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10. *Isotopic Ages of Uraninites from Japan.*

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Abstract

Isotopic age measurements were made on three samples of uraninite from Japan. Lead was determined by the isotope dilution technique using a spike of stable lead. The results for two samples give a discordant age pattern generally observed on many young uraninites: Pb-207/Pb-206 age is higher than Pb-206/U-238 age. Pb-207/U-235 age agrees with the Pb-206/U-238 age for three samples. It is concluded that the Pb-206/U-238 age is the most probable and that discordant ages result from uncertainties concerning the original lead. All the minerals have approximately the same age, 100×10^6 years.

Introduction

Age determination by the lead method has been investigated by many researchers. In addition, several studies have been made in connection with the age discordance problem, of which some interpretations were presented on the basis of experiments in laboratories.

Most of the radioactive minerals subjected to these studies are more than several hundreds million years old. The present work is concerned with the age determination of young uraninites from Japan.

Description of samples

The uraninite from Yamaguchi mine together with the galena from Tarō mine were supplied by Dr. H. Imai.[1] The uraninite occurred in a copper mine of skarn type which was a metasomatic deposit near the contact of Paleozoic formation with intruded granitic rocks. The size of uraninite crystals average 0.04 mm. to 0.40 mm. in diameter and

1) H. IMAI, N. SAITO, S. HAYASHI, K. SATŌ and Y. KAWACHI, *J. Geol. Soc. Japan*, **66** (1960), 405-409.

pleochroic halo is distinctly observed in thin section.

The galena from Tarō mine occurred in the ore formed in granitic rocks, 5 km. north-west of Tarō machi, Iwate prefecture, Japan. It is concluded that the galena has the same age as the granitic rocks related to the formation of the Yamaguchi mine. Then, its isotopic composition is assumed to be the same as the original lead in the uraninite.

The uraninite from Iisaka was collected by Dr. T. Iimori and Dr. K. Kimura in a pegmatite, a part of Abukuma plateau granite-pegmatite extended in north-east of Japanese Island.[2] It occurred in a rock body near Iisaka machi, Fukushima prefecture, Japan. The crystals existed as fine granules, 0.01 to 0.02 mm. in diameter, with co-genetic thorogummites, yttrialites and fergusonites. These co-genetic radioactive minerals were removed by elutriation and panning. The fine grains thus prepared were subjected to X-ray powder analysis, which proved the sample sufficiently pure for chemical analysis.

The uraninite from Masaki[3] was supplied by Mr. H. Inouye. The uraninite occurred in a chlorite vein cutting one of the pegmatite bodies formed in Masaki granitic rocks, 8 km. south of Tagawa City, Fukuoka prefecture, Japan. The crystals, 0.05 to 0.1 mm. in diameter, occurring in the vein were separated from co-genetic minerals by elutriation and by means of an isodynamic separator.

Chemical and isotopic analysis

A powdered sample, whose purity was checked by X-ray diffraction pattern, was weighed and then decomposed by heating with 6 N nitric acid. The resulting solution was dried up and water containing a small amount of hydrochloric acid was added. After the procedure was repeated, the insoluble part was removed by a centrifuge, and the solution was subjected to analysis.

For the isotopic analysis, lead was precipitated with hydrogen sulfide from the 0.1 N hydrochloric acid solution and lead sulfide was dissolved in nitric acid. When the amount of lead separated from the sample was small (less than 1 mg.), a large part of the nitric acid solution was introduced into a specially designed vessel[4] and evaporated up. After lead nitrate was converted into iodide with hydriodic acid, tetramethyl

2) T. IIMORI, *Sci. Pap. I. P. C. R.*, **39** (1941), 208.

3) H. INOUYE and K. SATŌ, *Jour. Japanese Ass. Min. Petr. Econ. Geologists*, **46** (1961), 133-137.

