RADIOACTIVE EQUILIBRIUM IN THE NINGYOTOGE URANIUM ORES, ESPECIALLY BETWEEN IONIUM AND URANIUM

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ABSTRACT

The radioactive equilibrium states in the uranium ores of the Ningyotoge mine were investigated in relation to their ionium content and to their microscopic features.

An analytical method of Io/U was examined and applied to the ores. The method is characterized by not being necessary to determine the chemical yield in the separation of thorium and by simplicity for obtaining the absolute value of Io/U. In order to investigate the states being different in phases of a specimen, variation of Io/Th-234 under chemical leaching was traced. Autoradiography and radioactivity measurements were also done.

The states of the radioactive equilibrium in the Ningyotoge ores are thought to be a results of the differentiation of thorium from uranium. This may occur by oxidation and chemical leaching and by crystallization of uranium minerals. The radiocolloid is explained as being a product of this differentiation. The radioactive nuclides included in the radiocolloid are ionium and its daughter products.

Introduction

States of the radioactive equilibrium of uranium ores have been studied for two purposes; one is to remove the disturbances in uranium radiometry due to the existence of the disequilibrium¹⁾²⁾, and the other to measure the disequilibrium state itself and to explain its geological meanings³⁾⁴⁾⁵⁾⁶⁾. The present study was done for the

same purpose as the latter on the states of the radioactive equilibrium in the uranium ores of the Ningyotoge mine.

The ore deposits of the Ningyotoge mine are the representative ones of uranium deposits of sedimentary type in Japan. Concerning the ore deposits, N. Katayama et al. discussed beta-counts per unit uranium content in relation to the occurrences of the ores in 1957⁴⁾. I. Hayase reported and discussed the radioactive disequilibrium and the radiocolloid in 1959⁷⁾. Radium of autunite from the ore deposits was analyzed and discussed by M. Umemoto et al. in 1957⁸⁾ and by T. Soma in 1957⁹⁾. In these papers, the states of the radioactive equilibrium were considered mainly as a relationship between uranium and radium.

The states of the radioactive equilibrium are, in principle, determined by the ratios of uranium to its daughter products. Among these products, ^{230}Th and ^{234}U are supposed to affect the states during long time, because they have long half-lives and are situated in the upper positions of the uranium decay series. The disequilibrium between ^{230}Th and its daughter products may disappear comparatively in short time, 10^4 years. The radiocolloid was found in an altered pitchblende by H. Yagoda in 1946¹⁰⁾. It is also found widely in the Ningyotoge uranium deposits. The Ningyotoge ores are classified into two kinds: unoxidized ores and oxidized ores. The oxidation has been thought to have a close relationship with these equilibrium phenomena. In this paper the author wishes to present an explanation of the relationships of ^{230}Th to (1) the states of the radioactive equilibrium in the ores, especially the differences of the states between the unoxidized ore and the oxidized ore, and to (2) the radiocolloid.

Experimental

The radioactive nuclides of the uranium decay series are divided, for convenience, into four groups: U-group (^{238}U ~ ^{234}U), ^{230}Th , Ra-group (^{226}Ra ~ ^{210}Po), and Pb-group (^{210}Pb ~ ^{210}Po). $N_{\lambda\lambda}$ is

abbreviated to A^* , where N_A is number of atoms of nuclide A, and λ_A is decay constant of nuclide A.

I. Samples

The uranium ore deposits of the Ningyotoge mine are formed in Neogene Tertiary lacustrine sediments, chiefly conglomerate and shale, lying horizontally on a granite base. The deposits of the Togo mine, which bounds the Ningyotoge mine on the south, belong to the same type. In the unoxidized zone, uranium occurs principally as ningyoite, $U_{1-x}Ca_{1-x}R.E_{.2x}(PO_4)_2 \cdot 1\sim 2 H_2O$, accompanied with pyrite and carbonaceous matter. The ningyoite is so fine in crystal size, less than 5μ , that it is difficult to obtain pure samples by separation. Uraninite is also found in this zone in very small quantities. In the oxidized zone, the main uranium mineral is autunite. Beta-uranophane, uranophane, and carnotite are found. The pyrite has been oxidized to limonite. The autunite, 1~3 mm in size, crystallizes often on the surface of the limonite. The beta-uranophane is formed for the most part by replacing fossil woods and is often associated with autunite. Details of the mineralogy and the geology of the Ningyotoge ore deposits should be referred to other papers¹¹⁾¹²⁾¹³⁾¹⁴⁾¹⁵⁾. The samples listed in Table 1 were investigated.

