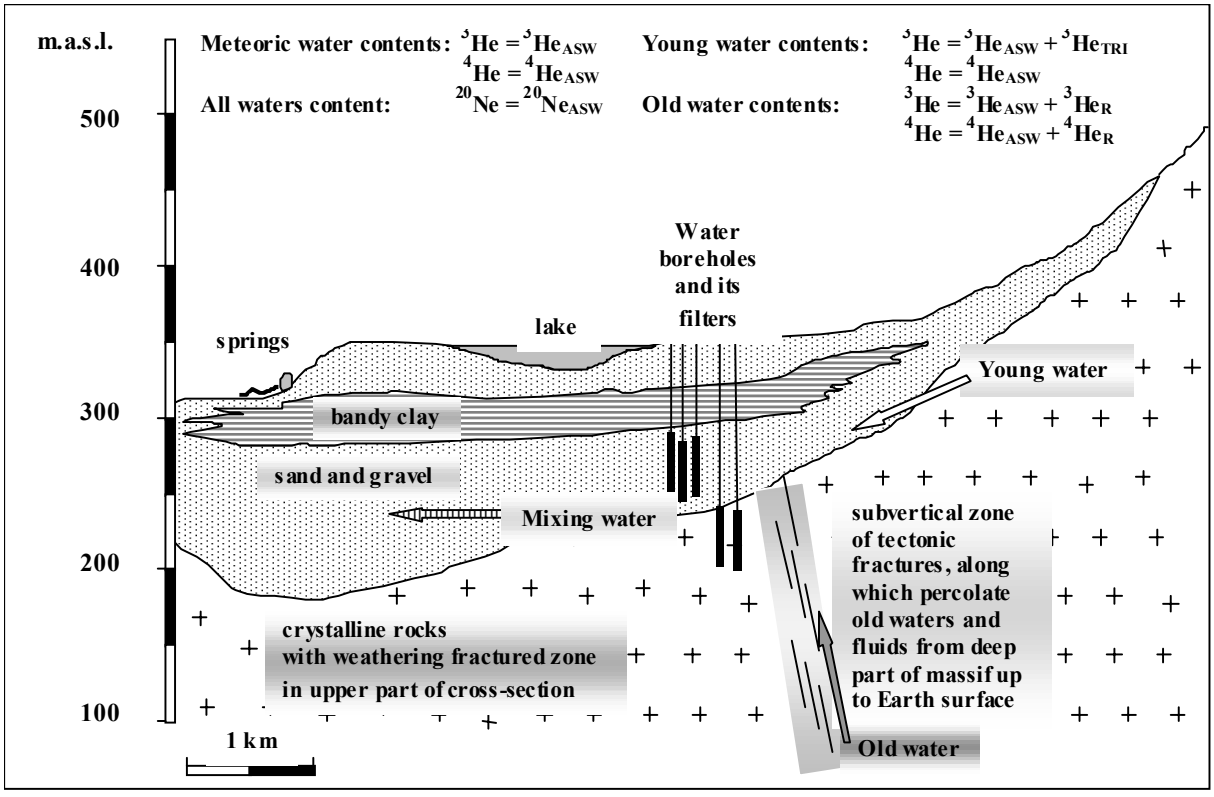

Fig. 2: Typical geological cross-section of Khibiny and Kovdor crystalline massifs, and eventuality of young and old water mixing.

Mixing of the young water and the old fluid is the general case for the shallow aquifers (SCHLOSSER et al., 1989; KAMENSKY et al., 1991; SOLOMON et al., 1994; KIPFER et al., 1997). In the helium-neon systematic it means mixing of He_Y and He_O (but not directly He_Y and He_R), therefore He_Y denotes the young water itself, and He_O has in mind both the old water and helium as a component of a gas phase. The ratios $(^3He/^4He)_Y$, and $(^3He/^4He)_O$ and $(^{20}Ne/^4He)_O$ can have any allowed values, so in the mathematical terms the isotope characteristics of the mixing water can take any place between the streak **I** and the evolution lines **II** or **II'** (see Fig. 1). In the two-component case the mixing line is a straight line in $^3He/^4He$ versus $^{20}Ne/^4He$ co-ordinates (see line **III** on Fig. 1):

$$Y = a*X + b \quad (7)$$

If the sampling points set sufficiently close on nature, then the young end-member has the tritium/helium-3 age t ≅ constant, the old end-member has the uranium/helium age T ≅ constant, and only proportions of mixing between He_Y and He_O are varied. In this case measured points are fitted on a regression line.