4) K. SATŌ and N. SAITO, *Mass Spectroscopy (Japan)*, **15** (1960), 43-51.

lead was synthesized in a vacuum system. Occasionally, lead iodide in the vessel contains a small quantity of bismuth as an impurity. This interferes with the isotopic analysis because ions of Bi-209 have the same mass as that of $^{208}PbH^+$ ions; the interference can be eliminated by the method using standard samples of lead as already reported.[4]

When a sufficient quantity of lead was available, lead was separated from the sample solution as sulfate. Lead sulfate was dissolved in a hot ammonium acetate solution containing acetic acid and converted into lead sulfide by the use of hydrogen sulfide. Then, lead nitrate solution was prepared, but for mass spectrometry lead iodide was precipitated from the solution by 10% solution of potassium iodide. The precipitate was separated by a centrifuge and suspended in pure water. The process was repeated until lead samples of sufficient purity was obtained.

For the purpose of determining the lead content of minerals, the solution of the mineral sample was mixed with a spike solution of lead of known volume (containing 3.07 mg. Pb per 1 ml.). Lead iodide was prepared in the same way as in the case of the isotopic analysis. In order to establish the isotopic exchange equilibrium between the species in solution, the solution was heated and stirred for at least two hours. Only in the case of the uraninite from Yamaguchi mine, was lead determined by the gravimetric method weighing lead as chromate and sulfate, and no isotope dilution method was applied.

Thorium was determined according to the ordinary gravimetric procedure. To the uraninite from Iisaka pegmatite, the separation method using anion exchange resin[5] was also applied. The result obtained was nearly the same as that of the gravimetry.

Uranium was determined by the ordinary method weighing U_3O_8.

Analytical data and age

The results of the isotopic analysis of leads are summarized in Table 1. It has been reported by Sakai and Satō that the isotopic compositions of leads in lead ores in Japan fall within a narrow range and the average value is nearly the same as the isotopic composition of the recent lead of *normal* type.[6] Since the chemical U–Pb ages of Iisaka and Masaki uraninites are less than 110×10^6 years, the isotopic compositions of the original lead in these uraninites were assumed as

5) T. SEKINE and N. SAITO, *Nature*, **81** (1958), 1464-5.
6) H. SAKAI and K. SATŌ, *Geochim. et Cosmochim. Acta*, **15** (1958), 1-5.

Table 1. Isotopic data for lead.

Sample	Isotopic composition (atom %)				Isotope ratio	
	Pb-204	Pb-206	Pb-207	Pb-208	Pb-207/Pb-206	Pb-208/Pb-206
Lead from Yamaguchi uraninite	0.032±0.006	93.484±0.007	5.185±0.032	1.299±0.036		
Lead from galena, Tarō mine	1.361±0.003	25.41±0.03	21.17±0.04	52.06±0.04		
Lead from Iisaka uraninite	0.027±0.008	92.460±0.044	4.84±0.03	2.678±0.014		
Estimated composition of original lead	1.355±0.002	25.05±0.07	21.13±0.07	52.46±0.20		
Uraninite 1.8303 g. +spike Pb 6.14 mg.	1.00±0.09	47.16±0.14	15.82±0.07	36.03±0.11	0.3358±0.0024	0.764±0.004
Uraninite 0.7875 g. +spike Pb 15.35 mg.					0.122±0.003	0.208±0.003
Lead from Masaki uraninite	0.1	91.07±0.71	4.94±0.17	3.82±0.19	0.0542±0.0015	0.0419±0.0017
	0.1	91.85±0.30	4.75±0.14	3.42±0.11	0.0516±0.0015	0.0372±0.0016
Estimated composition of original lead	1.355±0.002	25.05±0.07	21.13±0.07	52.46±0.20		
Uraninte 0.09367 g. +spike Pb 3.07 mg.	1.068±0.029	40.92±0.16	17.39±0.23	40.63±0.37	0.425±0.004	0.993±0.005
	1.131±0.018	41.14±0.28	17.24±0.46	40.49±0.60	0.419±0.008	0.984±0.008
Spike lead	1.364±0.002	24.93±0.05	21.38±0.04	52.33±0.20		

Table 2. Analytical data and ages of uraninites.