(1) Sample I, no. 1~no. 6, are the unoxidized ores: no. 1~no. 4 were collected from the unoxidized zone of the Ningyotoge uranium deposits, and the other two sampled for comparison. No. 5 is representative specimen occurring in the Ogamo uranium ore deposits, which are characterized by coffinite¹⁶⁾. No. 6 is a typical specimen of pitchblende collected by Dr. M. Sato from the MiVida mine, Utah, U. S. A., and is principally composed of uraninite with minor amount of calcite. The radioactive equilibrium is supposed to be established in it, considering its unweathered features and the geological age of the MiVida deposits.

(2) Sample II, no. 7~no. 14, were collected from the oxidized

Table 1. List of the samples investigated.

Sample	Rock Type	Uranium Mineral	Locality	
I	no. 1	Conglomerate	Ningyoite	Toge area, Ningyotoge Mine
	no. 2	Conglomerate	Ningyoite	Toge area, Ningyotoge Mine
	no. 3	Conglomerate	Ningyoite	Toge area, Ningyotoge Mine
	no. 4	Tuff-breccia	Ningyoite	Asabatake area, Togo Mine
	no. 5	Quartz vein	Coffinite	Ogame Mine
	no. 6	Pitchblende	Uraninite	MiVida Mine, Utah, U. S. A.
II	no. 7	Conglomerate	Autunite	Toge area, Ningyotoge Mine
	no. 8	Conglomerate	Autunite	Toge area, Ningyotoge Mine
	no. 9	Conglomerate	Autunite	Toge area, Ningyotoge Mine
	no. 10	Conglomerate	Autunite	Toge area, Ningyotoge Mine
	no. 11	Conglomerate	Autunite	Toge area, Ningyotoge Mine
	no. 12	Conglomerate	Autunite	Toge area, Ningyotoge Mine
	no. 13	Conglomerate	Autunite	Yotsugi area, Ningyotoge Mine
	no. 14	Conglomerate	Autunite	Yotsugi area, Ningyotoge Mine
III	no. 15	Fossil wood replaced by U	Beta-uranophane	Katamo area, Togo Mine
	no. 16	Same as no. 15	Autunite	Katamo area, Togo Mine

zone of the Ningyotoge deposits: no. 7~no. 9 are crude ores, while, no. 10~no. 14 are samples of autunite separated under binocular microscope.

(3) Sample III, no. 15 and no. 16, are the oxidized ores collected from the Togo mine. No. 15 is beta-uranophane replacing fossil wood and no. 16 is autunite found on the surface of the sample no. 15.

II. Radibactivity measurements

The equilibrium states within U-group*, within Ra-group, and between Ra-group and Pb-group are established in short time. In natural uranium ores these equilibrium states are generally found, and are used for uranium radiometry¹⁾²⁾. In order to check these

* In this case U-234 is not included in U-group.

states in the samples beta and gamma countings were done. The counters used were a G-M tube and a gamma-ray spectrometer accompanied with a well type thallium activated NaI crystal, 1 3/4" dia. 2" high, and a twenty-channel pulse height analyzer. Then were calculated three ratios: beta-counts per unit uranium content (beta/U), area of 610 kev-gamma peak to uranium content (610 kev/U), and height of 80 kev-gamma peak to uranium content (80 kev/U). The peak of 80 kev-gamma is composed of 93 kev and 64 kev, gammas of Th-234 and 74 kev, KX-ray of Pb¹⁷). The peak of 610 kev-gamma is due to Bi-214.

The results of the measurements are shown in Table 2. Linear

Table 2. Results of the radioactive measurements of the uranium ores.

Sample	80 kev/U	610 kev/U	Beta/U
no. 1	2032	552	3028
no. 2	5650	1630	6010
no. 3	4476	1365	5309
no. 4	1765	392	2795
no. 5	1505	359	2428
no. 7	1387	249	2334
no. 8	2211	507	3344
no. 17	1569	357	2532
no. 18	1539	310	2499

Fig. 1. Beta/U vs. 610 kev-gamma/U of the uranium ores.

