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Progress Report

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Natural Repository Analogue Program

October 1—December 31, 1981

Compiled by
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ABSTRACT

The final draft of a paper entitled "The Oklo Reactors: Natural Analogs To Nuclear Waste Repositories" has been submitted for publication. This paper discusses the chemical stability of the fossil reactors with respect to uranium, neodymium, ruthenium, and technetium, the transport of elements in the geologic environment at Oklo; and the geochemical conditions that may have influenced these processes. Measurements of barium isotopic ratios limit the abundance of fissiogenic barium to $<10^{-7}$ g/g and $<2 \times 10^{-6}$ g/g in two samples peripheral of Oklo reactor zone 9. Samples from the Oklo mines have been sent to Australia for cooperative studies on the geochemistry of palladium, silver, cadmium, tin, and tellurium. Four samples representing a traverse to the east of reactor zone 9 are being analyzed to determine the isotopic composition of molybdenum and ruthenium.

I. PERSONNEL

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

Los Alamos National Laboratory

T. M. Benjamin

E. A. Bryant

J. H. Cappis

D. B. Curtis

D. J. Frank

A. J. Gancarz

A. E. Norris

D. J. Rokop

II. PROGRAM OBJECTIVE

The Natural Repository Analogue program is a research effort to study the chemical processes and conditions that affect the retention and transport of elements in the earth's crust.

Geologic burial is the favored method being considered for the disposal of commercially generated radioactive wastes. Appropriately chosen sites are thought to be relatively inert environments with respect to the stability of engineered waste containers. In addition, the geologic media itself will provide the ultimate containment, assuring that the wastes will remain isolated from the biosphere for adequate periods of time. However, efforts to evaluate the effectiveness of the geologic environment in this regard are limited by our understanding of the effects of natural, physical, and chemical processes acting over periods of time much longer than that recorded by human experiences. The work of this program examines the stability of elements in the geologic record and their response to natural conditions over appropriately long periods of time.

III. PROGRESS REPORTED PREVIOUSLY

Funding for the United States' participation in the international investigation of the Oklo natural fission reactor phenomenon began 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 is the occurrence of self-sustaining fission chain reactions in a series of very rich uranium ore pockets located in a Precambrian pitchblende deposit in Gabon, Africa. The uranium formed critical masses 2×10^9 years ago. During criticality $\sim 10^4$ kg of ^{235}U were fissioned.

Early work in the program determined the inventory of elements produced and destroyed by the nuclear reactions. Comparisons between the abundances of nuclear products produced in the natural reactors and those measured in them today provided a quantitative measure of the loss of elements from these rocks in the two-billion years since the reactors were critical. Uranium, the principal nuclear fuel, appears to have been extremely stable during this time. Individual grains of uraninite have been mechanically intact since the nuclear reactions, and uranium isotopic ratios seem to mimic the spatial distribution of reactor operating characteristics with extremely high resolution. Despite the apparent stability of the minerals that contained the nuclear fuel, many

of the nuclear products have been lost from these mineral grains and redistributed into the geologic surroundings. Of particular interest has been the loss of the long-lived radioactive species ^{99}Tc, its stable daughter ^{99}Ru, and the other fission-produced ruthenium isotopes. These two elements were chemically fractionated during or within one-million years after the few hundred-thousand-year period of sustained nuclear reactions.

Isotopes of cesium are also of prime concern to the management of high level radioactive wastes. One isotope, ^{137}Cs, has a 30-year half-life, while another, ^{135}Cs, has a 2×10^6 year half-life. Transport and retention of these isotopes at Oklo can be studied by measuring their stable daughter products ^{137}Ba and ^{135}Ba. Procedures to obtain high precision measurements of barium isotopic ratios have been developed. The results of such measurements on salts of isotopically normal barium were presented in the last quarterly report.

IV. ACTIVITIES DURING THE REPORTING PERIOD.

A final manuscript entitled "The Oklo Reactors: Natural Analogs To Nuclear Waste Repositories" has been submitted for publication in the first of a series of books entitled Advances in the Science and Technology of the Management of High Level Nuclear Waste. The paper examines possible geochemical conditions and processes that influenced the chemical stability of the reactors and the ability of the geologic environment to contain nuclear products that have been released from their host phase. This phase, crystalline uraninite, has been mechanically unaltered in the two-billion years since the period of sustained nuclear reactions. In spite of this mechanical stability, selected radio-nuclides have been released from the uraninite, probably by solid state diffusion. The quantities removed from the rocks were limited by the rate of diffusion from the host; a rate that appears to have been dramatically accelerated by high temperatures and/or large radiation doses associated with the nuclear reactions. These losses occurred on a time scale of less than 10^6 years.

After release from their host phase, ruthenium, ^{99}Tc, and neodymium were removed from the reactors and redistributed into the surroundings. Conditions in the host sedimentary rocks were extremely effective in containing these elements. Their apparent rate of movement was on the order of 10^{-5} m/year in the presence of fluids that may have been convecting as fast as 5 m/year.

Temperature-dependent reduction-oxidation reactions provide an excellent accounting of both the transport and redeposition of ruthenium and technetium at Oklo. At electrochemical potentials and pH conditions that must have prevailed there, equilibrium concentrations of ruthenate and pertechnetate in waters at elevated temperatures could have been sufficiently large to transport the missing quantities away from the reactor zones. As the temperature decreased, equilibrium concentrations of both anionic species decreased dramatically. The insoluble reduced form could have been deposited from cooling fluids in rocks adjacent to the hot regions of nuclear criticality. The equilibrium concentration of Nd^{+3} at elevated temperatures was too small for the same hot fluids to remove neodymium; therefore, the redistribution of neodymium may have occurred at later times, after the reactors had cooled.

Procedures to measure barium isotopic ratios were applied to samples peripheral to reactor zone 9 (ORZ-9). Two samples, one ~45 m away from ORZ-9 in the F_B strata and one from ~4 m stratigraphically beneath the reactor zone, contain barium that is isotopically indistinguishable from normal. The uncertainties in the analyses limit the concentration of fissiogenic barium to <100 ppb in the sample from F_B and <2 ppm in the underlying sample.

At the request of Dr. J. R. DeLaeter, 13 samples, duplicates of those included in our ORZ-9 experiment, have been sent to the Western Australia Institute of Technology. Arrangements are being made to ship another 10 samples. Dr. DeLaeter and his group have worked on Oklo samples in the past, measuring isotopic ratios of palladium, silver, cadmium, tin, and tellurium. Their efforts on the same elements will provide new information about the chemical stability of ORZ-9, the transport of fission products in crustal rocks, and the geochemical conditions that influence these processes.

In the first quarterly report for fiscal year 1981, we reported the results of analyses for fissiogenic elements in rocks peripheral to ORZ-9. A composite representing three samples from stratigraphically above the reactor zone contained large abundances of several fissiogenic elements. The individuals that make up this composite and an additional sample from another location in this same traverse have been sent to the Exxon Nuclear Idaho Company for isotopic analyses of molybdenum and ruthenium.

V. FUTURE ACTIVITIES

(A) Finish the analyses of barium isotopic abundances in ORZ-9 samples.

(B) Complete the analyses of molybdenum, ruthenium, and uranium abundances in four samples from the traverse east of ORZ-9.

(C) Begin a manuscript on the geochemistry of lead, uranium, plutonium, and thorium at the Oklo uranium deposit.