The aim of dating is an evaluation of the isotope characteristics of the end-members (He_Y and He_O), therefore KAMENSKY et al. (1991) suggested to carry out sampling so that the line of correlation is obtained. This line enables to estimate the isotope characteristics of the young water due to crossing line **III** with streak **I**. For that equation (7) is solved with the coefficients "a" and "b", which are obtained from the regression line, which approximate measured points. The parameter "X" is assumed equal $(^{20}Ne/^4He)_{ASW}$, then the isotope coordinates of the young water $(^3He/^4He)_Y$ are obtained and the tritiogenic helium-3 concentration is calculated as:

$$[^3He_{TRI}] = \{(^3He/^4He)_Y - {}^3He/^4He)_{ASW}\}*[^4He_{ASW}] \quad (8)$$

The tritium/helium-3 age is calculated from equation (3), if the tritium concentration was measured.

The correlation line enables to estimate the isotope characteristics of old water due to crossing line **III** with the helium accumulation line **II**, for that need to solve combined equations 5, 6, 7.

Fairly often the sampling points set so far one from another that the helium-neon correlation has not obtained (see case of the single sample on Fig. 1). In this situation the isotope characteristics of "deep" helium ($(^3He/^4He)_O$ and $(^{20}Ne/^4He)_O$) must be measured, calculated or assumed, then coefficients "a" and "b" in (eq. 7) can be calculate from the two points line (the mixing water and the old end-member). After that the isotope coordinate of the young water $(^3He/^4He)_Y$ is calculated. This method has a strong risk to give a false age, if the concentration of neon-20 differ from $[^{20}Ne]_{ASW}$, due to degassing or "excess" air in water.

Technique and examples of groundwater dating.

This part will demonstrate using $^3He/^4He$ versus ^{20}Ne /^4He correlation for the tritium/helium-3 and the uranium/helium dating. The detailed study shown best results then the boreholes with the electrical rotary down-pump, the self-spring wells and sometimes the springs are sampled. Of course sampling of the soluble noble gases must be executed so that a gas exchange between water and air is excluded. The prior operations for the noble gases extraction and purifying carried out on a high-vacuum apparatus. The noble gases must be analysed on the mass-spectrometer with the high resolution to resolve the interfering ion peaks from the peak of $^3He^+$.

We carried out of sampling on two regions of Baltic shield (Kola peninsula), and on north-west and east flanks of Russian platform (Izjora plateau near St.-Petersburg and Tatarian Republic, respectively).

Hydrogeological setting of sampling sites and age data on Kola pepinsula

Khibiny and Kovdor crystalline massifs are close by circle on a geological map. Both crystalline massifs formed about 360 Ma ago due to the multistage intrusion of the mantle melts (GALAKHOV, 1975). There are several river's and like's valleys inside massifs, which fill partially of the fluvioglacial, alluvium and other Qarternary sediments (see Fig. 2).

We studied waters of several small intramounting artesian basins with a total area from 45 up to 130 km^2. The recharge areas of these basins are situated on the mounting crystalline frames, which are the fractured reservoirs (see Fig.2). Waters are filtrated through the weathering fractured zone in the upper part of the cross-section of the crystalline rocks and through the porous sediments in the transit area and are discharged in the mouths of valleys.

