Characteristics of Distribution of Uranium Isotopes in the Groundwater on the Yusung Area

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Abstract

Characteristics of distribution of uranium isotopes in the groundwater on the Yusung area was studied with measuring the concentrations and activity ratios of uranium isotopes in the groundwater. Most of the uranium isotopes in the groundwater was found in the filtered water. Only less than 1 % of total uranium isotopes was detected in the particulate fraction. The concentrations and activity ratios of uranium isotopes in the groundwater measured in this study were variable, depending upon sampling site. Owing to a rapid material exchange between the subterranean hot waters and the rock strata, the concentrations of ^{238}U in the ground water at the hot spring area were found to be about four times higher than those at the other area. Because of α-particle recoil effect, the activity ratios of ^{234}U/^{238}U in the groundwater taken at "cold" spring sites were variable with the range from 1.20 to 3.58, depending on residence time of groundwater. In the hot spring area, the activity ratios of ^{234}U/^{238}U were close to the equilibrium value (1.10 $\pm$ 0.07) due to rapid erosions of the rock strata by the hot spring water.

1. Introduction

Natural radionuclides in the environment are important in the general study of radionuclide migration. Among natural radionuclides occurred in the environment, uranium isotopes are good tracers to study the migration of radionuclides, because natural uranium can be easily detected in nearly all materials from the environment. Most groundwaters contain a few ppb of dissolved uranium. The uranium concentration in most surface and near surface continental waters is somewhat lower and more variable, ranging from less than 0.1 ppb to more than 1000 ppb. In the groundwater, uranium concentrations greater than 50 ppb are quite rare, and have generally been found only in aquifers containing uranium mineralizations. Uranium accumulated in humans may have a dual effect due to its chemical and radioactive properties. The chemical toxicity of natural uranium is a major hazard to the kidneys. Radiotoxicity also arises from the irradiation of bone surfaces and red bone marrow by uranium isotopes. Therefore, it is necessary to determine the concentration of uranium isotopes in the groundwater for radiological dose assessment. During the last few years, a number of studies has been carried out to investigate the anomalous behavior of uranium isotopes in soils[1], surface water[2,3], groundwater[4-5], and sediment [6-8], but there is not much[9] information available on the concentration of uranium isotopes in the groundwater of the Korean Peninsula. The present work was carried out to determine the concentrations and the activity ratios of uranium isotopes in the groundwater on the Yusung Area. The result may be used as reference data in case of an accident in a radioactive waste repository or in a nuclear plant, and elucidated the migration characteristics of uranium isotopes in the groundwater under natural conditions.

2. Experimental methods

Sampling sites were chosen to cover the Chungcheng area. The groundwater samples were taken

at 19 sites from the hot spring area and 14 sites from the "cold" spring area located in the Chungcheng region in 1998-1999. Samples of about 20 L of ground water were collected at the sampling sites. With the exception of two sampling sites, H 18 and H 19, most of the ground water samples are used for drinking water by the local in habitants. The sampling depths were in the range of 70 m ~ 400 m.

The suspended matters in the water samples were separated by filtration through Nuclepore filters of 0.45 μm pore size. The pH and Eh (Model; Orion 290 A) were measured at the sampling area. Total carbon contents were measured by Shimadzu TOC Analyzer (Model; TOC-5000 A).

^{232}U as a yield tracer was added to the filtered water and the particulate fraction. Fifteen liters of filtered water were evaporated to a final volume of 100 ml. The condensed filtered water was transferred into a 250 ml beaker and evaporated to dryness. The particulate fraction with the membrane filter was calcined at 550 ^{o}C for 24 hours. The residue was dissolved with 7.2 M HNO_3. Uranium isotopes were extracted from the dissolved sample materials using TBP (tributyl phosphate) in carbon tetrachloride. The radiochemical purification of the U fraction was performed with 8 M hydrochloric acid. Back extraction was done using 1 M HCl. Finally, purified uranium isotopes were electrodeposited on a polished stainless steel disc and measured by α-ray spectrometry. Detailed description of the experimental procedure has been well described elsewhere[10,11].