Fig. 2. 80 kev-gamma/U vs. 610 kev-gamma/U of the uranium ores.

relationships are found among these three ratios; between 610 kev/U and beta/U; between 610 kev/U and 80 kev/U. Fig. 1 and 2 illustrate them. These results indicate that (1) beta-counts due to U-group are nearly constant, (2) beta-counts due to Ra-group and Pb-group nearly proportional to 610 kev-gamma or Ra-group content, and (3) gamma-counts due to U-group nearly constant too. Consequently, it may be said that the equilibrium states above stated are recognized in these samples.

In order to investigate the microscopic distribution of alpha-emitters in the ores, microautoradiographs were taken with alpha sensitive nuclear emulsion (Fuji contact type autoradiographic plate)¹⁸⁾¹⁹⁾. Alpha-tracks were observed corresponding to limonite and radiocolloid besides the uranium minerals. Sometimes biotite contains alpha-emitters.

III. Analysis for U-234*/U-238*

Uranium was separated from the sample by solvent extraction with tributyl phosphate, and by anion exchange with Dowex 1-X8. The alpha-ray spectrum of the separated uranium was obtained by a gridded ionization chamber accompanied with a twenty-channel pulse height analyzer. This gridded ionization chamber was described in detail by T. Doke et al. in 1960²⁰⁾.

Two representative samples, no. 1 (unoxidized ore) and no. 7 (oxidized ore), were analyzed in this way. The alpha-ray spectra for no. 1 is shown by Fig. 3, the

Fig. 3. Alpha-ray spectra of uranium separated from the unoxidized uranium ores.

spectra for no. 7 are almost the same. In both spectra, 4.18 Mev-alpha of U-238 and 4.76 Mev-alpha of U-234 are observed distinctly. Difference in the areas of these two peaks is about 3% for both samples, which is not significant in consideration of the experimental error, about 5%. Thus the disequilibrium is not found between U-234 and U-238.

IV. Radiocolloid concentration

The concentration of the radiocolloid in the samples was measured as following. Pulverized sample, about 2 g, was packed in a glass tube, 22 mm in diameter, about 15 mm long, without use of binding material. The tube packed with the sample was placed in contact with the autoradiographic plate for about 100 hours. The plate was developed, fixed and then examined under a nuclear track research microscope. The radiocolloids were recorded as stars of alpha tracks. Total number of the stars (N) was counted. The concentration of the radiocolloid may be expressed as $N/U/A$, where U is uranium content (%), A is area (cm^2) of the glass tube. The results obtained are shown in Table 3.

V. Analysis for $\text{Io}^*/\text{U-238}^*$

(1) Principle The thorium isotopes in uranium ores are Io, Th-234, Th-231 and Th-227, which are expressed in Fig. 4 with dotted lines. Among these isotopes, Io and Th-234 belong to the uranium decay series, and the others to the actinium series. The radioactivities of the separated thorium are derived from Io and

Fig. 4. Upper parts of the uranium and actinium decay series.

Th-234, if the radioactivities due to the other isotopes are neglected. The Th-234 will be in equilibrium with Pa-234 in about 10 minutes. Thus the separated thorium contains Io as an alpha-emitter, and Th-234 and Pa-234 as beta-emitters. When Th_β are the beta-counts of the separated thorium and Th_α its alpha-counts, Th_α/Th_β is proportional to $Io^*/Th-234^*$ or $Io^*/U-238^*$, if U-238 is in equilibrium with Th-234. A thin film of uranium, in which U-238 is in equilibrium with U-234 and Th-234 is formed on a Pt-foil and is counted to obtain the alpha-counts (U_α) and the beta-counts (U_β) under the same condition as the countings of the thorium. $Io^*/U-238^*$ may be expressed as follows:

$$Io^*/U-238^*=2 \cdot Th_\alpha/Th_\beta \cdot U_\beta U_\alpha.$$

Correction of Th_α/Th_β for the disintegration of Th-234 and Th-227 is necessary. But there is no need to consider the correction for Th-231, because Th-231 is thought to be in equilibrium with U-238 both in the sample and in the uranium foil. The error due to the contamination of Th-232, 1% for uranium, is about 0.6%.

