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**Investigations of the Natural Fission
Reactor Program**

October 1976—September 1977

Edited by
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INVESTIGATIONS OF THE NATURAL FISSION

REACTOR PROGRAM

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ABSTRACT

During Fiscal Year 1977, efforts of the Natural Fission Reactor Program have been directed toward (1) further measurements and predictions of reactor product migration at Oklo, (2) uraninite solubility studies, (3) radiogenic equilibria studies of natural Pu, Ra, and Th in U ores, (4) search for evidence of other natural fission reactors, and (5) supportive analytical measurements and procedures development. These investigations are conducted by personnel at the Los Alamos Scientific Laboratory, the Allied Chemical Idaho National Engineering Laboratory, and the Department of Geology of the University of New Mexico.

I. INTRODUCTION

The objectives of the Natural Fission Reactor Program (NFRP) are (1) continued isotopic, chemical, and petrographic investigation of the Oklo natural reactor system, (2) predictive and experimental studies of the geochemical behavior of reactor products and uraninite host matrix, (3) study of the geochemical behavior of the natural radiogenic species radium, thorium, and plutonium in uranium ores, and (4) search for other natural reactors where additional knowledge of the long-term behavior of radionuclides can be obtained. It is expected that this program will elucidate fundamental concepts that describe radionuclide fixation in natural geologic systems and that

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can be applied to geologic disposal of radioactive wastes. These studies are conducted by personnel at the Los Alamos Scientific Laboratory, the Allied Chemical Idaho National Engineering Laboratory, and the Department of Geology of the University of New Mexico.

II. ISOTOPIC DETERMINATIONS OF OKLO SAMPLES

A suite of approximately 47 Oklo samples has been received through the French Project Franceville. The samples represent seven different geologic categories of the Oklo system including reactor zones, traverses across reactor zone boundaries, and regions peripheral to the reactor zones. These samples are being studied by petrographic, chemical, and isotopic techniques in order to determine the extent of radionuclide redistribution. Particular attention is being given to peripheral samples where it is possible to find material that has migrated from reactor core regions. An isotopic Pb analysis is being devised and will be used on these samples to indicate the possible hydrologic gradient responsible for the dispersion of such species as ^{137}Cs , ^{99}Tc , and ^{90}Sr .

Ruthenium isotopic analyses conducted on an initial group of 10 peripheral samples are presented in Table I. The samples were from regions between 2 and 10 m from the known boundaries of the Oklo reactor zones. In all samples, the majority of the Ru was from the thermal-neutron induced fission of ^{235}U , with small fractions of natural Ru and Ru from the spontaneous fission of ^{238}U . Initial U isotopic measurements on these samples show normal $^{235}\text{U}/^{238}\text{U}$ ratios (within ± 0.002 rel wt%) indicating that the samples are not from reactor zones. Thus, the fission-product Ru in the samples must represent material that migrated from the reactor zones.

The $^{99}\text{Ru}/^{101}\text{Ru}$ ratio in these samples gives valuable information on the migration behavior of Tc relative to that of Ru. The progenitor of ^{99}Ru is ^{99}Tc , which has a half-life of 2.1×10^5 yr. As indicated in Table I, the ^{99}Ru content is highly variable in these samples; the ratio of the fission-product $^{99}\text{Ru}/^{101}\text{Ru}$ ranges from 0.74 to 3.8. In contrast, both the $^{101}\text{Ru}/^{102}\text{Ru}$ and $^{101}\text{Ru}/^{104}\text{Ru}$ ratios are constant to within about 5%. If Tc behaved similarly to Ru during the period of redistribution, then the $^{99}\text{Ru}/^{101}\text{Ru}$ ratio

TABLE I
RUTHENIUM MEASUREMENTS OF PERIPHERAL OKLO SAMPLES

Sample Number	U (wt%)	Total Ru (ng/g)	Relative ^{99}Ru Content ^a
KN224	3.1	665	high
KN236	1.5	0.6	~ normal
KN241	8.6	40	~ normal
KN244	3.0	n.d.	----
KN255	5.3	850	high
KN258	1.7	19	~ normal
KN266	8.3	35	depleted
KN268	1.0	1.7	~ normal
KN270	12.2	1500	depleted
SCO	3.0	7.5	high

^aOf the fission-product Ru, ^{99}Ru varies by factors of 2 to 3 from the expected amount (based on mass yields) because of precursor ^{99}Tc mobility.

would be approximately 1. Therefore, for samples KN270 and KN266, the reactor-product Ru was concentrated preferentially relative to Tc; for samples KN224, KN255, and SCO, Tc was concentrated relative to Ru. For the remaining samples, the fission-product ratio of $^{99}\text{Ru}/^{101}\text{Ru}$ is observed, and we can conclude that Tc and Ru migrated similarly or that Ru migration occurred more than about 10^6 yr after production, when ~ 95% of the ^{99}Tc had decayed to ^{99}Ru . There does not appear to be any spatial correlation of the migration/fixation behavior for either Tc or Ru, which suggests that mineralogical rather than hydrological factors are more important in the behavior of these species. Petrographic and U, Nd, and Gd isotopic analyses are

planned for these and other peripheral samples to further characterize the nature of radionuclide migration.