KAMENSKY et al. (1991) realized tritium/helium-3 dating of groundwaters on the water supply system (WSS) of Kirovsk town (it situated in Vud'javr lake's valley in Khibiny massif, boreholes pump water only from the fluvial-glacial aquifer). After two years they repeated sampling and obtained the perfect coincidence of the isotopic data (see joint line, which approximate the measured points by the least square method, Fig. 3). The tritium/helium-3 age $t = 15.8\pm1.5$ years was calculated taking into account the mean concentration of tritium in wells $^3H = 31$ TU and $(^3He/^4He)_Y = 3.66*10^{-6}$.

Specially note the triple crossing of the mixing lines for the several test sites, which locate inside Khibiny massif (see the big black open square in the left down corner of Fig. 3), lies very close to $(^3He/^4He)_R = 1.7*10^{-7}$ ratio, which was measured for the Khibiny rocks composite sample. Therefore this $^3He/^4He$ ratio and corresponding ratio $^{20}Ne/^4He = 0.2$, which calculated from accumulation line (eqs 5, 6) may be assume as the isotope characteristics of the old waters in the deep parts of Khibiny massif. In this case order of its uranium/helium age calculated by equation (4) is about $T \approx 10^5$ years. Because of the distance between the flank test sites on nature is about 40 km, so this isotope characteristics may be used as the regional constant for calculation of $(^3He/^4He)_Y$, if the single well with the mixing water is sampled.

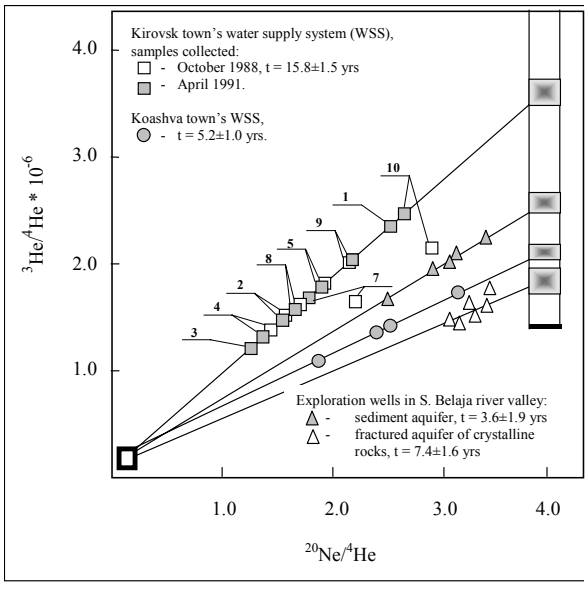

Fig. 3: Examples of tritium/helium-3 dating of young and uranium/helium dating of old waters. Shift of points 7 and 10 for earliest collection of water on Kirovsk town's WSS is explained air contamination. Note the new points (boreholes 1 and 3) also coincidence fit on approximation line.

It is interesting the proportion of the tritium/helium-3 ages of the young waters, which was calculated for the sediment and the fractured aquifers in valley of M. Belaja river. The residence time of water for the Quaternary aquifer is more in two times than age of water from the fractured aquifer of the crystalline rocks although the test boreholes situated closely (on distance about 50-70 m). We explain this proportion in the following way. The porosity of the Quarternary sediments more by order than the active porosity of the crystalline rocks. Therefore the water volume in the sediments equals the water volume in the fractured rocks, though volumes of the sediments and the fractured crystalline rock are differenced about in ten times. The hydraulic gradient in the sediment aquifer less by half than the hydraulic gradient in the fractured aquifer, so ages are differenced in two.

Hydrogeological setting and age data of Izjora plateau

The Izjora plateau is situated near St.-Petersbourg on the north-west flank of the Moscow artesian basin. The aquifer of the fractured limestones and dolomites, and sandstone is underplayed of the regional aquitard of bandy clay and is covered of the devonian semi-penetrable loam. The groundwaters are recharged in the central part of plateau where the carbonate rocks are opened for infiltration of the meteoric waters (Fig. 4).

The groundwaters are mainly discharged into the rivers and as the springs along the clint of the plateau. The water supply system of Petersburg institute of nuclear physic of RAS is situated on the south-east part of plateau. It fills area about 1300×1200 m, distances between neighbors boreholes are from 250 to 300 m. The total production of 10 boreholes is Q ~ 6500 m^3/day.

