COMPARISON OF THE ISOTOPIC ABUNDANCE

OF U^{235} AND U^{238} AND THE RADIUM ACTIVITY

RATIOS IN COLORADO PLATEAU URANIUM ORES

By   F. E. Senftle, Lorin Stieff, Frank Cuttitta, and P. K. Kuroda

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

March 25, 1957

AEC-405/7

Dr. T. H. Johnson, Director
Division of Research
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Dr. Johnson:

Transmitted herewith is one copy of TEI-485, "Comparison of

the isotopic abundance of U^{235} and U^{238} and the radium activity ratios

in Colorado Plateau uranium ores," by F. E. Senftle, Lorin Stieff,

Frank Cuttitta, and P. K. Kuroda, May 1956.

The authors plan to submit this report for publication in

Geochimica et Cosmochimica Acta.

Sincerely yours,

John H. Eric

for W. H. Bradley
Chief Geologist

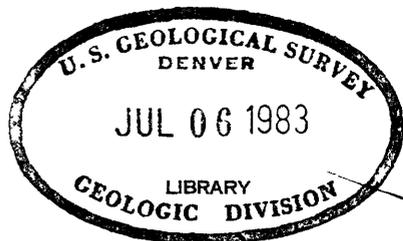UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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AND THE RADIUM ACTIVITY RATIOS IN COLORADO

PLATEAU URANIUM ORES*

By

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COMPARISON OF THE ISOTOPIC ABUNDANCE OF U^{235} AND U^{238}

AND THE RADIUM ACTIVITY RATIOS IN COLORADO

PLATEAU URANIUM ORES

By F. E. Senftle,[1] Lorin Stieff,[1] Frank Cuttitta,[1]

and P. K. Kuroda [2]

ABSTRACT

The isotopic abundances of uranium and the radium activity ratios
of 11 samples of uranium ore from the Colorado Plateau have been measured.
No significant variation in the isotopic abundance of the uranium was
noted; within the experimental error, the average U^{238}/U^{235} ratio is 137.7.
There is a significant variation in the Ra^{226}/Ra^{223} activity ratios
(0.048 - 0.143), which indicates a relatively recent alteration of the ore
samples. The variations do not, however, explain the lead-uranium and
lead-lead age discrepancies.

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Both the published and the unpublished data on the natural variations in isotopic abundance of U^{235} and U^{238} in different geologic materials are limited (Nier, 1939a,b; Inghram, private communication). Although Inghram showed that there were no significant variations in the U^{238}/U^{235} abundance ratio greater than 0.03 percent (see Katz and Rabinowitch, 1951), the possibility has been suggested that the observed variation in the Ra^{223}/Ra^{226} activity ratios and the discrepancies between the Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages may be due, at least in part, to variations in the U^{238}/U^{235} ratio (Kuroda, 1955). For this reason the U^{238}/U^{235} ratios of 11 samples from a selected group of uranium deposits of the Colorado Plateau area and uranium ores from two other areas have been isotopically analyzed. These samples represent a wide variety of uranium ore types. Ra^{223}/Ra^{226} ratios have been determined by Kuroda on many of these samples and Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages have been determined by Stieff and others (1953) on the same samples or similar materials from the same mines. We are indebted to personnel of the Mass Assay Laboratory of Union Carbide Nuclear Company, Y-12 Plant, at Oak Ridge, Tennessee, for the uranium isotope analyses. This study is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

The uranium was completely extracted from the specimens and a minimum of four separate conversions of U_3O_8 to UF_6 and mass spectrographic determinations were made on each. All the results were compared with those of the Oak Ridge National Laboratory "N" Standard (0.7115 wt percent U^{235}). The expressed error is the limit of error of the mean in the 95-percent confidence level. The results shown in table 1 are for 11 ore

Table 1.—Comparison of the radium activity ratios and the uranium isotope abundances in samples from the Colorado Plateau.