III. URANINITE SOLUBILITY STUDIES

The Oklo reactor zones are part of an ore body of generally much lower U content. For this reason, it was postulated that aqueous solutions entering the reactor zones would contain U with natural isotopic abundances. If, after reactor shutdown, such fluids were in contact with the reactor zones, then uraninite grains might have formed a "rim" where the ^{235}U depletion would not be so great as in the interior of the grains. This hypothesis was tested by conducting heavy-ion microprobe analyses on a petrographic thin section of Oklo ore from within a reactor zone of high burnup. The microprobe technique determined $^{235}\text{U}/^{238}\text{U}$ values for 10- μm -diam spots; the uraninite grains were irregularly shaped with dimensions of about 10^2 to 10^3 μm . The $^{235}\text{U}/^{238}\text{U}$ values obtained using microprobe analysis were in good agreement with the whole-rock U analysis obtained for the same sample. However, within the approximate 5% accuracy of the microprobe measurement, no isotopic alteration of grain surfaces was observed. The absence of detectable zonation at the surface of uraninite grains may be a result of such factors as homogenization of the grains by solid diffusion or extremely low solubility of uraninite.

In order to assess uraninite solubility in the Oklo system, concentrations of uranium oxide, hydroxide, and carbonate species in equilibrium with uraninite were calculated¹ for solutions with various values of pH and of O_2 and CO_2 fugacities. The total dissolved U was the sum of the equilibrium concentrations of U^{3+} , U^{4+} , UO_2^+ , UO_2^{2+} , $\text{UO}_2(\text{OH})^+$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $\text{U}(\text{OH})^{3+}$, UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{UO}_2(\text{CO}_3)_3^{2-}$, and $\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2^{2-}$ at 298 K and 1 bar. If these were the only important aqueous species and the concentrations of CO_2 and O_2 were fixed by the equilibrium among the graphite, magnetite, and hematite phases, then for pH $\sim$ 6 the equilibrium concentration of uranium would have been sufficiently low to preclude the formation of observable rims on the uraninite grains for any plausible fluid flow rates. In general, intermediate pH values (5 to 7) and low fugacities of CO_2 and O_2 favor low uranium solubility. The

assemblage of graphite, magnetite, and hematite provides sufficiently low CO_2 fugacities (~ 1 bar) and O_2 fugacities ($\sim 10^{-69}$ bar) to limit the total molality of uranium to less than 10^{-12} at pH of 5 and 10^{-8} at pH of 7. For higher O_2 fugacities or more acidic or basic conditions, however, other constraints would be necessary to explain the persistence of the Oklo uraninite. In these cases, low fluid flow rates or slow dissolution kinetics might be invoked. Nevertheless, suitable control of CO_2 and O_2 fugacities and pH is sufficient to explain the persistence of ^{235}U -depleted uraninite in the Oklo system for times $> 10^9$ yr.

IV. Eh-pH STABILITY FIELD STUDIES

The extreme insolubility of uraninite under the physiochemical conditions in the Oklo system appears to have limited reactor product migration from uraninite grains to processes of solid diffusion and, for fission products, atomic recoil. The behavior of these reactor products, once liberated from the uraninite lattice, is indicated by recent predictions,^{2,3,4} which show that the stabilities of hydrolysis products and other compounds may be in part responsible for the observed retention or migration of reactor products.

The French investigators have presented data suggesting restricted ranges in both Eh and pH at Oklo. Both primary hematite and pyrite are present and suggest a range of Eh from approximately -0.15 to -0.25 V in the pH range from 7.0 to 8.5. For elements with $Z = 40$ to 52, a clear distinction can be made between those elements with a strong affinity for sulfur relative to those with affinities for oxygen (including oxides, hydroxides, carbonates, and silicates) in the solid phases. The French investigators have shown that the chalcophile elements, fixed in sulfides, have been locally redistributed and occur in veins within or at the boundaries of uraninite grains. This probably results from the fact that slight Eh-pH fluctuations would allow migration of chalcophile elements and their incorporation into either sulfides (pyrite-stable field) or oxides/hydroxides (hematite-stable field). Thus, for elements with stable compounds in both the pyrite-stable and hematite-stable fields, retention is predicted. Eh-pH diagrams indicate that Tc, Ru, Pd, Ag,

Sb, In, and Te should have been retained at Oklo, whereas Mo and Cd may have migrated because of lack of a field for a stable oxide/hydroxide phase in the hematite field. These predictions are inconsistent with the Tc and Ru data, which indicate substantial redistribution. Measurements of Sb and In have not been attempted, but Pd, Ag, and Te were mostly retained. Loss of Mo and Cd has been confirmed. For siderophile and lithophile elements in the $Z = 40$ to 52 range, retention of Zr, Rh, Sn, Nb is predicted. Tin measurements have not been made, but Zr, Rh, and Nb were at least partly retained.