(2) Procedure

(a) Separation Thorium was separated by coprecipitation with Pr carrier²¹⁾, and by a cation exchange resin²²⁾. There is no need for quantitative separation in this analytical method.

Pulverized sample, 1~3 g, was dissolved with aqua regia, evaporated and filtrated to remove the insoluble material. The filtrate was added with Bi and Pb carriers, each of 20 mg, then saturated with H_2S and filtrated to remove Pb, Bi, Po, and other heavy metals. The filtrate was boiled to drive out H_2S gas and diluted to 50 ml with 0.5 M oxalic acid. Th in the solution was coprecipitated with Pr carrier, 20 mg, under boiling. The precipitate was dissolved in 10 ml of 2 N HNO_3 , added with distilled water to 20 ml. Th was separated from the Pr carrier and others by cation exchange. The column used was 0.6 mm in diameter and 15 cm long. As cation exchange resin, Dowex 50-X4, 50~100 mesh, 2 ml, was used. After

absorption, the resin was washed with 20 ml of 3N HCl and 10 ml of distilled water, then, Th was eluted with 0.5 M oxalic acid.

Completeness of the separation and contamination of Th-232 were checked by beta counting and gamma and alpha spectrometries.

Fig. 5. Alpha-ray spectrum of thorium separated from the un-oxidized ores.

Decrease of the beta-counts due to the half-life (24.1 days) of Te-234, (93 kev-gamma) was observed. The alpha-ray spectrum of the separated thorium is shown in Fig. 5, in which 4.68 Mev-alpha of Io is observed, and any contamination of other alpha-emitters is not found. The calibration of energy in the spectrometry was made with 5.15 Mev-alpha

of Pu-239.

(b) Sample preparation and counting. On a Pt-foil, 0.03 mm in thickness, and 25 by 25 mm square, 0.3 ml of the eluted solution was dropped from the column directly. It was evaporated quietly to dryness by an infrared lamp, heated to about 180°C by taking the lamp near the Pt-foil to sublimate the oxalic acid, then heated to red in flame. The sample thus prepared was counted for its alpha and beta activities. The counter used was a two pi proportional counter (Type PC-3A, Nuclear Measurement Co.) with PR-gas, 95% of argon and 5% of methane.

The standard deviation for seven values obtained from repeated analyses for one sample was 2.75%.

(3) Results

(a) Sample no. 6 (MiVida pitchblende) was analyzed repeatedly, for Io*/U-238* were obtained two values: 1.02 and 0.98. It may be proved that the equilibrium of Io to U-238 is established in this specimen. This result has been expected beforehand as already

Table 3. Experimental results for $\text{Io}^*/\text{U-238}^*$ analyses and for radiocolloid concentration measurements. (Analysts for U: S. Watanabe and S. Motoyama, Atomic Fuel Research Institute)

Sample	U(%)	Io*/U-238*	Radiocolloid N/U/cm	Beta/U	
I	no. 1	0.98	1.14	33	3028
	no. 2	0.20	1.75	334	6010
	no. 3	0.17	1.43	179	5309
	no. 4	0.31	1.03	1	2795
	no. 5	0.99	1.11	49	2428
	no. 6	50.5	1.00	0	—
II	no. 7	2.04	1.00	1	2334
	no. 8	0.09	1.25	23	3344
	no. 9	0.39	1.21	30	3108
	no. 10	—	0.82	0	—
	no. 11	—	0.62	0	—
	no. 12	—	0.70	0	—
	no. 13	—	0.71	0	—
	no. 14	—	0.72	0	—
III	no. 15	—	1.06	0	—
	no. 16	—	0.72	0	—

stated.

Analytical results of the samples listed in Table 1 are shown in Table 3.

(b) Relationship between beta-counts/U and $\text{Io}^*/\text{U-238}^*$ is expressed in Fig. 6. It indicates a trend that beta-counts are increased with Io content.

(c) Relationship of $\text{Io}^*/\text{U-238}^*$ to the radiocolloid concentration in the unoxidized ores is illustrated by Fig. 7. When $\text{Io}^*/\text{U-238}^*$ is less than 1.00, radiocolloid is not found. But the radiocolloid concentration increases with increasing Io, when $\text{Io}/\text{U-238}^*$ is more than 1.00. A probable explanation of these relationships is that Io is in equilibrium with U-238 in the uranium mineral, ningyoite, and the excess amount of Io is included in the radiocolloid free from

Fig. 6. Beta/U vs. $Io^*/U-238^*$ in the uranium ores.