3. Results and discussion

3.1 Concentration of uranium isotopes

The concentrations and activity ratios of uranium isotopes in the groundwater were measured and the results are presented in Table 1 and Table 2. In the groundwater, most of uranium isotopes (> 99 %) were found in the filtered water. Only less than 1 % were detected in the particulate

fraction. The activity concentrations of ^{238}U in the filtered water were plotted as a function of total carbon (organic and inorganic) contents, as shown in Fig. 1. The correlation of the uranium activity concentrations with total carbon contents was found to be significant (r = 0.73), though two outlier points (H-18, H-19) found in Fig. 1. The results suggest that most of uranium isotopes in the groundwater exist as a dissolved uranium, forming complexes with carbonate ions such as uranyl carbonates ($UO_2(CO_3)_2^{2-}$ or $UO_2(CO_3)_3^{4-}$) and dissolved organic matters including humic substances[12,13] rather than associated with a solid fraction. The total carbon contents at the hot spring area were ranged from 7.5 to 21.9 ppm, and were higher than those at the non hot spring area, which showing that high amount of organic and inorganic carbon is dissolved in the groundwater of the hot spring water.

The concentration of uranium isotopes at the different sampling points was variable, as shown in Table 1 and Table 2. The concentration of uranium isotopes largely depends upon its solubility in the groundwater as well as the geological characteristics of the aquifer [14]. Comparing Table 1 with Table 2, the concentrations of ^{238}U in the groundwater at the hot spring area were relatively higher than those at the "cold" spring area. The mean activity concentration of ^{238}U in the filtered water was found to be 730 mBq/l with the range from 125 to 3273 mBq/l for the hot spring area and 174 mBq/l with the range from 6.75 to 606 mBq/l for the "cold" spring area, respectively. The increase in the concentrations of ^{238}U at the hot spring area could be attributed to a rapid material exchange between the groundwater and the mother rocks such as U black shales and granite[15]. The uranium isotopes in the ground water are mainly from uranium which are leached by the water from U black shales and granite rocks. Owing to the material exchange between the subterranean hot waters and the rock strata, the erosion of the rocks has been greatly increased. Hence, uranium isotopes in U black shales area is easily dissolved in the hot spring water, resulting in high concentration of uranium as indicated by comparing the concentrations of ^{238}U in the groundwater taken at H-18 and H-19 site with those

taken at the hot spring sites (H-1 ~ H-17) in Table 1. The concentrations of uranium isotopes taken at H-18 and H-19 site were higher than those collected from any other site in the hot spring area. This result may be explained by the effect of the temperature in the groundwater. The temperature in the groundwater taken at H-18 and H-19 site is about 49 ^{o}C. Because of the high temperature in the groundwater, the reactive characteristics of hot spring water and rock may increase the concentrations of uranium isotopes. Kim *et al*. reported that the mineral contents such as Na and Ca in the hot spring water were higher than those in other areas in Korea, due to the erosion of granite rocks in U black shales area[16]. A similar behavior has been observed in the Ta-Tun volcanic group area in Taiwan [15].

3.2 Activity ratios of uranium isotopes

Activity ratios of uranium isotopes can be utilized to identify the different sources of release. In general, the activity of ^{238}U is nearly equal to that of ^{234}U in natural conditions, because of radioactive equilibrium. However, some studies showed that the ^{234}U/^{238}U activity ratio in the groundwater is not constant but variable, depending on several parameters[17,18] such as redox conditions, the difference in the chemical characteristics of uranium and its daughter elements, reactive characteristics of groundwater and rock stratum and residence time of groundwater.

In the present study, the activity ratio of ^{234}U/^{238}U in the groundwater varied between 1.01 to 3.58, as shown Table 1 and Table 2. The mean activity ratio of ^{234}U/^{238}U (1.10 ± 0.07) in the filtered water at the hot spring area is close to the equilibrium value. The activity ratios of ^{234}U/^{238}U in the filtered water at the "cold" spring sites were variable with the range from 1.20 to 3.58 due to disequilibrium. There was no systematic variation of the ^{234}U/^{238}U activity ratios in the particulate fractions, and most data were close to the equilibrium value.

Figure 2 shows a plot of the ^{234}U/^{238}U activity ratio versus uranium concentration for filtered water.

The $^{234}U/^{238}U$ activity ratios have a tendency to decrease with increasing concentration of uranium. The high $^{234}U/^{238}U$ activity ratios calculated in the "cold" spring water are due to the alpha recoil effect in the reducing conditions. As shown in Fig. 3, Eh values measured in the "cold" spring water were lower than those in the hot spring water. Under reducing conditions, the dissolution of ^{234}U with alpha recoil mechanism becomes more dominant. Similar results has been reported elsewhere[17-19]. Osmond $al.$ explained this with the redox potentials in the aquifer system : high concentration of uranium and low activity ratio occur in oxidizing zone, while low concentration and high activity ratios occur in reducing zones[17]. The main mechanism which may contribute to disequilibrium in the groundwater includes α-particle recoil ejection of ^{234}Th into a solution, preferential dissolution of ^{234}U due to radiation damage, and the change of ^{234}U to more soluble U(VI) species in the associated rocks[17,18]. Therefore, if the residence time of the groundwater is long enough, the accumulation of ^{234}U from α-recoil effects will increase. Hence, isotopic data may be used to investigate the movement and history of groundwater.