Yttrium and the rare earth elements (REE) have been retained within the reactor zones. This is in agreement with Eh-pH diagrams, which show that if these elements should escape from host uraninite, they would be incorporated into stable oxides-hydroxides or carbonates. Most of the REE are soluble as M^{3+} below $pH = 5$, but above this value a sequence of stable carbonate $M_2(CO_3)_3$ and oxide M_2O_3 species exists. For Eu and Pr, the hydroxides are stable with respect to the oxides, but this does not apparently affect their retention. The compound Bi_2S_3 or possibly Bi_2O_3 can account for the retention of Bi, but its crystal chemistry is also compatible with substitution of Bi^{3+} for U^{4+} in uraninite. Lead redistribution has been firmly established. The stability of galena (PbS) in the pyrite field and either anglesite ($PbSO_4$) or cerussite ($PbCO_3$) in the hematite field over wide ranges in Eh-pH suggests Pb should be retained.

Eh-pH diagrams, in conjunction with crystal chemical considerations, indicate retention of Th, U, Np, Pu, and Am. Of these, Th should be stable over a wide range of Eh and pH values, whereas U may be locally soluble due to oxidation of some U^{4+} to U^{6+} in the hematite field. The extent of U solubility must have been slight, however, as widespread destruction of uraninite would have allowed escape of many of the fissiogenic isotopes, which in fact were retained. NpO_2 and PuO_2 are predicted to be stable in the Oklo Eh-pH range; Am could have been retained as the oxide, hydroxide, or carbonate.

Eh-pH diagrams are not useful for the alkali or alkaline earth elements because these elements are insensitive to oxidation reduction.

V. EQUILIBRIUM OF NATURAL Pu IN U ORES

Plutonium-239 is formed naturally in U ores by neutron capture of ^{238}U followed by two beta decays. Hence, ^{239}Pu can be thought of as a naturally emplaced waste species, and comparison of measurements and calculations of ^{239}Pu concentration in U ores can provide information on the long-term geochemical behavior of Pu.

Plutonium analyses were run on a number of U ore samples. The ores were ground and dissolved, and Pu analyses were conducted soon after dissolution in order to prevent reprecipitation. The chemistry⁵ was performed in a clean air-down-flow area specially set aside for this work. Every effort was made to limit contact of the sample with any item that might contribute alpha activity.

The results of the Pu analyses are shown in Table II. An earlier analysis of a Cluff Lake sample is included for comparison. The data of Table II are plotted in Fig. 1, which also shows the calculated ^{239}Pu concentration resulting from neutron capture by ^{238}U . These calculations⁶ assume that the primary source of neutrons in the ore assemblage is from spontaneous fission of ^{238}U , and that a secondary source is from induced fission of ^{235}U and ^{238}U . The

TABLE II
NATURAL PLUTONIUM IN URANIUM ORES

Sample Number	Sample Weight (g)	^{239}Pu d/m/g of Ore	^{239}Pu Atoms/g ($\times 10^{10}$)	$\frac{\text{g U}}{\text{g Ore}}$	$\frac{\text{g UO}_2}{\text{g Ore}}$	$\frac{^{238}\text{U} \text{ Atoms}}{\text{g of Ore}} (\times 10^{20})$	$\frac{\text{Atoms } ^{239}\text{Pu}}{\text{Atoms } ^{238}\text{U}} (\times 10^{-12})$
9.16-22	9.7654	0.043 $\pm$ 0.004	0.085 $\pm$ 0.006	0.337	0.382	8.477	1.003 $\pm$ 0.07
9.16-34	5.8510	0.039 $\pm$ 0.006	0.071 $\pm$ 1.070	0.270	0.306	6.78	1.047 $\pm$ 0.16
9.71-22	9.7542	0.071 $\pm$ 0.004	0.129 $\pm$ 0.007	0.138	0.157	3.467	3.721 $\pm$ 0.02
9.77-34	9.7567	0.0507 $\pm$ 0.005	0.092 $\pm$ 0.009	0.404	0.458	10.15	0.906 $\pm$ 0.09
10.14-12	9.7509	0.0590 $\pm$ 0.019	0.107 $\pm$ 0.034	0.196	0.222	4.934	2.169 $\pm$ 0.69
10.31-12	9.7507	0.0297 $\pm$ 0.003	0.054 $\pm$ 0.005	0.274	0.311	6.883	0.785 $\pm$ 0.07
10.33-12	9.8652	0.391 $\pm$ 0.013	0.712 $\pm$ 0.023	0.619	0.702	15.56	4.576 $\pm$ 0.15
9.77-25 ^a	6.3387			0.381	0.432	9.565	
Cluff Lake	10.545	0.024 $\pm$ 0.003	0.043 $\pm$ 0.005	0.266	0.302	6.732	0.636 $\pm$ 0.07

^aThe yield on this sample was too low for an accurate determination.

Fig. 1.
Estimates of maximum ²³⁹Pu activity expected in uranium ore, for geometries that result in neutron leakage fractions, L , as a function of UO₂ concentration. Circles represent measured values.

neutron spectrum was calculated as a function of the U concentration and the composition of the gangue, which was assumed to be similar to that found in the Oklo system. Capture of thermal and epithermal neutrons by ²³⁸U was calculated for different U concentrations and the multiplication of secondary neutrons was considered.

Because the ores are of finite dimensions, the amount of neutron "leakage" L was a variable in the calculations.