Uraninite from Yamaguchi mine

Concentration of isotopes (mg./g.)				age in million years	
U-238	705±5	radiogenic Pb-206	8.92±0.96	Pb-206/U-238 age	94±11
U-235	5.08±0.04	radiogenic Pb-207	0.448±0.060	Pb-207/U-235 age	99±12
Th-232	9.66	radiogenic Pb-208	0.007±0.026	Pb-208/Th-232 age	<80
				Pb-207/Pb-206 age	235±75

U: 710.1 mg./g., Th: 9.66 mg./g., Pb: (9.56±1.01) mg./g.

Uraninite from Iisaka pegmatite

concentration of isotopes (mg./g.)				age in million years	
U-238	668.7±8.3	radiogenic Pb-206	8.82±0.17	Pb-206/U-238 age	98±3
U-235	4.81±0.06	radiogenic Pb-207	0.423±0.022	Pb-207/U-235 age	98±6
Th-232	33.8	radiogenic Pb-208	0.156±0.030	Pb-208/Th-232 age	102±19
				Pb-207/Pb-206 age	115±78

U: 673.5 mg./g., Th: 33.8 mg./g., Pb: (9.59±0.16) mg./g.

Uraninite from Masaki pegmatite

concentration of isotopes (mg./g.)				age in million years	
U-238	635±9.5	radiogenic Pb-206	9.47±0.37	Pb-206/U-238 age	111±5
U-235	4.61±0.03	radiogenic Pb-207	0.431±0.097	Pb-207/U-235 age	104±23

U: 639.6 mg/g., Pb: (10.45±0.24) mg./g.

Decay constants used in age calculation

U-238: $\lambda=1.54\times10^{-10}$/year; A. F. KOVARIK and N. I. ADAMS JR., *Phys. Rev.*, **98** (1955), 46.
U-235: $\lambda=9.72\times10^{-10}$/year; E. H. FLEMING JR., A. GHIORSO and B. B. CUNNINGHAM, *Phys. Rev.*, **88** (1952), 642.
Th-232: $\lambda=4.99\times10^{-11}$/year; E. PICCIOTTO and S. WILGAIN, *Nuovo Cimento*, **4** (1956), 1525.

Isotopic ratio of uranium at present time

U-238/U-235=137.8±1.0; M. G. INGHRAM, *Manhattan Project Technical Series Div. 2, Gaseous Diffusion Project*, **14** (1946), **Chap. V.**, 35.

being the same as the average value for the common leads of Japan. The isotopic composition of original lead in the Yamaguchi mine uraninite was assumed to be the same as that of lead in the galena from Tarō mine as already mentioned.

The results of the chemical analyses and the calculated ages are shown in Table 2. For each of the uraninites, the Pb-206/U-238 age is consistent with the Pb-207/U-235 age within estimated errors. For Yamaguchi uraninite, the Pb-207/Pb-206 age is higher than other ages. The abundance of Pb-207 of lead in Masaki uraninite could not be measured accurately so that it is difficult to estimate the Pb-207/Pb-206 age. It is also difficult to estimate the Pb-208/Th-232 ages for Yamaguchi and Masaki uraninites because of uncertainties of the content of radiogenic Pb-208. Four isotopic ages of Iisaka uraninite coincide with each other within estimated errors.

Discussion

As seem from Table 2, the Pb-207/Pb-206 age of Yamaguchi uraninite is extraordinarily higher than other ages and the Pb-207/Pb-206 age of Iisaka uraninite is somewhat higher than other ages. Even these discordances have to be taken into account when minerals used for age determination are young.

The type of age discordance varies with the different kinds of minerals. When the age discordances obtained in this research are

Table 3. Original leads

Locality	Total lead content (mg./g.)	Original lead content estimated from Pb-204 (mg./g.)
Joachimstal[8]	27.4	14.4
Masaki pegmatite	10.45	<0.76
Iisaka pegmatite	9.59	0.192
Yamaguchi mine	9.56	0.225
Colorado plateau[8]	13.4	9.73
Colorado plateau[8]	7.9	3.37
Marysvale, Utah[8]	0.25	ca. 0.14

discussed, the errors of isotopic analysis of lead and the uncertainty concerning the original lead in the mineral have to be considered as main factors. So far as the determination of isotopic composition and

the mass spectrometric isotope dilution analysis are concerned, it is generally said that errors have hardly any effect on the evaluation of ages.[7]

However, the available data supporting this statement are mainly relating to samples containing an almost negligible amount of original leads, having ages older than about 2×10^8 years. In the case of young minerals, the situation differs from the above. It is extremely difficult to estimate the amount of radiogenic leads of young minerals containing original lead on account of the following circumstances.