Fig. 7. Relationship between Io and the radiocolloid in the oxidized ores.

Fig. 8. Relationship between Io and the radiocolloid in the unoxidized ores.

uranium. Sample no. 5 plotted in Fig. 7 with symbol $\square$ seems to have the same relationships as the others. This is also reasonable, because the coffinite is a primary mineral of the Ogamo ore deposits and expected to have Io in equilibrium with U-238.

(d) In the autunite samples $Io^*/U-238^*$ is lesser than 1.00 as shown in Table 3. This seems to correspond to the fact that the autunite is a secondary mineral. But Io in the oxidized ores, as a whole, is in excess for the equilibrium state. Fig. 8 illustrates the relationships between $Io^*/U-238^*$ and the radiocolloid concentration in the oxidized ores. Even if $Io^*/U-238^*$ for the autunite is assumed to be 0.82, the maximum value for the autunite samples, the radiocolloid concentration is too small to explain the Io content. Limonite is the only phase containing radioactive nuclides except the autunite and the radiocolloid. Thus, it may be said that Io in

the limonite is in excess for the equilibrium state.

(e) Table 3 shows that the ratio, $\text{Io}^*/\text{U-238}^*$, of sample no. 16 is less than 1.00, while that of sample no. 15 is nearly 1.00. These results explain that the autunite is the secondary mineral after beta-uranophane.

VI. Variation of $\text{Io}^*/\text{Th-234}^*$ under leaching

A method of investigation by means of chemical leaching is available for studying the states of the radioactive equilibrium of a specimen in which these states are different in phases.

(1) Principle. Two models are illustrated in Fig. 9, where (A) is a case in which U and Io are contained in one phase, while (B) is a case in which they are contained separately into two phases which are different in chemical properties. In both cases, it is assumed that U-238 is in equilibrium with Th-234, and Th-232 is not contained or negligible.

When a sample is leached in the case of (A), $\text{Io}/\text{Th-234}$ is kept to be constant throughout leaching, although the ratio of U to these Th isotopes may vary. While in the case of (B), $\text{Io}/\text{Th-234}$ possibly varies in the course of leaching. If the behaviors of these two phases under chemical leaching are known, it may become clear which phase contains Io or U by tracing the variation of $\text{Io}^*/\text{Th-235}^*$ under leaching. On the contrary, if the phase which contains Io or U is known, the differences in the behaviors of these phases under leaching may be found in the same way.

This method seems to be applicable to and useful for studying the Ningyotoge ores whose radiocolloid and ningyoite are too fine to be separated from each other.

Fig. 9. Schematic diagram illustrating the difference of leaching effect on Th-isotopic ratio in two models of uranium ores.

(2) Procedure. Sample, 10g of the pulverized ore, was weighed into a glass column, 10 mm in diameter and 20 mm long, accompanied with a glass filter and a cock like that used in ion exchange. At first, distilled water, about 10 ml, was pushed into the column from its bottom, so that the bubbles in the column were removed. Then the sample was leached with 10 ml of 6N HCl allowed to flow through the column at a rate of about 2 ml per minute. Thus the filtrate F_1 was obtained. Next the sample was leached with another 10 ml of 6 N HCl and the filtrate F_2 was obtained in the same way. Finally the sample was carried from the column to a flask, added with 20 ml of aqua regia, and evaporated. The insoluble material was removed by dilution and filtration, and the filtrate F_3 was obtained. These three filtrates, F_1 , F_2 and F_3 , were analyzed for $\text{Io}^*/\text{Th-234}^*$ by the same method as that for $\text{Io}^*/\text{U-238}^*$. The same experiments were done with 6 N H_2SO_4 instead of 6 N HCl.

(3) Results. The method was applied to the samples, no. 2 and no. 7. Sample no. 2 is characterized with ningyoite and much radiocolloid, no. 7 is characterized with autunite and radioactive limonite. The radiocolloid concentration is very small for no. 7 as shown in Table 3. The experimental results are presented in Fig. 10. It is indicated that $\text{Io}^*/\text{Th-234}^*$ is not constant for both the samples. Consequently each sample has two phases which are different in $\text{Io}^*/\text{U-238}^*$ from each other.