The ^{239}Pu values observed in the nine samples are in qualitative agreement with the calculated values. The actual geometries of the ores from which the samples were collected are not known, but neutron leakage factors between about 10 and 50% are expected. Likewise, information on neutron poison content is not available. The ^{239}Pu content was clearly higher than expected for one ore sample, the most dilute of eight. And it was clearly lower than expected for five others, probably because of excess neutron poisons. These data demonstrate the capability of this Pu equilibrium measurement technique, and they show that for these samples no extreme geochemical loss or gain of Pu has occurred over the last $\sim 50\,000$ yr.

VI. RADIOGENIC EQUILIBRIA OF Th AND Ra IN U ORES

Uranium ores can be considered as long-term experiments in geologic isolation of certain radioactive waste species. The decay of U produces natural quantities of Th and Ra, and by determining the relative concentrations of U, Th, and Ra, the extent of redistribution of these species can be compared for different geochemical environments.

The ratios of the activities of ^{230}Th and ^{226}Ra in selected ore samples have been determined. The method was based on the determination of the activity ratios for $^{230}\text{Th}/^{227}\text{Th}$ and $^{226}\text{Ra}/^{223}\text{Ra}$ in the samples, and on the assumption that equilibrium had been established between $18.2\text{-d } ^{227}\text{Th}$ and $11.4\text{-d } ^{223}\text{Ra}$ in the ^{235}U natural decay chain.

The literature branching ratios for ^{226}Ra and ^{223}Ra are discrepant, and therefore, they were remeasured. The ^{226}Ra values were obtained by comparison of a calibrated standard obtained from the National Bureau of Standards. The ^{223}Ra values were obtained by preparing stippled sources of calibrated ^{227}Th and observing the growth of ^{223}Ra in the samples. The ^{227}Th was obtained from an aged ^{227}Ac solution. The stippled source was also gamma counted directly.

The results of these experiments are given in Table III. The estimated uncertainty in the final ratios is 5 to 7%, mostly from the uncertainties in the gamma-ray branching ratios.

Table III
Th-Ra ACTIVITY RATIOS IN ORE SAMPLES

Sample	Activity Ratios		
	$^{230}\text{Th}/^{227}\text{Th}$	$^{226}\text{Ra}/^{223}\text{Ra}$	$^{230}\text{Th}/^{226}\text{Ra}$
9.16-23A	21.69	21.73	0.998
9.71-23A	21.44	22.35	0.959
	20.90 ^a	21.62 ^a	0.967 ^a
9.77-33A	21.50	22.04	0.980
10.14-13A	21.56	22.23	0.970
	21.45 ^a	21.48 ^a	0.999 ^a
10.23-11A	20.84	20.59	1.012
10.27-11A	21.56	23.17	0.931
10.31-13A	21.58	21.12	1.022
10.33-13A	21.70	21.88	0.992

^aSamples dissolved in HNO₃. All other samples are from HCl solutions.

The absolute activity of ^{226}Ra in selected ore samples has been determined using Ge(Li) detection of the ^{226}Ra equilibrium gamma-ray intensities. Table IV summarizes the results for the $^{238}\text{U}/^{226}\text{Ra}$ disintegration rate ratios. The samples were aliquots of the same dissolved materials used in the earlier measurements of the $^{230}\text{Th}-^{226}\text{Ra}$ activity ratios. Known amounts of the dissolved samples were contained in sealed ampoules having a minimum gas volume, and these were then used for counting on a Ge(Li) detector system. The detector system, with this particular geometry, was calibrated

Table IV

U-Ra DISINTEGRATION RATE RATIOS FOR ORE SAMPLES

Sample	DPM (^{238}U)/DPM (^{226}Ra)
3.42	0.809 ^a
9.16-23A	1.090
9.71-23A	0.892
-22A ^b	0.866
9.77-33A	1.002
10.14-13A	0.895
10.31-13A	0.972
10.33-13A	0.971
1177 ^c	0.884 ^a
1183 ^c	0.913

^aThe errors associated with these samples may be somewhat larger since the concentration of ore in the dissolved samples was a factor of 10 lower than that currently in use.

^bSample dissolved in 1M HNO₃. All other samples were in 3M HCl solutions.

^cOklo sample.

by preparing a similar sample of standard ^{226}Ra solution obtained from the National Bureau of Standards. Because ^{238}U is not identified absolutely by this method, the ^{238}U disintegration rate was calculated using the concentration of ^{238}U in the samples determined by delayed-neutron counting. The ^{238}U half-life was taken to be 4.5×10^9 yr, and the U was assumed to have a natural isotopic abundance. The errors involved in the ^{226}Ra absolute disintegration rate are typically 2 to 4% for counting statistics and 3% for detection

efficiency. The principal error involved in the calculation of the ^{238}U disintegration rate is the 5% error of the total U analysis.

