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Progress Report

C.3

Oklo-Natural Fission Reactor Program

October 1—December 31, 1979

University of California

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

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October 1—December 31, 1979

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OKLO-NATURAL FISSION REACTOR PROGRAM

October 1 - December 31, 1979

by

A. E. Norris

ABSTRACT

The study of lead, ruthenium, and technetium transport in nature requires the mass spectrometric analyses of large numbers of geologic samples. This quarter about 200 samples arrived from Gabon, which were collected at the Oklo mine in September. Work was performed to improve the lead and ruthenium chemical procedures and the mass spectrometric instrumentation in preparation for analyzing many of the Oklo samples and a large number of the 402 samples on hand from Key Lake, Canada. Data concerning ruthenium isotopic alterations from samples near an Oklo natural fission reactor zone indicated that ruthenium or technetium were not transported to distances greater than the 10 meters detected previously.

I. PERSONNEL

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

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E. A. Bryant
D. B. Curtis
A. J. Gancarz
A. E. Norris

Idaho National Engineering Laboratory

J. E. Delmore
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W. J. Maeck
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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 this program, which includes 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 this time, approximately 6 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. Principal objectives of our current studies of the Oklo phenomenon are identification of the migration paths of some of the mobile fission products and reconstruction of the paleohydrology and transport history of the Oklo site.

Lead was chosen as the first element to be investigated for tracing transport paths. Lead is not a fission product, but it is formed from the radioactive decay of uranium. Previous work has shown that ~70% of the radiogenic lead is missing from the Oklo reactor site. The Oklo setting appears to be favorable for tracing lead transport, because the common lead background is low and the quantity of radiogenic lead that was produced can be calculated. However, when this work was begun, we did not know whether we would be able to obtain requisite samples from the Oklo location. Therefore, we undertook the measurement of radiogenic lead transport in the vicinity of a rich uranium ore body in Canada. This undertaking is proving valuable, because the geologic setting differs from the Oklo provenance and should provide useful information concerning lead transport in a high grade metamorphic rock.

Analyses of the first set of Oklo samples shipped to us for lead transport studies indicated that a major transport path and repository involved the conglomerate material underlying the Oklo natural reactor zones. The data could not be used to infer the method of lead transport from the uraninite grains to the basal conglomerate, but diffusion appeared to be the mechanism by which lead was removed from the uraninite grains, where it was formed. Water flow, we presume, was the means of transport.

Ruthenium was chosen as the second element to be investigated for tracing transport paths. Measurements of ruthenium isotope abundances in conjunction with uranium analyses permit the determination of the gain or loss of fissiogenic ruthenium relative to uranium. Furthermore, because ^{99}Ru is formed by the decay of 2.13 x 10^5 year ^{99}Tc, it is possible to determine from ^{99}Ru measurements the gain or loss of ^{99}Tc relative to uranium and ruthenium during the time when the ^{99}Tc was decaying. Our spectrometric analyses have detected isotopic anomalies in samples as far as 10 meters from a natural fission reactor. These anomalies indicated the redistribution of fissiogenic ruthenium and technetium relative to each other and to uranium. This observation is a significant step toward determining element transport paths and migration rates in a natural environment. Additional work in these ruthenium migration studies has involved development of a uranium-ruthenium age dating technique and isotopic analyses of ruthenium in nanogram quantities.

IV. PROGRESS DURING THE CURRENT QUARTER

A. Mass Spectrometric Analyses of Lead

Work has concentrated on improving both the instrument capabilities and the chemical procedures for lead isotopic analyses that will be required by the many samples from the Oklo mine in Gabon and from Key Lake, Canada. A new, 12-inch radius of curvature mass spectrometer was placed in operation this quarter. This instrument provides better resolution of lead isotopes than the 6-inch mass spectrometer used previously. The better resolution results in more accurate lead analyses. In addition, a new mass spectrometer operator has been trained to measure lead isotope ratios.

The chemical procedure used to prepare lead samples for mass spectrometric analysis was improved to make it applicable to a wider variety of materials than could be analyzed by the previous procedure. The new method incorporates a step to separate lead from the bulk of a sample by anion exchange in a 1 N HBr solution. The final separation of lead from traces of elements that interfere in the mass spectrometric analysis is achieved by electrodeposition.

The new separation method and the new mass spectrometer are being used to continue the analyses of samples from the Key Lake uranium mineralization.

B. Mass Spectrometric Analyses of Ruthenium

The procedure developed to measure nanogram quantities of ruthenium in Oklo samples, which frequently contain organic material, has been tested and refined in three areas. First, the method described in the previous quarterly report to remove organic interferences by co-precipitating the distilled ruthenium with ferric hydroxide has been tested now with ore samples spiked with ^{96}Ru. Each sample was divided after the first distillation for comparison of interferences in the mass 100 peak from duplicate aliquots. The tests indicated that the ferric hydroxide precipitation generally resulted in samples free from interferences.

Second, an improvement was made in the ore dissolution procedure. Some ore samples contain cations that are insoluble in sulfuric acid. These insoluble sulfates cause excessive bumping and spattering during sulfuric acid fuming to remove reductants. We showed this quarter that these samples can be filtered after the addition of sulfuric acid without loss of ruthenium.

