224
9-12-80

Dr.

LA-8479-PR

ONWI/Sub/80/E511-01100-5

Progress Report

MASTER

Oklo-Natural Fission Reactor Program

January 1—March 31, 1980

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545

The four most recent reports in this series, unclassified, are LA-7816-PR, LA-8054-PR, LA-8189-PR, and LA-8281-PR.

This report was not edited by the Technical Information staff.

This report was prepared by the Los Alamos Scientific Laboratory of the University of California under Subcontract E511-01100 with Battelle Memorial Institute, Project Management Division, under Contract EY-76-C-06-1830 with the US Department of Energy. The subcontract was administered by the Office of Nuclear Waste Isolation.

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

Printed in the United States of America. Available from
National Technical Information Service
US Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Microfiche $3.00

001-025	4.00	126-150	7.25	251-275	10.75	376-400	13.00	501-525	15.25
026-050	4.50	151-175	8.00	276-300	11.00	401-425	13.25	526-550	15.50
051-075	5.25	176-200	9.00	301-325	11.75	426-450	14.00	551-575	16.25
076-100	6.00	201-225	9.25	326-350	12.00	451-475	14.50	576-600	16.50
101-125	6.50	226-250	9.50	351-375	12.50	476-500	15.00	601-up	

Note Add $2.50 for each additional 100-page increment from 601 pages up.

LA-8479-PR
Progress Report
ONWI/Sub/80/E511-01100-5

UC-11
Issued: August 1980

Oklo-Natural Fission Reactor Program

January 1—March 31, 1980

Compiled by

A. E. Norris

CONTENTS

Department of Energy
Mr. C. R. Cooley
Bld. Code GTN
MS B107
Washington, D. C. 20545

Department of Energy
Dr. John A. Patterson
Bld. Code FED
RA-224, MS-6521
Washington, D.C. 20461

Battelle Project Management Division
Attention: Dr. Norman Hubbard
505 King Avenue
Columbus, OH 43201

Battelle Project Management Division
Attention: Ms. B. A. Rawles
505 King Avenue
Columbus, OH 43201

Mr. R. Y. Lowrey
Weapons Production Division
Albuquerque Operations Office
P. O. Box 5400
Albuquerque, NM 87115

Prof. Paul Kruger
Department of Civil Engineering
Stanford University
Stanford, California 94305

Prof. Douglas G. Brookins
Department of Geology
University of New Mexico
Albuquerque, New Mexico 87131

Mr. W. J. Maeck
Exxon Nuclear Idaho Company, Inc.
Radiochemistry Subsection
Post Office Box 2800
Idaho Falls, Idaho 83401

Dr. J. E. Delmore
Exxon Nuclear Idaho Company, Inc.
Radiochemistry Subsection
Post Office Box 2800
Idaho Falls, Idaho 83401

Los Alamos Scientific Laboratory
G. A. Cowan, ADCEL, MS-102
D. C. Hoffman, CNC-DO, MS-760
J. E. Sattizahn, CNC-11
E. A. Bryant, CNC-11
J. H. Cappis, CNC-11
D. B. Curtis, CNC-11
C. J. Duffy, CNC-11
B. R. Erdal, CNC-11
A. J. Gancarz, CNC-11
A. E. Norris, CNC-11
R. J. Vidale, CNC-11

OKLO - NATURAL FISSION REACTOR PROGRAM

January 1 - March 31, 1980

Compiled by

A. E. Norris

ABSTRACT

The techniques to measure lead isotopic abundances in geologic material have been refined and tested with National Bureau of Standards lead isotope standards. The results from 28 analyses show that our measurements of ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios are both reproducible and accurate. However, our data for the ^{204}Pb/^{206}Pb ratio indicate that our mass 204 background correction may be causing problems. The initial work to measure gadolinium isotopic abundances has been accomplished. Studies of rubidium and strontium isotopic ratios in the Oklo reactor zone #2 and adjacent areas indicate that fissiogenic rubidium and strontium are observed in solution when the samples adjacent to the reactor zone are leached for 20 minutes with 0.5 N HCl, while fissiogenic rubidium and strontium are observed in the insoluble residues of samples from reactor zone #2 that are leached in the same manner. Additional work will be done to see if some quantitative conclusions about rubidium and strontium transport at the Oklo site can be deduced.

I. PERSONNEL

This report covers some of the activities of the following individuals.