It is interesting to compare the activity ratios of $^{234}U/^{238}U$ in the groundwater at the hot spring and the "cold" spring areas. As shown in Fig. 2, the $^{234}U/^{238}U$ activity ratios in the hot spring area samples showed lower $^{234}U/^{238}U$ activity ratios than those at the non hot spring area in the Okchun Metamorphic Belt, although the concentrations of ^{238}U at the hot spring area were higher than those at the "cold" spring area. These results may be explained by the reactive characteristics of hot spring water and rock rather than residence time of water based on redox potentials. In the hot spring water, the leaching of uranium is more important than the effects of reducing conditions. The leaching of uranium generally prevail on the acidic conditions[15]. However, much of the ^{238}U located in the U black shales is easily dissolved due to a extensive erosion and chemical reactions between the hot spring waters and the rock strata even alkali conditions (H-19 site, pH; 8.1), decreasing the alpha recoil effects. Hence, the activity ratio of $^{234}U/^{238}U$ in the hot spring water is close to that in the rock

strata.

4. Conclusions

In the groundwater samples most of the uranium isotopes was found in the filtered water and only less than 1 % of total uranium isotopes was detected in the particulate fraction. Owing to a rapid material exchange between the subterranean hot waters and the rock strata, the concentrations of ^{238}U in the ground water at the hot spring area were found to be about four times higher than those at the other area. The activity ratios of ^{234}U/^{238}U in the groundwater taken at "cold" spring sites were higher than those taken hot spring sites, due to α-particle recoil effect. In the hot spring area, the activity ratios of ^{234}U/^{238}U were close to the equilibrium value due to the leaching of uranium from rock strata by the hot spring water.

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Table 1. Concentrations and activity ratios of uranium isotopes of the ground water at the hot spring area

Sampling Site	pH	Temp. (^{o}C)	Filtered water fraction			Particulate fraction		
			^{238}U(mBq/l)	U_{total} (ppb)	^{234}U/^{238}U	^{238}U(mBq/l)	U_{total} (ppb)	^{234}U/^{238}U
H-1	6.9	29.4	674 ± 24.7	54.2 ± 1.99	1.02 ± 0.12	0.31 ± 0.02	2.49E-2 ± 1.61E-3	1.05 ± 0.11
H-2	6.5	23.6	804 ± 32.1	64.7 ± 2.58	1.05 ± 0.05	0.51 ± 0.04	4.10E-2 ± 3.22E-3	1.02 ± 0.11
H-3	7.6	12.6	142 ± 8.83	11.5 ± 0.71	1.20 ± 0.13	0.99 ± 0.06	7.96E-2 ± 4.83E-3	1.06 ± 0.10
H-4	6.9	24.1	722 ± 21.8	58.1 ± 1.75	1.03 ± 0.11	0.12 ± 0.03	9.65E-3 ± 2.41E-3	1.01 ± 0.12
H-5	7.5	18.1	170 ± 16.4	13.7 ± 1.32	1.14 ± 0.10	2.94 ± 0.36	0.24 ± 2.90E-2	1.10 ± 0.10
H-6	8.2	13.4	383 ± 20.9	30.8 ± 1.68	1.19 ± 0.14	1.92 ± 0.21	0.15 ± 1.69E-2	1.20 ± 0.12
H-7	7.4	25.4	693 ± 13.4	55.8 ± 1.08	1.05 ± 0.08	0.46 ± 0.03	3.70E-2 ± 2.41E-3	1.02 ± 0.10
H-8	7.1	30.6	842 ± 35.1	67.7 ± 2.82	1.04 ± 0.13	0.19 ± 0.02	1.53E-2 ± 1.61E-3	1.06 ± 0.06
H-9	6.7	22.4	481 ± 13.7	38.7 ± 1.10	1.22 ± 0.13	0.69 ± 0.05	5.55E-2 ± 4.02E-3	1.04 ± 0.12
H-10	8.0	21.4	553 ± 12.5	44.5 ± 1.00	1.13 ± 0.10	0.39 ± 0.04	3.14E-2 ± 3.22E-3	1.09 ± 0.15
H-11	6.4	23.5	715 ± 34.1	57.5 ± 2.74	1.01 ± 0.08	0.17 ± 0.01	1.37E-2 ± 8.04E-4	0.99 ± 0.10
H-12	6.7	29.4	871 ± 28.7	70.1 ± 2.31	1.03 ± 0.10	0.20 ± 0.01	1.61E-2 ± 8.04E-4	1.05 ± 0.07
H-13	6.5	19.8	628 ± 28.3	50.5 ± 2.28	1.06 ± 0.05	0.51 ± 0.06	4.10E-2 ± 4.83E-3	1.00 ± 0.11
H-14	6.8	16.8	318 ± 19.1	25.6 ± 1.54	1.15 ± 0.12	0.27 ± 0.02	2.17E-2 ± 1.61E-3	1.09 ± 0.08
H-15	7.0	17.0	414 ± 12.1	33.3 ± 0.97	1.16 ± 0.14	0.25 ± 0.03	2.01E-2 ± 2.41E-3	1.04 ± 0.10
H-16	7.2	14.7	125 ± 10.2	10.1 ± 0.82	1.19 ± 0.13	0.34 ± 0.03	2.73E-2 ± 2.41E-3	1.10 ± 0.08
H-17	8.4	16.1	204 ± 18.6	16.4 ± 1.50	1.09 ± 0.07	1.24 ± 0.14	9.97E-2 ± 1.13E-2	1.12 ± 0.10
H-18	6.4	43.8	1861 ± 55.2	149.7 ± 4.44	1.01 ± 0.12	0.51 ± 0.03	4.10E-2 ± 2.41E-3	1.01 ± 0.11
H-19	8.1	49.1	3273 ± 94.3	263.2 ± 10.9	1.07 ± 0.09	0.38 ± 0.04	3.06E-2 ± 3.22E-3	1.08 ± 0.15