1) When the content of radiogenic lead is compared with that of original lead, the fraction of radiogenic lead is not so large as that of lead in the old minerals. The error of measurement of Pb–204 and the imperfect estimation of the ratios: Pb–207/Pb–204 and Pb–208/Pb–204 of the original lead may affect the calculation of ages.

2) Even though the content of original lead is satisfactorily small, the ratios; Pb–207/Pb–206 and Pb–208/Pb–206 are, in general, extremely small and even minute errors in the isotopic analysis make it difficult to estimate the contents of radiogenic Pb–207 and Pb–208.

In Table 3 are shown the contents of original leads in the uraninites investigated in this research and those of the comparatively young uraninites reported by other investigators.

Kulp et al.[8] concluded that Pb–206/U–238 age is the most reliable for young minerals. When the ages of three uraninites are compared

and ages of uraninites.

Isotope ratio			Age in million years		
$\frac{\text{Pb-204}}{\text{Pb-206}}$	$\frac{\text{Pb-207}}{\text{Pb-206}}$	$\frac{\text{Pb-208}}{\text{Pb-206}}$	$\frac{\text{Pb-206}}{\text{U-238}}$	$\frac{\text{Pb-207}}{\text{U-235}}$	$\frac{\text{Pb-207}}{\text{Pb-206}}$
0.010	0.216	0.42	179±3	197±15	425±200
0.0011	0.053	0.044	111±5	104±23	—
0.0003	0.052	0.029	98±3	98±6	115±78
0.00034	0.055	0.014	94±11	99±12	235±75
0.022	0.37	0.84	55±2	58±10	220±500
0.0087	0.18	0.34	51±1	56+5	250±250
0.021	0.84	0.83	9.8±1.2	24±10	—

7) L. T. ALDRICH and G. W. WETHERILL, *Ann. Rev. Nucl. Sci.*, **8** (1958), 257-298.

8) J. L. KULP, G. L. BATE and B. J. GILETTI, *Proc. Geol. Assoc. Canada*, **7-11** (1955), 15-24.

in Table 4 with the K–Ar or U–Pb ages reported by other investigators, the data strongly suggest that Pb–206/U–238 ages are the most probable, although the data in the Table 4 are scanty for establishing the true ages for the respective rocks concerned. Japanese uraninites, however, contain less original leads than the uraninites from other localities. The content of original lead of Iisaka uraninite is small and all lead ages

Table 4. Comparisons of U–Pb ages of radioactive minerals with K–Ar ages of related rocks.

Rock	Location	Age in million years	Mineral and method
Granitic rocks, Miyako-Taro district	Yamaguchi mine	94	uraninite, isotopic U-Pb (this paper)
Pegmatite, Abukuma plateau	Suisyō-yama, Fukushima	131	yttrialite, chemical U-Pb[9]
	Suishō-yama, Fukushima	111	allanite, chemical U-Pb[9]
	Hayamadake, Fukushima	109	fergusonite chemical U-Pb[9]
	Ishikawa, Fukushima	132, 123	samarskite, chemical U-Pb[9]
	Iisaka, Fukushima	98	uraninite, isotopic U-Pb (this paper)
	Iisaka, Fukushima	111	microcline perthite, isotopic K-Ar[10]
	Iisaka, Fukushima	112, 126	biotite, isotopic K-Ar[10]
Diorite, Abukuma plateau	Furudono, Fukushima	102	biotite, isotopic K-Ar[11]
	Orimatsu, Fukushima	95	biotite, isotopic K-Ar[11]
Masaki pegmatite (a)	Masaki, Fukuoka	96	uraninite, chemical U-Pb[12]
Masaki pegmatite (c)	Masaki, Fukuoka	111	uraninite, isotopic U-Pb (this paper)
Ko-tōge pegmatite	Ko-tōge Fukuoka	102	uraninite, chemical U-Pb[12]

9) A. KATO, *Chikyū Kagaku (in Japanese)*, **34** (1957), 40.