Third, analysis of the mass 100 peak has been corrected for molybdenum interferences. Natural molybdenum can be introduced into the ruthenium samples from the ion source filament, from the sample, or from both. Zirconium can be introduced in the hydrochloric acid that traps the distilled ruthenium. The presence of these two contaminants results in interferences with ruthenium at masses 96, 98, and 100. The calculation to separate fission product ruthenium from natural ruthenium requires accurate data from the mass 100 peak. The data in the peak now are corrected by using the measured ^{95}Mo or ^{97}Mo peaks. Without this correction, the natural ruthenium from samples containing 20 ng of ruthenium would be calculated to be as much as 30% high.

Ruthenium isotopic analyses are being used to determine the distances to which fissiogenic ruthenium has been transported from its origin in natural fission reactors at the Oklo mine. The data in Table II of report ONWI/Sub/79/E511-01100-7 (Los Alamos report LA-8054-PR) can be supplemented by the data shown in Table I below, which have just become available.

TABLE I

Ruthenium Data from Oklo Samples

Sample	Plan Distance From Reactor Zone	$\frac{\text{pg } ^{101}\text{Ru}}{\text{g rock}}$	$\frac{^{99}\text{Ru}}{^{101}\text{Ru}}$	$\frac{^{102}\text{Ru}}{^{101}\text{Ru}}$	$\frac{^{104}\text{Ru}}{^{101}\text{Ru}}$	Radiogenic Pb enrichment
KN 6	<5 m	<8	0.90	1.05	0.53	No
KN 230	<5 m	<8	1.46	0.96	0.56	Yes
SC 48b	<5 m	--	--	--	--	Yes
KN 56	30 m	<5	0.91	1.04	0.53	No
KN 5	40 m	<3	0.95	1.02	0.50	No
KN 76	40 m	<7	1.03	0.85	0.46	No
KN 187		38	1.00	0.98	0.48	No
^{235}U (thermal fission)†			1.20	0.83	0.36	
^{238}U (spontaneous fission)†			0.83	1.11	0.58	

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†W. J. Maeck, J. E. Delmore, R. L. Eggleston, and F. W. Spraktes in Natural Fission Reactors, I.A.E.A. TC-119, p. 521 (1977).

The absence of mass 100 data precluded correcting Table I data for natural ruthenium abundances in the same manner as the data reported previously. Even without this precise correction, it is possible to draw the following conclusions by comparing the data from the samples with the ratios from thermal-neutron-induced fission of ^{235}U and spontaneous fission of ^{238}U, which are shown at the bottom of Table I for reference.

1. The basal conglomerate sample KN 230, which is enriched in radiogenic lead, is enriched in ^{99}Ru.
2. Remaining samples show no large excesses or depletions of ^{99}Ru.

When the data from the samples that were listed in the earlier report are combined with these, two more conclusions can be stated.

3. The current samples contain significantly smaller amounts of fission products than those reported previously that showed isotopic alterations of ruthenium. The basis for this conclusion is the observation that all the samples in Table I except one contained <8 pg ^{101}Ru/g rock, compared to the average of ~100 pg ^{101}Ru/g rock in the samples with ruthenium isotopic alterations.
4. There is no evidence for ruthenium isotopic alterations, indicating possible ruthenium or technetium transport, at distances greater than 10 meters from the reactor zones.

C. Eh - pH Diagrams

The first draft of a report presenting the Eh - pH diagrams for most fission product elements, uranium decay products, and transuranic elements was completed this quarter. Thermodynamic data were used to construct Eh - pH diagrams at 25°C for all 28 elements considered. In addition, there were sufficient thermodynamic data to permit construction of Eh - pH diagrams at 200°C for 19 of the elements. We expect to use the relationships shown in these diagrams to enhance our understanding of the chemical forms and migration characteristics of the migrating elements of the Oklo site.

D. Conclusions

The efforts to improve the ruthenium isotopic analyses for very small samples appear to be fruitful. The correction for ^{100}Mo contamination in the ^{100}Ru peak is a significant advance. The work to improve both the lead chemical procedure and the mass spectrometric instrumentation should result in more accurate and more rapid analyses of the many samples on hand.

The most recent data concerning ruthenium and technetium require no change in our previous conclusion that the transport of these elements has not been observed at distances greater than 10 meters from a natural fission reactor zone.

E. Communications and Publications

Dissemination of the results of this work is an important part of our program. The following talks were presented this quarter:

A. J. Gancarz, "Nuclide Migration in Natural Systems," U. S.-Swedish Symposium on Radioactive Waste Disposal, October 11-13, 1979, Lawrence Berkeley Laboratory.

A. J. Gancarz, G. A. Cowan, and A. E. Norris, "Oklo - Natural Fission Reactor Program," O.N.W.I. Information Meeting, October 30 - November 1, 1979, Columbus, Ohio.

A. J. Gancarz, G. A. Cowan, D. B. Curtis, and W. J. Maeck, "^{99}Tc, Pb, and Ru Migration Around the Oklo Natural Fission Reactors," International Symposium on the Scientific Basis for Nuclear Waste Management, November 27-30, 1979, Boston, Massachusetts.

A. J. Gancarz, "A Potpourri of Uranium Deposits," Earth Sciences Colloquium, December 14, 1979, Los Alamos Scientific Laboratory.

V. PROBLEMS

No problems are hindering the progress of this work within its funding and manpower levels.

VI. ACTIVITIES PLANNED FOR NEXT QUARTER

The samples collected at Oklo in September for additional studies of ruthenium and lead transport arrived in Los Alamos from Gabon in December. They will be unpacked, catalogued, and sorted for mass spectrometric analyses. The mass spectrometric analyses of these samples will commence, and the analyses of samples from Key Lake, Canada, will continue.

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