Los Alamos Scientific Laboratory

J. C. Banar
E. A. Bryant
J. H. Cappis
D. B. Curtis
A. J. Gancarz
A. E. Norris

Idaho National Engineering Laboratory

J. E. Delmore
F. A. Duce
W. J. Maeck
R. A. Nielson

University of New Mexico

D. G. Brookins

II. PROGRAM OBJECTIVE

The goal of this program is the determination of rates of reactor product migration and the mechanisms of transport in geologic media that include natural fission reactors or rich uranium ore bodies.

III. PROGRESS REPORTED PREVIOUSLY

Funding for the United States' participation in the international investigation of the Oklo natural fission reactor phenomenon commenced in fiscal year 1975. The first formal report of progress in this program was the annual report of fiscal year 1976, issued in November, 1976. The Oklo phenomenon refers to the occurrence of self-sustaining fission chain reactions in a series of very rich uranium ore pockets located in an extensive Precambrian pitchblende deposit in Gabon, Africa. The uranium formed critical masses about 2×10^9 years ago. The duration of criticality was several hundred thousand years. During criticality, approximately 10 tons of uranium were fissioned. Studies of the Oklo phenomenon have shown that many fission products were retained at the sites where they were generated. Other products from uranium decay or fission have been shown to be missing in whole or in part from the fossil reactor cores.

Our studies have utilized mass spectrometric techniques to investigate the migration of technetium, ruthenium, and lead. The first two elements are formed from the thermal-neutron-induced fission of ^{235}U and ^{239}Pu and the spontaneous fission of ^{238}U, while the lead isotopes ^{207}Pb and ^{206}Pb are formed as the stable end members of the decay chains that originate with ^{235}U and ^{238}U, respectively.

The following results have been obtained from the technetium and ruthenium studies: 1. Both technetium and ruthenium appear to have migrated to distances of ~10 meters in the vicinity of the reactor zones, but we have been unable to detect evidence of migration to greater distances. 2. The migration that we observe occurred during the operation of the reactors or within approximately one million years after the cessation of criticality. 3. Conditions during the migration time were such that technetium was more mobile than ruthenium, and ruthenium was more mobile than uranium. 4. The migration is in the direction from below the reactor zones to above the zones. This transport most likely was facilitated by aqueous fluids whose circulation may have been induced by thermal effects from the nuclear reactors.

We have concluded from our uranium-lead isotopic studies that lead in the uraninite grains, including that which resulted from uranium decay, diffused continuously during the past two billion years with a fractional loss rate of 10^{-9} to 10^{-11} per year. Some of the lead that diffused out of the uraninite grains was transported 3 to 5 meters below the ore and the reactor zones, where it was immobilized by sulfide precipitation.

The development of new techniques is an important part of these studies. Extensive work has been required to make ruthenium isotopic analyses routine for samples containing ~10 nanograms of ruhenium, but these efforts have been successful. The ruthenium isotopic analysis technique has been used to develop a uranium-ruthenium dating procedure, which has been validated by comparison with the results of uranium-lead dates from the same ore samples. This uranium-ruthenium dating procedure is expected to be used to obtain additional information about the migration of ruthenium in the vicinity of rich uranium ore bodies.

IV. PROGRESS DURING THE CURRENT QUARTER

A. Lead Isotope Analyses

1. Chemical Separation of Lead. The chemical procedure developed for the lead isotope analyses in this work, which was mentioned in the previous quarterly report, produced erratic yields. The problem was traced to

non-quantitative retention of lead during the anion exchange portion of the separation. The difficulty was surmounted this quarter by controlling the concentration of the dissolved rock in the 1 N HBr solution that is the influent to the anion exchange column. Satisfactory performance of the chemical procedure is obtained when the dissolved rock is no greater than 10 mg/mℓ in this HBr solution. After the lead is adsorbed onto the anion exchange resin, it is eluted with 10 N HCl, converted to the perchlorate salt, then electrodeposited before being transferred to the mass spectrometer filament. The overall chemical yields are routinely 80%, now that the dissolved rock concentration in the anion exchange column influent solution is carefully controlled.

2. Mass Spectrometric Measurements. Analyses of lead isotope standards supplied by the National Bureau of Standards (NBS) have been performed to determine the accuracy of our measurements. The results of 28 analyses are shown in Table I. Our analyses are performed with a minor modification of the NBS procedure for loading the lead samples onto the thermal ionization filament of the mass spectrometer, but the results in the table show that our procedure is both reproducible and accurate for the major lead isotopes. Our data are corrected for mass fractionation and normalized to the NBS certified values. The low abundance of ^{204}Pb, relative to the major lead isotopes, appears to have resulted in less accurate results for the ^{204}Pb/^{206}Pb ratio, in comparison to the NBS standard values, than for the ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios. We believe that difficulties in making appropriate mass 204 background corrections are the cause of the lower accuracy for the ^{204}Pb/^{206}Pb ratios. The significance of the mass 204 background correction is magnified for measurements of ^{204}Pb in NBS standard 983, where ^{204}Pb is two orders of magnitude smaller than in the other two NBS standards. Therefore, the NBS standard 983 values for the ^{204}Pb/^{206}Pb ratio are listed separately in Table I. We are examining methods to increase the accuracy of mass 204 background corrections.