Sample no.	Location and description	Activity ratio $N_{Ra223}\lambda_{Ra223}/N_{Ra226}\lambda_{Ra226}$	Weight percent U^{235}	N_{U238}/N_{U235}
G	Heavily oxidized uranium ore, Mineral Joe mine, Colo.	--	0.7147 ± 0.0025	137.1 ± 0.35
S	Oxidized ore, composite sample, Mineral Joe mine, Colo.	--	0.7121 ± 0.0033	137.7 ± 0.64
J	Oxidized ore, Mineral Joe mine, Colo.	--	0.7115 ± 0.0022	137.8 ± 0.31
N	Partly oxidized uranium ore, Mineral Joe mine, Colo.	0.048 ± 0.002	0.7118 ± 0.0022	137.7 ± 0.31
GS-64	Fresh uraninite, Happy Jack mine, Utah	0.048 ± 0.002	0.7115 ± 0.0013	137.8 ± 0.26
GS-87	Oxidized ore, Happy Jack mine, Utah	0.052 ± 0.002	0.7115 ± 0.0022	137.8 ± 0.31
PK-18	Carbonaceous ore, Temple Mountain, Utah	0.055 ± 0.002	0.7115 ± 0.0022	137.8 ± 0.31
AE-1165	Fresh unaltered uraninite, Mi Vida mine, Utah	0.048 ± 0.002	0.7119 ± 0.0022	137.7 ± 0.31
AE-1260	Coffinite, Woodrow Pipe mine, New Mexico	0.064 ± 0.005	0.7124 ± 0.0017	137.6 ± 0.24
AE-1271	Coffinite, Poison Canyon mine, New Mexico	0.143 ± 0.010	0.7116 ± 0.0022	137.8 ± 0.31
AE-1288	Oxidized ore, black, J. J. mine, Paradox Valley, Colo.	0.052 ± 0.002	0.7116 ± 0.0022	137.8 ± 0.31
PK-2	Apparently altered uraninite, Joachimsthal	0.051 ± 0.002	0.7112 ± 0.0020	137.8 ± 0.28
PK-5	Uraninite, Great Bear Lake, Canada	0.048 ± 0.002	0.7114 ± 0.0018	137.8 ± 0.25

specimens from mines on or near the Colorado Plateau. The isotopic data for samples of pitchblende from Great Bear Lake and Joachimsthal are shown for comparison. The following geologic information concerning these specimens is known:

Samples G, J, S, and N are from a series of samples from a channel sample collected from the Mineral Joe mine, Montrose County, Colorado, and are fully described by Garrels and others (1956). The mine is in the Morrison formation of Jurassic age. The channel was cut across a mineral-ized zone which graded from black, partly oxidized uranium ore, through oxidized yellow-brown ores, into unmineralized rock. Sample N is partly oxidized ore, J is yellow-brown oxidized ore, and G is low-grade thoroughly oxidized yellow-brown sandstone. S is a composite sample of three channel samples, F, G, and H (F and H being adjacent to and on either side of sample G).

Samples GS-64 and GS-87 are from the Happy Jack mine, San Juan County, Utah. The mine is in the Shinarump member of the Chinle formation of Triassic age. GS-64 has been described by Stieff and Stern (1952) and is, to the authors knowledge, the freshest, least altered uraninite yet found on the Colorado Plateau. GS-87 is a composite mill pulp sample representing tons of altered and oxidized ore from the same mine.

Professor John W. Gruner of the University of Minnesota has kindly provided the following samples and sample descriptions:

Sample AE-1165 is a specimen of very fresh, unaltered uraninite from the Mi Vida mine, San Juan County, Utah. Montroseite, $VO(OH)$, is also present in the sample.

Sample AE-1260 is a specimen of coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$, from the Woodrow Pipe mine near Laguna, Valencia County, New Mexico. The mine is in the Morrison formation of Jurassic age. The sample was obtained from the Anaconda Mining Company and is believed to have been collected near the bottom of the shaft, about 80 feet from the surface. The pyrite and marcasite associated with the coffinite are quite fresh.

Sample AE-1271 is a specimen of coffinite from the Poison Canyon mine, McKinley County, New Mexico. The mine is in the Morrison formation. The sample came from a depth of approximately 100 feet below the surface of the ground and contained some slightly reddish material, possibly primary hematite. [The extremely high radium activity ratio of this sample, however, suggests to the authors that it has been subjected to extreme alteration and oxidation, as explained below, and that the hematite is probably secondary.]

Sample AE-1288 is from the J. J. mine, Montrose County, Colorado. The mine is in the Morrison formation. This ore contained oxidized vanadium minerals and it may be assumed that the uranium minerals had also been oxidized.

Sample PK-18 is from the Temple Mountain district, Emery County, Utah. The mines in this district occur in the Moss Back member of the Chinle formation of Late Triassic age. The sample is representative of the black uranium-bearing carbonaceous ores of the area. In general, this material shows very little evidence of oxidation and alteration.

Sample PK-2 is a specimen of uraninite from the Joachimsthal district, Czechoslovakia and was obtained from Ward's Scientific Company.