Table 2. Concentrations and activity ratios of uranium isotopes of the ground water at the "cold" spring area

Sampling Site	pH	Temp. (°C)	Filtered water fraction			Particulate fraction		
			^{238}U(mBq/l)	U_{total} (ppb)	^{234}U/^{238}U	^{238}U(mBq/l)	U_{total} (ppb)	^{234}U/^{238}U
C-1	7.8	17.1	46.0 ± 2.61	3.70 ± 0.21	2.33 ± 0.18	3.94E-2 ± 1.41E-3	3.17E-3 ± 1.13E-4	1.61 ± 0.22
C-2	6.7	16.9	407 ± 20.1	32.7 ± 1.62	1.83 ± 0.17	0.11 ± 0.001	8.85E-3 ± 8.04E-5	1.24 ± 0.12
C-3	6.5	17.1	293 ± 17.8	23.6 ± 1.43	1.75 ± 0.18	0.10 ± 0.001	8.04E-3 ± 8.04E-5	1.18 ± 0.21
C-4	8.6	20.7	364 ± 19.8	29.3 ± 1.59	1.20 ± 0.11	0.09 ± 0.001	7.24E-3 ± 8.04E-5	1.02 ± 0.08
C-5	7.4	18.2	287 ± 17.3	23.1 ± 1.39	1.23 ± 0.15	0.10 ± 0.001	8.04E-3 ± 8.04E-5	1.10 ± 0.14
C-6	7.1	18.4	150 ± 10.0	12.1 ± 0.81	2.20 ± 0.21	0.12 ± 0.001	9.65E-3 ± 8.04E-5	1.20 ± 0.14
C-7	8.2	17.5	134 ± 11.4	10.8 ± 0.92	3.12 ± 0.24	9.24E-2 ± 1.02E-3	7.43E-3 ± 8.20E-5	1.59 ± 0.21
C-8	6.9	18.4	53.6 ± 6.34	4.31 ± 0.51	2.69 ± 0.19	7.42E-3 ± 5.42E-4	5.97E-4 ± 4.36E-5	1.41 ± 0.20
C-9	7.4	19.5	10.6 ± 1.12	0.85 ± 0.09	2.83 ± 0.27	1.08E-2 ± 1.32E-3	8.69E-4 ± 1.06E-4	1.06 ± 0.16
C-10	7.2	18.8	19.9 ± 1.37	1.60 ± 0.11	2.10 ± 0.26	4.32E-3 ± 6.21E-4	3.47E-4 ± 4.99E-5	1.26 ± 0.18
C-11	7.4	16.5	6.75 ± 0.91	0.54 ± 0.07	3.58 ± 0.29	1.27E-3 ± 9.34E-5	1.02E-4 ± 7.51E-6	1.50 ± 0.27
C-12	8.3	18.2	17.4 ± 2.61	1.40 ± 0.08	3.42 ± 0.31	1.59E-3 ± 1.72E-4	1.28E-4 ± 1.38E-5	1.37 ± 0.12
C-13	9.2	19.5	606 ± 21.3	48.7 ± 1.71	1.52 ± 0.12	9.94E-2 ± 1.31E-3	7.99E-3 ± 1.05E-4	1.21 ± 0.18
C-14	8.5	16.6	38.8 ± 6.34	3.12 ± 0.51	2.52 ± 0.21	5.74E-2 ± 3.21E-3	4.62E-3 ± 2.58E-4	1.34 ± 0.16