B. Gadolinium Isotope Analyses

A procedure to measure gadolinium isotopic abundances is being developed to expand our capabilities for analyses of samples from the Oklo mine. The results of our current mass spectrometric analyses are given in Table II. Our results are compared to those measured at the California Institute of Technology over a period of several years. For this comparison, the data in Table II are

TABLE I

A COMPARISON OF LASL LEAD ISOTOPE RATIOS WITH NBS CERTIFIED STANDARDS

Measured Ratio	Number of Measurements	Mean Value, $\frac{\text{LASL}}{\text{NBS}}$	Standard Deviation of the Mean
$^{208}Pb/^{206}Pb$	28	1.0002	± 0.0003
$^{207}Pb/^{206}Pb$	28	0.99999	± 0.00025
$^{204}Pb/^{206}Pb$	24[a]	0.9992	± 0.0006
	4[b]	0.98	± 0.01

---

[a] Data from NBS-981 and NBS-982 standards.

[b] Data from NBS-983 standard.

normalized to $^{160}Gd/^{158}Gd = 0.88042$ to correct for bias from mass fractionation in the mass spectrometers.

The standard deviations shown in Table II indicate that the precision of our five analyses is reasonable. However, the variations of the three light isotopes relative to the "historic" ratios are outside the calculated standard deviations. It is likely that the bias shown in the $^{155}Gd/^{158}Gd$ ratio reflects an interference at mass 155. The apparent overabundance of masses 154 and 152 also may be attributable to interfering species of the same masses. Inaccurate subtraction of the background is another potential problem for the ^{154}Gd and ^{152}Gd measurements. Additional work will be done to solve these problems.

C. Element Migration at Oklo

The samples from the Oklo mine that were collected by Dr. A. J. Gancarz last September were catalogued, packaged, and stored this quarter. A natural fission reactor was exposed on the floor of the mine at the time these samples were being collected. Consequently, samples were collected that should provide an excellent opportunity to study the migration of fission-produced elements within and around a well-defined source. Rock samples are being selected and

TABLE II

A COMPARISON OF LASL GADOLINIUM ISOTOPE RATIOS WITH "HISTORIC" RATIOS

Ratio	LASL RESULT[a]	Δ[b]
$^{152}Gd/^{158}Gd$	0.00828± 0.00007	+ 1.4%
$^{154}Gd/^{158}Gd$	0.0880 ± 0.0001	+ 0.24%
$^{155}Gd/^{158}Gd$	0.5967 ± 0.0002	+ 0.13%
$^{156}Gd/^{158}Gd$	0.8243 ± 0.0002	+ 0.022%
$^{157}Gd/^{158}Gd$	0.6306 ± 0.0001	+ 0.044%
$^{160}Gd/^{158}Gd$	≡ 0.88042	

---

[a] Mean and standard deviation of 5 measurements.

[b] $\Delta = \left(\frac{\text{LASL Ratio}}{\text{"Historic" Ratio}} - 1\right) \times 100.$ "Historic" ratios are from G. P. Russ, III, "Neutron Stratigraphy in the Lunar Regolith," Ph.D. thesis, California Insititute of Technology, 1974.

prepared for this purpose. Analyses will be undertaken for uranium and for fissiogenic elements that appear to be fractionated from uranium, such as rubidium, strontium, molybdenum, and ruthenium.

Work is in progress to assess the quantities of fissiogenic rubidium and strontium observed in samples at the edges of reactor zones #2 and #3. Previous investigations[1] have shown that >99% of the rubidium and >90% of the strontium is missing from the cores of these reactor zones. Detailed work of Brookins, et al.,[2] on reactor zone #2 samples showed that a fraction of the reactor zone material could be leached for 20 minutes in 0.5 N HCl to yield a soluble component that contained natural isotopic abundances of rubidium and strontium. The insoluble residues, in contrast, contained a mixture of natural and fissiogenic rubidium and strontium. The amount of the fissiogenic strontium relative to the natural strontium in the residue generally increased with increasing depletion of ^{235}U relative to ^{238}U. Therefore, it seems reasonable that the rubidium and strontium in the insoluble residues represents a small fraction of the fissiogenic components not leached by natural processes from the reactor zones.