The data show that, within the 5 to 7% uncertainty, the ^{230}Th and ^{226}Ra are in equilibrium. Values of the $^{230}\text{Th}/^{226}\text{Ra}$ activity ratio range from 0.93 to 1.02. Therefore, these different ores have experienced geochemical conditions, which apparently retained Th and Ra quantitatively for the last 5 000 yr. Furthermore, the ratios of $^{230}\text{Th}/^{227}\text{Th}$ are nearly constant suggesting that U and Th also behaved similarly. Similar conclusions may be drawn for the equilibria between ^{238}U and ^{226}Ra , where the values of the $^{238}\text{U}/^{226}\text{Ra}$ activity ratio range from 0.87 to 1.09. Further U-Th-Ra radiogenic equilibrium studies are in progress for a suite of samples believed to have been subjected to the action of ground water.

VII. WORLDWIDE U ORE SURVEY FOR OTHER NATURAL REACTORS

Studies of the Oklo natural reactor system have provided valuable information on reactor waste-product geochemistry, U ore formation, isotope geology, and the geochemistry of the primordial earth. Study of other natural reactors, if they exist, would extend our knowledge of these important topics. It appears that another natural reactor system occurred in a deposit adjacent to Oklo,⁷ but evidence for other natural reactors has not yet been found. A systematic search⁸ is under way to find such systems. By studying the actual behavior of natural reactor products in other locations, the long-term, geologic behavior of high-level nuclear wastes can be predicted.

Precambrian U ores are being surveyed for evidence of natural fission reactors. The requirements^{9,10} for a natural reactor direct this investigation to U deposits with large, high-grade ore zones. Massive zones with volumes $\gtrsim 1 \text{ m}^3$ and concentrations $\gtrsim 20\%$ U are likely places for a fossil reactor if they are $\gtrsim 0.6$ Gyr old and if they contained sufficient water of saturation but lacked neutron-absorbing impurities.

Such zones meeting the first three requirements have been discovered in northern Saskatchewan and northern Australia. Data on water and impurity content of the Precambrian configurations,

however, are generally unavailable. Ore samples from these two locations were collected, and additional samples have been received through exploration and mining companies. Uranium ore samples have been obtained from the following worldwide locations: The Skinkolobwe and Katanga regions of Zaire; Southwest Africa; Rio Grande do Norte, Brazil; the Jabiluka, Nabarlek, Koongarra, Jabiru, and El Sharana ore bodies of the Northern Territory, Australia; the Beaverlodge, Maurice Bay, Key Lake, Cluff Lake, and Rabbit Lake ore bodies and the Great Bear Lake region, Canada.

The ore samples were tested for isotopic variations in U, Nd, Sm, and Ru, and selected samples received multielement analysis. If a natural reactor had existed, ^{235}U would show a relative depletion, whereas Nd, Sm, and Ru would have relative increases in their respective fission-product isotopes.

Results of the isotopic measurements are shown in Table V. The ^{235}U concentrations were measured by thermionic mass spectrometry, with a precision of about 0.2%. The relative ^{235}U content values for these ores are all normal to within the precision of the technique. But because of nuclear conversion of ^{238}U to ^{235}U , U from a natural reactor might give ^{235}U values that are indistinguishable from normal values. The $^{143}\text{Nd}/^{142}\text{Nd}$ ratio, however, would indicate an increment of fission produced ^{143}Nd compared to the non-fission product ^{142}Nd . The normalized values given in Table V suggest that there are systematic tendencies in the $^{143}\text{Nd}/^{142}\text{Nd}$ ratio for different ore bodies, but fission produced ^{143}Nd (in excess of $\sim 1\%$ of the natural ^{143}Nd) is not indicated. The $^{150}\text{Sm}/^{149}\text{Sm}$ ratio is also a sensitive indicator of a natural reactor, but an increment in this ratio would result from the high neutron fluence associated with a chain reaction. The measured Sm ratios likewise give no indication of a natural reactor.

There is a possibility that other natural fission reactors, if they existed, may have been redistributed or dispersed by geochemical or erosional processes. If this is so, there may be evidence for them in subtle ^{235}U isotopic depletions in present-day U ore bodies. Ore samples from around the world have been tested for variations in the $^{235}\text{U}/^{238}\text{U}$ ratio using precise gas (UF_6) mass

Table V

ANALYSIS OF SELECTED URANIUM ORES

Sample Number	Location	Isotopic Analysis			
		U (wt%)	²³⁵ U (rel wt%)	¹⁴³ Nd/ ¹⁴² Nd ^a	¹⁵⁰ Sm/ ¹⁴⁹ Sm ^b
8.01	Jabiluka, Australia	63	0.711	1.012	
8.02	Jabiluka, Australia	56	0.710	1.012	
8.03	Jabiluka, Australia	57	0.711	1.011	
8.04	Jabiluka, Australia		0.710	1.017	
8.10	Koongarra, Australia		0.710	1.017	
8.14	Nabarlek, Australia	59	0.712	1.020	
8.15	El Sherana, Australia		0.711		
9.05	Key Lake, Canada		0.713	1.001	
9.13	Key Lake, Canada			1.022	
9.16	Key Lake, Canada	29	0.711	1.014	
9.20	Key Lake, Canada			1.016	
9.23	Key Lake, Canada			1.014	
9.27	Key Lake, Canada			1.017	
9.68	Fay Mine, Canada		0.711	1.012	
9.71	Fay Mine, Canada	12		1.007	
9.77	Port Radium, Canada	40		1.010	
9.80	Port Radium, Canada			1.019	
10.08	Rabbit Lake, Canada			1.003	1.002
10.11	Rabbit Lake, Canada			1.002	1.000
10.13	Rabbit Lake, Canada			1.004	1.000
10.14	Rabbit Lake, Canada	19		1.003	1.000
10.29	Rabbit Lake, Canada			1.003	1.000
10.30	Rabbit Lake, Canada			1.005	1.001
10.31	Rabbit Lake, Canada	27	0.712	1.006	0.999
10.32	Rabbit Lake, Canada			1.003	1.001
10.33	Cluff Lake, Canada	57		1.013	1.001