10) H. NAGASAWA, Private communication.

11) J. MILLER, F. SHIDO, S. BANNO and S. UYEDA, *Japan. Jour. Geol. Geogr.*, **32** (1961), 145-151.

12) K. KIMURA and T. IIMORI, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **58** (1937), 1135.

roughly coincide with each other. The uraninite such as above is a good specimen for age determination, because Pb–206/U–238 age can be compared with other lead ages.

It can be seen in Table 3 that Pb–206/U–238 ages agree with Pb–207/U–235 ages except for Marysvale uraninite. This shows that the error of estimation of radiogenic Pb–207 does not affect the calculation of Pb–207/U–235 age.

The Pb–207/Pb–206 ages are considerably higher than other ages. For example, radon leakage in the past may be considered as a cause of the discordances above.

On the mass spectrometry in this research, considerable error is inevitable in the measurement of the abundance of Pb–204. On the other hand, the most abundant Pb–206 seems to affect the experimental result in such a way as to overestimate the Pb–204. As a result of this, the radiogenic Pb–207 is underestimated and the age pattern: Pb–206/U–238 age > Pb–207/U–235 age > Pb–207/Pb–206 age must be observed. Consequently, very high Pb–207/Pb–206 age cannot be explained.

The most probable cause of the high Pb–207/Pb–206 age is the uncertainty of the isotopic composition of original lead, since the true value of this is never known.

In conclusion, it is very likely that the Pb–206/U–238 ages obtained for three uraninites of Japan are close to their true ages. It may be concluded that uraninite is useful in determining ages of 100 million years or less, provided that lead in the mineral contains Pb–204 of less than 0.1%. A high Pb–207/Pb–206 age of young uraninite is far from being a true age. The age pattern: Pb–207/Pb–206 age > Pb–206/U–238 age generally observed on many young uraninites may be attributed to the obscurity of the amount and isotopic composition of original lead in the mineral.

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10. 日本の閃ウラン鉱の同位体年令について

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鉛法による各種同位体年令間の不一致については，2×10^9 年またはそれ以上の年令の鉱物に関する研究が多く行われている．年令が新しい鉱物の場合は radiogenic isotope/parent isotope の測定誤差は一般に大きい．鉛法による見かけ上の年令不一致が測定によつて得られたときは，放射性起源の鉛の同位体の集積量が小であることおよび鉱物中の非放射性起源の鉛の同位体の量と存在比の不確実さが考慮すべき問題となる．

以上の観点から年令の比較的新しい日本の閃ウラン鉱について年令決定を行なつた．対象としてえらんだ閃ウラン鉱はペグマタイトから採取されたもの 2 種および銅鉱床から採取されたもの 1 種である．

鉛の定量法としてペグマタイトから採取された閃ウラン鉱については普通の鉛を spike とする同位体希釈分析を適用した．得られた年令はいずれも約 10^9 年であつたが，各鉱物について若干の年令不一致が認められた．従来報告されている結果および分析誤差から見て，$^{206}Pb/^{238}U$-年令が最も確からしいこと，$^{207}Pb/^{206}Pb$-年令は最も不正確であること，および $^{208}Pb/^{232}Th$-年令は若干低い値を示すことが見出され，さらに $^{207}Pb/^{235}U$-年令は $^{206}Pb/^{238}U$-年令とほぼ一致することが見出された．

これらの諸結果から，鉱物の年令が 10^9 年程度でその中の鉛の非放射性起源の同位体 ^{204}Pb の含有量が 0.1% 以下であれば，年令決定の対象として閃ウラン鉱の有用性は大であること，および年令の新しい閃ウラン鉱中の非放射性起源の鉛の含有量が上記のものより大きいものでは，その同位体存在比の不確実さのために年令不一致が生じ，従来報告されているこのような鉱物に関する不一致の例も，同様の原因に説明を求めることができることが推論された．