(a) Sample no. 2 (unoxidized ore) In Fig. 10, it is indicated that the phase of high $\text{Io}^*/\text{U-238}^*$ is more leachable than the other phase of low $\text{Io}^*/\text{U-238}^*$. Accordingly it may be thought that the high $\text{Io}^*/\text{U-238}^*$ phase corresponds to the radiocolloid and the other phase corresponds to ningyoite.

(b) Sample no. 7 (oxidized ore) In the case of no. 7, a reverse result is found in Fig. 10; the phase of low $\text{Io}^*/\text{U-238}^*$ is more leachable than the other. And it may be said that autunite corresponds to the phase which is low in the ratio and more leachable, and limonite corresponds to the other phase.

Fig. 10. Variation of $Io^*/Th-234^*$ by chemical leachings.

Discussions and conclusions

(1) The equilibrium between U-238 and U-234 has been assumed to be established without measurement. Isabaev et al. reported that $U-234^*/U-238^*$ fluctuated in some secondary uranium minerals and it arrived the maximum value of about 3^{23} . The results of the measurements of this ratio for two representative samples of the Ningyotoge ores indicate the establishment of the equilibrium. The conspicuous disequilibrium between these nuclides does not seem to exist in other samples. But it may rather be a future problem to measure the ratio more accurately and to investigate its geological and geochemical meanings in wider area including the Ningyotoge mine.

(2) An analytical method for $Io^*/U-238^*$ was examined and applied to the Ningyotoge ores. The method is based on the determination of isotopic ratio, $Io/Th-234$, and there is no need to determine the chemical yield in the separation of thorium. The absolute value of $Io^*/U-238^*$ is easily obtained by the use of uranium as

the standard. Analytical error can be limited within 5%.

As an application of this analytical method, was examined an experimental method by means of tracing the variation of $\text{Io}^*/\text{Th-234}^*$ under chemical leaching. This was proved to be useful to investigate the states of the equilibrium which are different in phases in one specimen.

(3) The ratio of beta-counts to uranium content, which depends on U-group, Ra-group and Pb-group, was turned out to vary with close relation to the Io content. It may be said that the Io content, in fact, affects considerably the states of the equilibrium between U-238 and its daughter products below Io. But Ra-226 and Pb-210 must be analyzed, at least, in order to discuss these states in detail.

According to the autoradiographic studies of the ores, the radioactive nuclides are contained not in uniform distribution but in microscopic units, in uranium minerals and radiocolloid. The states of the equilibrium, therefore, exist corresponding to such units.

In the unoxidized ores, Io is contained in excess for the equilibrium state, as a whole. This may be interpreted that Io in ningyoite is in equilibrium with U but Io in excess is contained in the radiocolloid free from U.

In the oxidized ores, Io is also contained in excess for the equilibrium state as a whole. In this cases, Io in autunite is deficient for the equilibrium state to U, but Io in limonite is in excess for it.

The processes, which have caused these states, may be described as follows:

It is known that differentiation of U from Th generally occurs by oxidation and chemical leaching. There is no doubt about

that the Ningyotoge uranium deposits have suffered from oxidation and chemical leaching. Process (a) shows that ningyoite has suffered from such reactions, and U has been separated from Io and removed in uranyl solution, while Io left as radiocolloid. Process (b); in the oxidized zone, it is supposed that U was fixed as uraniferous limonite at first, and then crystallized as autunite. The separation of Th from U has occurred during the crystallization.

Consequently, the states of the radioactive equilibrium in the Ningyotoge uranium ores are explained to be a result of the differentiation of uranium from thorium. On the contrary, these states are represent the various features of this differentiation.

(4) The radiocolloid was thought by H. Yagoda to be Ra-sulphate coprecipitated with Pb-sulphate from the facts that the specific activity of the radiocolloid was extremely high and lead was detected at the very points where the radiocolloids were found. Since then it has been thought that the radioactive nuclides in the radiocolloid are radium and its daughter products.

In this work, it was proved that they are ionium and its daughter products, in which radium is included.

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