Fig. 1. Concentration of ^{238}U vs. total carbon in the ground water

Fig. 2. Contents of ^{238}U vs. activity ratio of $^{234}U/^{238}U$ in the ground water
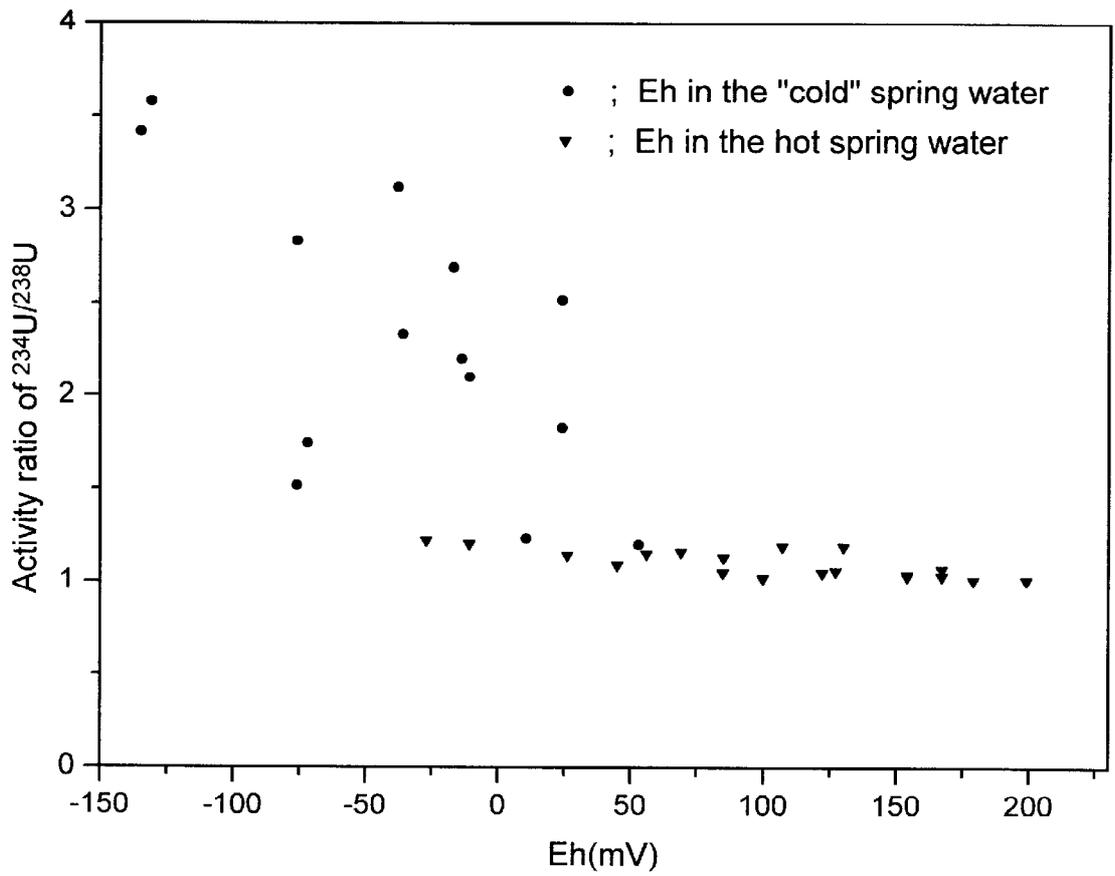
Fig. 3. Activity ratio of $^{234}U/^{238}U$ vs. Eh in the ground water