^aThe ratio ¹⁴³Nd/¹⁴²Nd measured for a sample has been normalized by dividing by the ratio measured for NBS standard material.

^bThe ratio ¹⁵⁰Sm/¹⁴⁹Sm measured for a sample has been normalized by dividing by the ratio measured for NBS standard material.

spectrometry. These data are presented in Table VI. The relative precision of this technique is ~ 0.01%, which is lower than the natural variability in the ²³⁵U/²³⁸U ratio.¹¹ The analyses presented

here are an extension of a previous study,¹¹ which identified a bimodal distribution of ^{235}U concentrations in natural ores; magmatic and vein-type ores had values around 0.7108 rel wt%, whereas the values of sandstone-type ores of the Colorado Plateau clustered around 0.7106 rel wt%. It was speculated that the lowered ^{235}U content in Colorado Plateau U could have resulted from isotopic fractionation brought about by the repeated oxidation-reduction depositional process of sandstone-type ores, or from ^{235}U -depleted U that had been geochemically redistributed from a Precambrian natural reactor. The data of Table VI bear on this question. Some of the samples are from deposits that are much older than the earliest epoch when a natural reactor is likely to have formed, and others are from recent sandstone deposits that have evidence for possible isotopic differentiation.

Four samples (3.13, 3.44, 8.04, and 10.14) have anomalously high ^{235}U values, which lie well outside the accepted range of ^{235}U content. Duplicate analyses of samples 8.04 and 10.14 were conducted by thermionic mass spectrometry, and the anomalously high ^{235}U content was not confirmed. Because there was good correlation between the gas mass spectrometric values and the other thermionic values, it is believed that the four high values resulted from some systematic measurement error or sample contamination. Interpretation of these data is continuing.

VIII. NONDESTRUCTIVE FIELD MEASUREMENT SYSTEM FOR $^{235}\text{U}/^{238}\text{U}$

An instrument has been constructed that uses the relative fission rates of ^{235}U and ^{238}U in fast and moderated neutron spectra to measure the isotopic ratio. This device¹² can be placed in the field, which allows continuous monitoring of natural fission reactor ore and can be used for laboratory screening of samples from potential reactor sites.

Several criteria must be satisfied to make this device practical and usable in the field. The neutron source must be reliable and easy to use and maintain. The measurement system must be simple, easy to operate, and not require exotic supplies to keep it in operation at a remote location. The precision and accuracy of the instrument

Table VI
PRECISE URANIUM ANALYSIS OF WORLDWIDE ORES

<u>Sample Number</u>	<u>Location</u>	^{235}U (rel wt%) ^a	^{235}U (rel wt%) ^b
3.1	Alligator Gorge, Australia	0.7110	
3.13	Rio Grande do Norte, Brazil	0.7139	
3.42	S. Alligator Gorge, Australia	0.7110	
3.61	Wilberforce, Canada	0.7108	
3.14	Shinkolobwe, Zaire	0.7111	
3.44	Shinkolobwe, Zaire	0.7134	
3.46	Katanga, Zaire	0.7110	
3.55	Kasolo, Zaire	0.7107	
6.1	Weddington Pit, Texas	>0.711 ^c	
8.01	Jabiluka, Australia	0.7112	0.711
8.04	Jabiluka, Australia	0.7128	0.710
8.14	Nabarlek, Australia	0.7112	0.712
9.16	Key Lake, Canada	0.7115	0.711
10.14	Rabbit Lake, Canada	0.7144	
11.02	Witwatersrand, SA	^c	
12.01	Elliot Lake, Canada	0.7110	

^aGas mass spectrometric analysis, 2 σ precision $\sim$ 0.0001 rel wt%.

^bThermionic mass spectrometric analysis, 2 σ precision $\sim$ 0.002 rel wt%.

^cInsufficient uranium in sample for gas mass spectrometry analysis.

must be sufficient to give a meaningful result. The unit must be of such a size that transport to remote locations is not difficult. Measurement times should be short to make data useful on an acceptable time scale. These requirements have been met in the finished instrument.

A neutron source consisting of three small containers of ^{252}Cf (1 mg total) is the excitation device, and an ion chamber is used as a fission-fragment detector. Any "fast" gas can be used as the counting gas (e.g., welding argon, natural gas, propane, etc.). The associated solid state electronics are simple, stable, and reliable. The entire counter and source configuration is contained at the center of a cylinder 25 cm in diameter and 25 cm high (Fig. 2). The neutron sources are placed symmetrically around the ion chamber for a uniform neutron flux distribution.