The water from boreholes of WSS was collected and the isotope composition of the noble gases and the concentrations of tritium (the mean concentration of tritium in wells $^3H = 29$ TU) was analysed. An amount of the parent elements, the composition of the helium isotopes and its concentration in the bandy clay were analysed and the helium accumulation line was calculated. The wide variations of the isotope ratios and the good fit of the measured points on the regression line shown on Figure 5. The crosses of the regression line with streak **I** (coordinates of the young waters) allowed to calculate the tritium/helium-3 (t

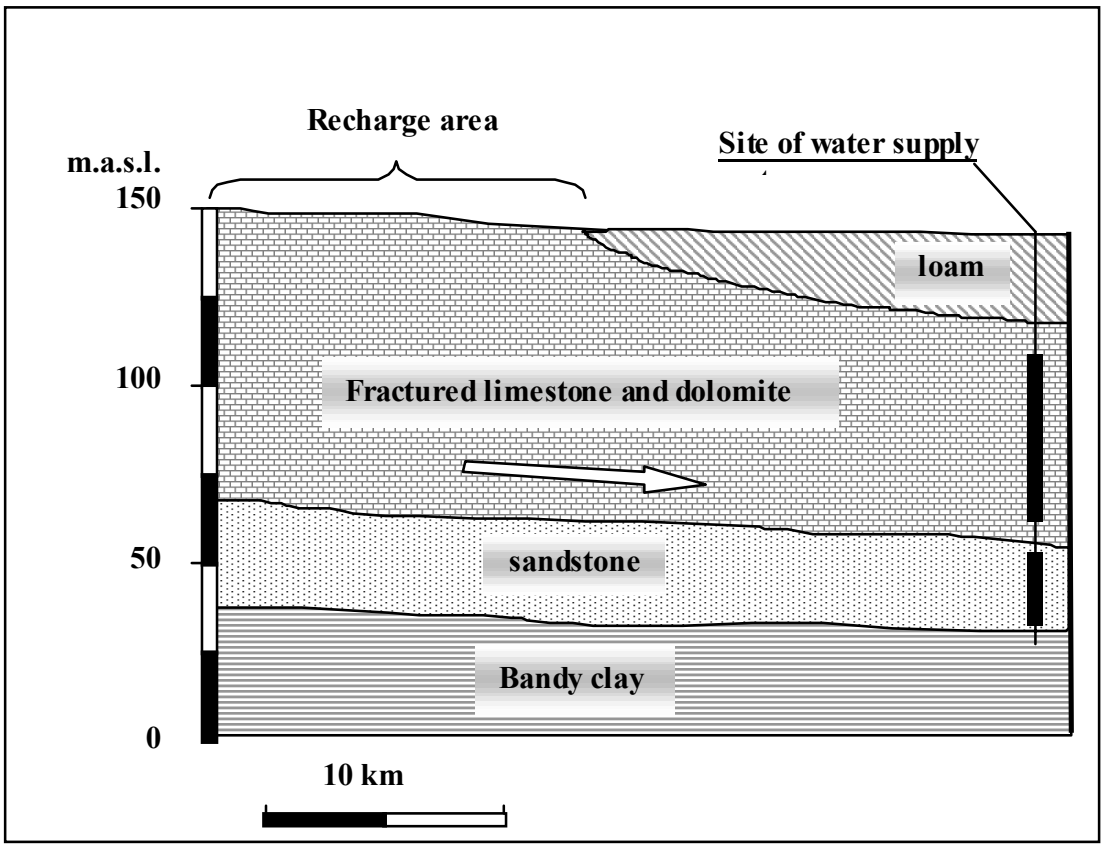

Fig. 4: Geological setting of Izjora plateau. Cross-section set from centre of plateau, which is recharge area, to southeast along one of flow line.