Sample PK-5 is a specimen obtained from the Eldorado Mining Company, Great Bear Lake, Canada. (For description, see Kuroda and Edwards, 1954.) Additional Great Bear Lake samples from Ward's Scientific Company gave Ra^{223}/Ra^{226} ratios in very close agreement with the value in the table.

With the exception of sample G the U^{238}/U^{235} abundance ratios of all the specimens are within the experimental error of 137.7--the average U^{238}/U^{235} ratio. Some difficulty was experienced in making the analyses of sample G and in preparing the UF_6, probably because of impurities present in the ore.

As shown in table 1 the Ra^{223}/Ra^{226} activity ratios of the samples vary markedly, in contrast to the uniform U^{238}/U^{235} abundance ratio. The calculated activity ratios using the most recent decay constants for U^{235} and U^{238} is 0.046. GS-64 and PK-5, the samples showing the least evidence of alteration, have Ra^{223}/Ra^{226} activity ratios of 0.048. The presence of abundant hematite in sample AE-1271 and the fact that this sample has the highest measured activity ratio of the group, namely 0.143, suggests that this sample has been subjected to extensive recent oxidation and alteration. It would seem, therefore, that the samples with radium activity ratios greater than 0.048 can be explained by the alteration of the ore and the simultaneous loss of Ra^{226} and Ra^{223} within the last 10,000 years (approximately 6 times the half-life of Ra^{226}). Under these conditions Ra^{223} ($T_{1/2}$ = 11.2 days) and its daughter products will grow back much more rapidly than Ra^{226} and its daughter products. This explanation is reasonable and will explain both the geologic field relations and the observed variation in the activity ratios of radium and its

daughter products. An alternative explanation can be found in the selective loss of Th^{230}. This would result in a deficiency of Ra^{226} and a high Ra^{223}/Ra^{226} ratio.

It has been suggested (Kuroda, 1955) that the disagreement between Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages calculated from the same sample can be reduced by using the measured radium activity ratio instead of the uranium activity ratio of 0.046 on the basis that the variations in the radium activity ratio reflected variations in the U^{238}/U^{235} abundance ratio. Significant variations of U^{238}/U^{235} abundance ratios have not been found in these samples. Continuous selective enrichment of any of the radioactive daughter products between U^{235} and Ra^{223} or selective depletion of the daughter products between U^{238} and Ra^{226} could produce the observed age discrepancies. Also, periodic loss of radium throughout a major portion of the samples' history could result in abnormally high Ra^{223}/Ra^{226} ratios. Under these unlikely conditions Pb^{207} would be enriched relative to Pb^{206} and the Pb^{207}/Pb^{206} age would be much greater than the Pb^{206}/U^{238} age.

Loss of radium is not supported by the data on samples GS-64 and PK-5 which show a low Ra^{223}/Ra^{226} activity ratio most nearly approaching the calculated value for the U^{235} and U^{238} series. These two samples still exhibit significant discrepancies between their Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages. (See table 2.) Sample GS-64 shows no mineralogic evidence of oxidation or alteration and therefore no visible mechanism for the continuous removal of radium. It would seem improbable that these samples would be in radium-uranium equilibrium now and yet could have lost significant quantities of radium in the past. Of equal significance, the

Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages on a sample of uraninite from Joachimsthal analyzed by A. O. Nier, sample N-1, are essentially in agreement, while the radium activity ratio of a similar sample from the same locality is high (0.051). Although recent loss of radium can account for the observed Ra^{223}/Ra^{226} activity ratios, it would not measurably affect the Pb^{207}/Pb^{206} ages. Thus, it seems that an alternative explanation for the lead-uranium and lead-lead age discrepancies must be found.

Table 2.--Comparison of Pb^{206}/U^{238} and Pb^{207}/Pb^{206} ages.

Sample no.	Location and description	Pb^{206}/U^{238} age in M.Y.	Pb^{207}/Pb^{206} age in M.Y.
N 1/	Relatively fresh ore, Mineral Joe mine, Colo.	55	590
GS-64 1/	Uraninite, Happy Jack mine, Utah	65	190
GS-87 1/	Mill pulp, Happy Jack mine, Utah	230	425
N-1 2/	Uraninite, Joachimsthal, Czechoslovakia	225	214
N-10 3/	Uraninite, Great Bear Lake, Canada	1251	1420

1/ Analysis and age, U. S. Geological Survey.
2/ Analysis of A. O. Nier (1939b). Age recalculated by A. Holmes (1946).
3/ Analysis and age by A. O. Nier (1939b).

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