Analyses of samples measured to date from the edges of reactor zones #2 and #3 indicate that the leachants are all enriched in fissiogenic strontium and rubidium compared to the insoluble residues. The insoluble portions all contain either normal rubidium and strontium or else show a very slight enrichment in fissiogenic rubidium. These analyses indicate a reversal from the results of the reactor zone assays. In the material outside the reactor cores, the soluble fraction contains the fissiogenic material, while the residue appears to be comprised of rubidium and strontium generally unaffected by the nuclear reactions. Estimation of the amounts of fissiogenic rubidium and strontium observed in the leachates of these samples exterior to the reactor cores requires completion of concentration measurements.

D. Uranium, Thorium, and Lead Migration at Key Lake

Analyses have continued to measure the migration of lead, thorium, and uranium in the vicinity of Key Lake uranium deposits. An interim report on this work is being issued.

E. Conclusions

The samples that were collected at the Oklo mine last quarter and shipped to Los Alamos appear to provide excellent material for studying element migration in the vicinity of a natural fission reactor. A large portion of natural reactor #9 was exposed on the floor of the mine at the time the samples were collected. Consequently, many samples could be collected from locations precisely determined with respect to this natural fission reactor, stratigraphically as well as dimensionally. This fortuitous circumstance should aid the interpretation of the sample analyses, when the results become available.

Analyses of samples collected previously are underway to determine the quantities of fissiogenic rubidium and strontium located adjacent to natural fission reactor zones #2 and #3. A leachable component of these samples is observed to contain fissiogenic rubidium and strontium, while the insoluble residule contains these elements mainly in their natural isotopic abundances. This observation is a reversal of the results obtained previously with samples from the reactor zones.

The chemical procedure that is used to prepare samples for lead isotopic analyses was modified to reduce and control the quantities of dissolved rock in the influent to the anion exchange column. This modification has eliminated the previously erratic lead yields obtained with this procedure. The results of analyzing 28 samples of NBS lead isotope standards showed that our procedure is both reproducible and accurate for $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios. The $^{204}Pb/^{206}Pb$ results indicate that the mass 204 background may not be subtracted correctly in all cases. The first results from a new gadolinium isotopic analysis procedure give reasonable values for the $^{156}Gd/^{158}Gd$ and $^{157}Gd/^{158}Gd$ ratios, when compared to the "historic" California Institute of Technology values. However, additional work must be done to obtain comparable values for the lighter gadolinium isotopes.

F. Communications

Dissemination of the results of this work is an important part of our program. The following talks were given on the dates shown.

J. E. Delmore, "Mass Spectrometric Analysis of Nanogram Levels of Ruthenium," Conference on Analytical Chemistry in Energy Technology, October 9, 1979, Gatlinburg, Tennessee.

A. J. Gancarz, "Radionuclide Migration," American Chemical Society, Wichita Falls - Duncan Section meeting, January 14, 1980, Duncan, Oklahoma.

A. J. Gancarz, "Natural Fission Reactors," American Chemical Society, Tulsa Section meeting, January 15, 1980, Tulsa, Oklahoma.

A. J. Gancarz, "Natural Fission Reactors," American Chemical Society, Northeast Oklahoma Section meeting, January 16, 1980, Bartlesville, Oklahoma.

A. J. Gancarz, "Natural Fission Reactors," American Chemical Society, North Central Oklahoma Section meeting, January 17, 1980, Ponca City, Oklahoma.

V. PROBLEMS

Problems associated with the preparation and writing of the Key Lake lead migration topical report resulted in the delay of this report. Now that the topical report has been written, future quarterly reports should be completed approximately on schedule.

VI. ACTIVITIES PLANNED FOR NEXT QUARTER

Experimental analyses of samples on hand will continue to obtain information about technetium and ruthenium migration in the vicinity of the Oklo reactor zone #9 and to study the transport of lead at the Key Lake uranium ore body.

REFERENCES

1. See, for example, E. A. Bryant, G. A. Cowan, W. R. Daniels, and W. J. Maeck, "Oklo, an Experiment in Long-Term Geologic Storage," in Actinides in the Environment, A. M. Friedman, ed., American Chemical Society Sypmposium Series, No. 35, pp. 89-102 (1976).
2. D. G. Brookins, M. J. Lee, B. Mukhopadhyay, and S. L. Bolivar, "Search for Fission-Produced Rb, Sr, Cs, and Ba at Oklo," International Atomic Energy Agency proceedings IAEA-SM-204, pp. 401-413 (1975).