⇒ natural flow of groundwater

construction of water supply boreholes – black is a filter

= 12.5±1.3 years) and the uranium/helium ages (T ≈ 1.6 Ma).

Hydrogeological setting and age data for region of Romashkinskoe oil deposit

The Romashkinskoe oil deposit situated on south-west of Tatarian Republic. Studied site with dimension about 3×5 km occupies an undulating country closely the regional watershed, which is the recharge area. Therefore the general direction of the shallow water filtration is vertically down. Part of waters are discharged here as spring. We collected water from springs, which situated chaotically on area. Distance between the neighbors springs vary from several tens of meters up to 1.5 km, therefore it was awaited strong variation of the tritium/helium-3 ages.

Naturally, as it is seen from Figure 5, the helium-neon data do not fit the common correlation, therefore it was used the “single” point method. We assumed $(^3He/^4He)_O = 2*10^{-8}$ and $(^{20}Ne/^4He)_O = 0.0005$, which measured for the accompanying gas (PRASOLOV E.M. oral com-

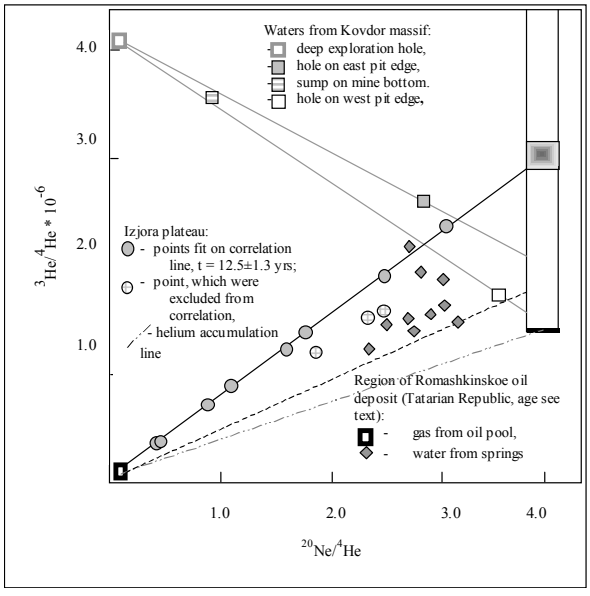

Fig. 5: $^3He/^4He$ versus $^{20}Ne/^4He$ systematic in waters for several regions of Russia. Three points was eliminated from discussion because of apparently they have contribution of “excess” air, which would have turned the data points aside from the regression.

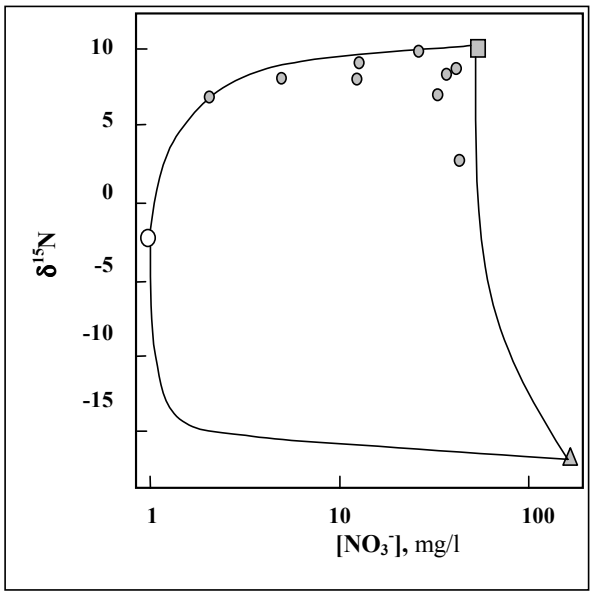

Fig. 6: Detection of contributions of two different waste sources in nitrates pollution of Kirovsk town's WSS.