Ore samples ($> 20\% \text{U}_3\text{O}_8$) are crushed to about 100- μm particles, and 0.5 g is uniformly distributed in a small planchet in the ion chamber. The neutron sources are remotely placed in reproducible locations around the sample, and a 30-min count is taken. The cylinder is then filled with water to moderate the neutrons, and a 10-min count is taken. The ratio of moderated to unmoderated count rates gives the isotopic composition directly.

A series of standards was prepared with National Bureau of Standards natural isotopic composition U_3O_8 and NBS depleted U_3O_8 ($^{238}\text{U}/^{235}\text{U} = 5700/1$). A calibration of the instrument with these standards is shown in Table VII.

A least squares fit to these data gives an equation for the line $y = 1.2911 + 608.4x$ where x is the ratio of moderated to fast count rates. Based on this calibration, samples from the Oklo reactor were isotopically analyzed, and the results compared with those from gas mass spectrometry. The results are shown in Table VIII. The relative error (1 σ) is 3%.

The instrument has been used to survey samples from the Australian Nabarlek deposit and more recently to survey samples obtained from the Key Lake and Maurice Bay deposits in Saskatchewan, Canada.

Fig. 2.
Schematic drawing of the nondestructive "Oklameter" used for field measurement of $^{235}U/^{238}U$ isotope ratios in ore samples.

Table VII
"OKLOMETER" CALIBRATION

Sample	$^{235}\text{U}/^{238}\text{U}$ ($\times 10^3$)	Fission Count Ratio
U-6	7.26	5.679
U-7		5.669
U-9	5.62	4.668
U-10	3.75	3.586
U-11	2.52	2.822
U-12	7.04	5.540
U-13	6.86	5.536

Table VIII
"OKLOMETER" SAMPLE ANALYSES

Oklo Sample	$^{235}\text{U}/^{238}\text{U}$ ($\times 10^3$)		Ratio A/B
	Fission Counter (A)	Mass Spectrometry (B)	
401/3	4.18	4.05	1.032
404/4	5.67	5.55	1.022
433/3	4.42	4.52	0.978

IX. U MILL MONITORING

Isotopically analyzing rich ore specimens from drill cores or from exposures in mines is an obvious way to search for other reactors. But such specimens represent only a small fraction of an ore body, and a natural reactor zone could easily be missed and subsequently exhumed. This sampling should be continued, but a more systematic and thorough search capability could be obtained by monitoring the output of mills servicing likely Precambrian deposits.

A plan has been proposed where "yellowcake" (U_3O_8) samples from operating mills would be routinely collected and analyzed for subtle decreases in the $^{235}U/^{238}U$ ratio. In this report,¹³ the effectiveness of mill monitoring is formulated in terms of the yellowcake sampling specifics and the sensitivity of the isotopic analysis. Both grab sampling and continuous sampling of the mill output are considered. For a given amount of reactor ore introduced into a mill, the requirements for detecting the isotopic anomaly are given in terms of the degree of ^{235}U depletion in the reactor ore, the grab or continuous sampling frequency, and the dilution half-time of the mill, i.e., the time required for the content of reactor U in the yellowcake output to be reduced by one-half. Situations are considered where reactor ore is introduced both episodically and continuously into the mill.

The results of this study suggest that for a natural reactor system the size of Oklo, many months would be required for processing of the affected ore. A rich zone such as this would be deliberately mined, stockpiled, and blended over a long time (compared to the mill half-time) in order to keep the average grade of the mill feed at an optimum concentration. Thus, reactor ore would eventually be introduced into the mill approximately continuously, but the isotopic anomaly in the yellowcake could fluctuate by an order of magnitude or more.

The objective of mill monitoring is early detection, so the sampling and analysis techniques should be capable of detecting the initial (probably erratic) amounts of reactor ore being processed. Mills with short half-times would therefore require continuous sampling, whereas those with longer half-times could safely use grab sampling without sacrificing sensitivity. The sampling frequency, though important to reactor ore detection, would probably be determined by convenience of collection and shipment and by sample analysis limitations.

The first throughput of reactor ore may not be easily detected, but as the anomalous U concentration in the mill increases as a result of continuous input, the anomaly would almost certainly be detected. For most mill monitoring scenarios, the detection limit

of the initial concentration of anomalous U introduced into the mill, C_0 , and its relative ^{235}U depletion, B , is $C_0 B \gtrsim 10$ to $100 (\%)^2$, where both C_0 and B are in per cent. For reactor ore similar to Oklo with $\sim 30\%$ depletion, an amount of reactor U between ~ 0.3 and $\sim 3\%$ of the total mill U would have to be introduced in order to insure early detection, i.e., between about ten and a few hundred kilograms of reactor U, depending on the mill capacity. Once anomalous ore was being continuously processed, however, the requirement for detection would be $BC_{ss} \gtrsim 8 (\%)^2$, where C_{ss} is the steady-state per cent of reactor U in the total mill-feed U. For reactor U with $\sim 30\%$ depletion and a typical mill operation, only ~ 10 kg/d of reactor U would have to be processed to insure detection.