○ blank water from clear area,
□ foul water from sewerage system of town,
△ drainage water from Juksporr apatit-mine,
○ water from wares-supply boreholes
Curves are the theoretical two-components mixing lines for each pair of end-members.

munication; age data see Fig. 7). We supposition this gas percolate in the shallow aquifer both a natural way and due to an exploitation of the oil deposit, which result in leakage of the accompanying brines from the product pipes. "Deep" helium percolates to shallow waters in small amount as it evident from small shift of $(^{20}Ne/^{4}He)_{MEASURED}$ from $(^{20}Ne/^{4}He)_{ASW}$.

Using of age data for the environmental protection aims

Tracing of drainage water genesis

We studied the inflow of water in the open mine of Kovdor iron-ore. Water from the deep exploration hole (1200 m) was collected and its isotope characteristics were compared with water from the drainage system of mine. As it seen from Figure 7 water from the drainage holes on the west edge of mine practically has not the tritium/helium-3 age and has a very small addition of the old water. It is explained the lake, which situated in 450 m from the mine edge, is a main source of watering of these ore flank. In contrast at the opposite ends of mine the drainage water has the noticeable tritium/helium-3 age, because it watering by the shallow groundwater.

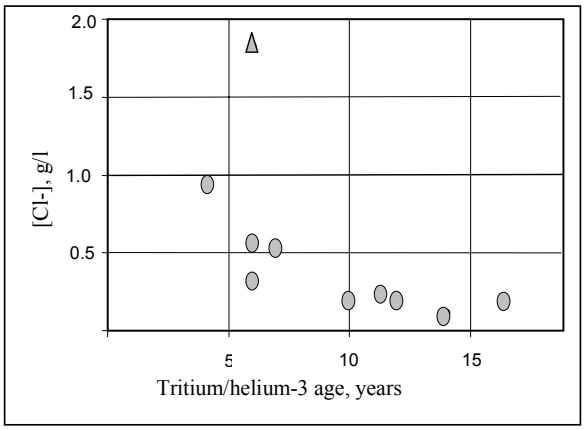

Fig. 7: Tritium/helium age of shallow groundwaters versus its chloride pollution.

○ springs,
△ shallow water-supply well

Here part of the old water is less than 0.1%. At last, the sump on the bottom of mine most likely contains mixing water, which is blend of the deep and shallow groundwaters, and the contemporary surface and the meteoric water. Here part of old water apparently is about 5%.

Tracing of nitrate pollution

Since starting of detail monitoring of water on the supply system of Kirovsk town in begin of 1980 was notice a growth of the nitrate concentrations. It was supposed this growth was explained of impact of the mine waters, which dissolute the nitrates from an explosive compound in blast-hole on mines. We carried out the isotope study of waters which result shows Figure 6. Note the contribution of the biogenic nitrates from the foul waters of the sewerage system of town is average about 90%. The contribution of nitrates from the drainage waters always is less 20%.

Comparison of the water age on WSS ($t \approx 15$ years) and time elapsed since the foundation of town (≈ 50 years) allows us make up the conclusion that water quality has steady-state regime. Variations of the nitrate concentration were artificial fact caused by the modification of the laboratory technique. In future the deterioration of the water quality is possible with degradation of the sewerage system of town.

Estimation of groundwater resources

Next we executed an estimation of the groundwater resources of aquifers in valley of Small

Belaja river. It was took into consideration follow equation:

$Q = V/t$

where Q is the groundwater resources, m^3/day; $V = V_{ROCKS}*p$ – value of water in aquifer, m^3; V_{ROCKS} – volume of the water-bearing rock, m^3; p – its porosity; t – the residence time of water in the hydrogeological system, i.e. age of groundwater. Taking into account age of groundwaters (see Fig. 3) and estimation of the water volume both the sediment and the fractured aquifers we calculated the groundwater resources as $Q \approx 63*10^3$ m^3/day. This estimation is very close, which obtained afterwards from the standard hydrogeological study $Q \approx 68*10^3$ m^3/day.

Tracing of shallow groundwater salinization

In 1997 we studied the oil-producing region near city Al'metevsk (the Romashkinskoe oil deposit, Tatarian Republic). One of main problem of this region is a reduction of resources of the drinking water due to salinization of the shallow aquifers by the accompanying oil-brines. Especially many of brines are lost from the pressure piping in flooding. In result the population uses the water with average salinity about 1.6 g/l for the drinking, housekeeping and agriculture aims. We compared the age data for springs, which used for the drinking water supply, with the concentrations of chloride-ion, which well marks the salinization (see Fig. 7).

The inverse correlation between the tritium/helium-3 ages and the chloride-ion concentrations indicates continued and increased the pollution of water. However the relatively small isotope ages (the residence time of water in the hydrogeological system) for part of springs enable us to suppose the fast rejuvenation of this waters after stopping of pollution.

Calculation of maximum possible of radioactive pollution

The residence time of the shallow waters on Izjora plateau (see above) was used for calculation of the maximum possible radioactive pollution of the water supply system of Peterbourg institute of nuclear physic of RAS (PINP). For calculation we took into consideration the modeling fallouts, which placed at our disposal the group of the simulation investigations of PINP, in follow situations a) the normal exploitation mode, b) the average accident and c) the massive fracture of the nuclear reactor (like Chernobyl). The maximum of the radionuclide concentrations will be less than the maximum concentration limit in any case. Time elapsed between accident and moment, when the maximum concentrations coming to WSS, is less than the tritium/helium-3 age of water (t = 12.5 yrs) and equals $\tau \approx 10$ yrs. Note the calculation of the radioactive pollution with the tritium/helium-3 age gives the upper limit of the concentrations because of two reasons:

- it is neglected of the residence time in the unsaturated zone,
- it is neglected the sorption of radionuclide on the water-bearing rocks.

In the actual situation the maximum of the radionuclide concentrations will be less than calculated one.

Conclusion

The isotope age, which is calculated from the noble gases and tritium, maybe successfully used for solution of the problems connected with the environmental protection aims. It clearly shows well results, which were got for the experimental validation of the helium-neon systematic for a diagnostic of two-components mixing and $^3He_{TRI}$ and ^4He_O calculation. The combination of the age data with the geochemical information, which is obtained during of dating procedure, and with other isotope methods gives best results.

It is the author's opinion some problems cannot be solved without using of the age information, for example burial in the ground disposal a toxic and radioactive waste.

Reference

GALAKHOV A.V. (1975): Petrology of the Khibiny alkaline massif. Nauka (in Russian).

KAMENSKY I.L., TOKAREV I.V. & TOLSTIKHIN I.N. (1991): ^3H-^3He dating: a case for mixing of young and old groundwaters. – Geoch. Cosmoch. Acta 55, 2895-2899.

KIPFER R. (1991): Primordiale Edelgase als Tracer fur Fluide aus dem Erdmantel. Zurich, ETH, Dissertation.

MAMYRIN B.A., ANUFRIEV G.S., KAMENSKY I.L. & TOLSTIKHIN I.N. (1970): A determination of atmospheric helium isotope composition. Geokhimija 6, 721-730 (in Russian).

SAVCHENKO V.P. (1935): On the problem of helium geochemistry. Natural gases 9, 53-107 (in Russian).

SCHLOSSER P, STUTE M., SONNTAG C. & MUNNICH K.O. (1989): Tritigenic ^{3}He in shallow groundwaters. Earth Planet. Sci. Lett. 94, 245-256.

SOLOMON D.K., SCHIFF S.L., POREDA R.J. & CLARKE W.B. (1993): A validation of the $^{3}H/^{3}He$ method for determining groundwater recharge. Water Res. Res. 29, 2951-2962.

TOLSTIKHIN I.N. & KAMENSKY I.L. (1969): On the possibility of tritium-helium-3 dating of underground waters. Geikhimija 8, 1027-1029 (in Russian).

TOP Z., EISMOND W.C. & CLARKE W.B. (1987): Helium isotope effect and solubility of helium and neon in distilled water and seawater. Deep-sea Res. 34, 1139-1148.

WEISS R.F. (1970): Helium isotope effect in solution in water and seawater. Science 168, 247-248.