X. Ru ISOTOPE GEOLOGY

Ruthenium is a sensitive indicator of natural fission because of its high yield in fission ($\sim 25\%$) and its low terrestrial abundance (~ 1 ppb). It is therefore a sensitive tool for tracing the migration of reactor-product Tc and Ru at Oklo and for searching for other possible natural reactors. These studies require a procedure for the chemical separation and mass spectrometric analysis of nanogram quantities of Ru from terrestrial samples; such a procedure¹⁴ was developed for this program at the Idaho National Engineering Laboratory. This Ru isotopic procedure is also being used to date Oklo and other Precambrian U ores by a U-Ru technique.¹⁵ According to this technique, if the amount of U in a sample is known and the amount of Ru that results from the spontaneous fission of ^{238}U (spontaneous fission $t_{1/2} = 8.2 \times 10^{15}$ yr) is known, then the duration, i.e., age, of Ru production can be inferred.

Recent measurements on more than 30 samples have demonstrated that the Ru in U ores is from three sources: (1) the natural abundance, (2) the spontaneous fission of ^{238}U , and (3) the neutron-induced fission of ^{235}U . The contribution of natural Ru is easily determined by noting the contribution of isotopes 96, 98, and 100, which are not produced in fission. Furthermore, the isotopic composition of Ru from ^{238}U spontaneous fission is significantly different from the composition of Ru from ^{235}U neutron-induced fission.¹⁶

Therefore, it is possible to determine the amount of Ru in an ore sample which results solely from ^{238}U spontaneous fission.

Approximately 20 Precambrian U ore samples have been dated using this technique. The component of Ru resulting from the neutron-induced fission of ^{235}U varied between about 5 and 50% of the amount resulting from ^{238}U spontaneous fission. The component from natural Ru was $\approx 25\%$ of the total Ru in the samples. These analyses indicate U-Ru ages for the deposits which are reasonable when compared to ages determined by standard U-Pb techniques. For instance, triplicate analyses on an ore from the Port Radium Eldorado Mine gave an age of 1.35 ± 0.07 Gyr, and the reported age of mineralization is 1.2 to 1.4 Gyr.

The U-Ru dating technique is advantageous because the product Ru isotopes (except for ^{99}Ru) are formed essentially instantaneously with no long-lived intermediate elements. This may be a distinct advantage over U-Pb dating where intermediates (e.g., Rn and Ra) and end-product Pb can be geochemically mobile. Hence, there may be less "discordia" resulting from loss of decay products with the U-Ru technique. This technique is limited, however, by the amount of ^{238}U fission-product Ru in the sample. Precambrian U mineral samples are particularly appropriate because the fission-product Ru content is at least equal to the natural Ru content. The U-Ru technique should compliment existing radiogenic age-dating techniques as it relies on a radiogenic product whose geochemistry is different from other such products. Further measurements are planned where the geochemical mobility of Ru in U ores will be determined relative to the U-Pb systematics.

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PUBLICATIONS AND COMMUNICATIONS

For the period of this report, the following publications have been made:

1. G. A. Cowan, "Nature's Nuclear Reactor," The 1978 Yearbook of Science and the Future (Encyclopaedia Britannica, 1977), 186.
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Presentations on the Oklo phenomenon and its relevance to radioactive waste disposal were made at the following meetings:

1. New Mexico Academy of Sciences, Socorro, NM, October 1976.
2. 10th Health Physics Society Topical Symposium, Saratoga Springs, New York, October 1976.
3. Symposium on Waste Management, Tucson, AZ, October 1976.
4. Sandia Laboratories Symposium, Albuquerque, NM, November 1976.
5. Joint Harvard-MIT Colloquium, Cambridge, MA, November 1976.
6. Iowa State University Seminar, Ames, IA, November 1976.
7. Symposium on Uranium in Saskatchewan, Regina, Sask., November 1976.

8. Annual Meeting of the Geological Society of America, Denver, CO, November 1976.
9. ERDA Workshop on Glass and Crystalline Ceramic Radioactive Waste Forms, Germantown, MD, January 1977.
10. University of British Columbia Physics Colloquium, Vancouver, BC, February 1977.
11. American Association for the Advancement of Science, Denver, CO, February 1977.
12. National Academy of Sciences Meeting, Washington, DC, February 1977.
13. Ohio State University Colloquium, Columbus, OH, March 1977.
14. Kansas State University Colloquium, Manhattan, KS, March 1977.
15. National Meeting of the American Chemical Society, New Orleans, LA, March 1977.
16. Brookhaven National Laboratory Seminar, Upton, NY, April 1977.
17. American Chemical Society Spring Lecture Tour, Bakersfield, China Lake, Fresno, CA, and Las Vegas, NV, May 1977.
18. University of California, Berkeley Seminar, Berkeley, CA, May 1977.
19. Oregon State University Physics-Chemistry Seminar, Corvallis, OR, May 1977.
20. Health Physics Society, Eastern Idaho Chapter, Idaho Falls, ID, May 1977.
21. 25th Annual Conference on Mass Spectrometry of the American Society for Mass Spectrometry, Washington, DC, June 1977.
22. Annual Meeting of the American Association of Petroleum Geologists, Washington, DC, June 1977.