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# Investigations of the Natural Fission Reactor Program

October 1977—September 1978

University of California

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Edited by

G. A. Cowan
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## ABSTRACT

The U.S. study of the Oklo natural reactor began in 1973 with the principal objectives of understanding the processes that produced the reactor and that led to the retention of many of its products. Major facets of the program have been the chemical separation and mass spectrometric analysis of the reactor components and products, the petrological and mineralogical examination of samples taken from the reactor zones, and an interdisciplinary modeling of possible processes consistent with reactor physics, geophysics, and geochemistry. Most of the past work has been on samples taken within the reactor zones. Presently, these studies give greater emphasis to the measurement of mobile products in additional suites of samples collected peripherally and "downstream" from the reactor zones.

This report summarizes the current status of research and the views of U.S. investigators, with particular reference to the extensive work of the French scientists, concerning the main features of the Oklo natural fission reactor. Also mentioned briefly is the U.S. search for natural fission reactors at other locations.

* * *

# I. OKLO STUDIES

## A. The Discovery of the First Natural Fission Reactor and Recent Additional Finds

The discovery of the "fossil" remains of a natural fission reactor was made by scientists of the French Commissariat à l'Energie Atomique in mid-1972. The history of the discovery and the technical background of the Oklo Phenomenon, as it is commonly called, have been described at length in a number of review articles.[1-3]

Briefly, the Oklo Phenomenon refers to the occurrence of self-sustaining fission chain reactions in a closely neighboring series of very rich uranium ore pockets located in an extensive Precambrian pitchblende deposit in Gabon, West Africa. Four neighboring zones, 20 to 30 m on a side, ∿ 1 m thick, and spread along a line ∿ 150 m long, were found in the initial investigations. The mining operation is in an open pit which, at the time of the initial discovery, was about 30 m deep (Fig. 1).

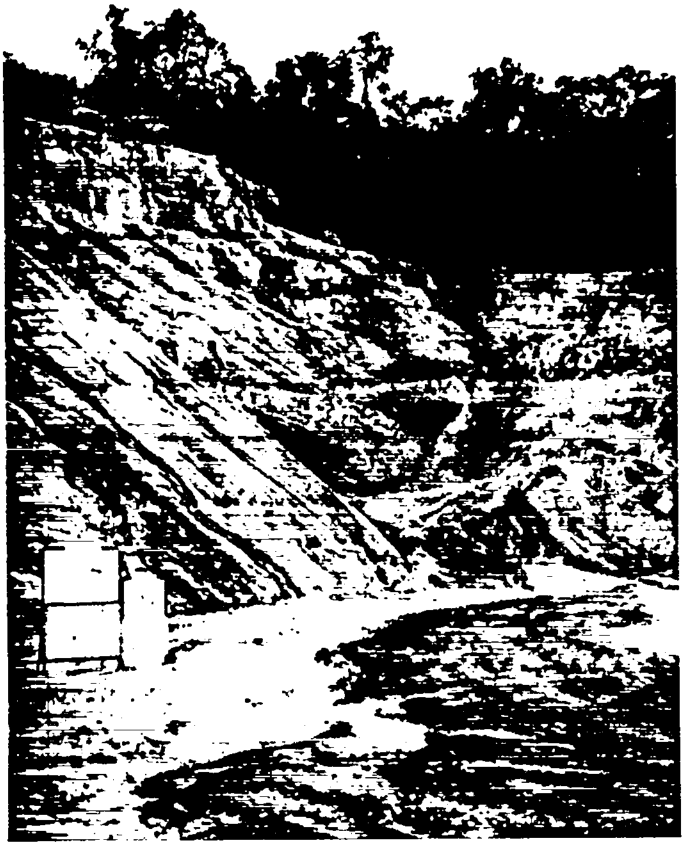


Fig. 1

Looking north in the Oklo mine toward reactor zone 2 at the base of an inclined sandstone wall on the left and immediately below some exposed uranium ore which is visible as an oxidized yellow uranate on the first vertical face.

In August 1977, evidence of another reactor zone was found ∿ 1000 m from the first group in an extension called Okelobondo.[4] In the spring of 1978 some new reactor zones were uncovered between these two groups, about 200 m from the first group, and are presently being extensively sampled.[5] It seems reasonable to assume that, in this environment, reactors were initiated in a predictable way whenever the uranium concentration reached a critical concentration and thickness.

## B. U.S. Participation in the Oklo Investigation

In May 1973, Ray Walton, a member of the Atomic Energy Commission's Waste Management staff in Washington, and George A. Cowan of Los Alamos visited with Roger Naudet, French manager of the Oklo investigation, to discuss a proposed U.S. program that would emphasize Oklo studies relevant to waste management technology. Naudet agreed to a French-U.S. collaboration on this problem and arranged to make samples available. The A.E.C. Waste Management Office provided support for the U.S. program, which was technically managed at Los Alamos and included investigators at LASL, the University of New Mexico, and the Idaho National Engineering Laboratory.

## C. Summaries of the Oklo Studies

Detailed summaries of work carried out in France, the U.S., and elsewhere through 1977 are contained in two I.A.E.A. publications of the proceedings of international meetings on Oklo held at Libreville, Gabon, in June 1975 and at Paris in December 1977.[6,7]

The Oklo program has also been the subject of review by members of an International Working Group on Natural Reactors, which was established by the I.A.E.A. at an organizing meeting in 1976 and subsequently met in Paris in December 1977. This group has focused on the importance of Oklo and, potentially, of other natural reactors to modern problems of nuclear technology and has contributed to initial planning for proposed collaborative studies of relative transport rates of reactor products away from the reactor sites.

## D. The Geological Setting of Oklo

The Oklo reactors occur within the uraniferous deposits of the Franceville sedimentary basin in Gabon. The geological environment has been described in detail at the 1977 Paris meeting. Rich uranium deposits within this basin have been found in the Francevillian series, an unmetamorphosed sequence of sedimentary and detrital volcanic rocks of middle Precambrian age. The uraniferous mineralization is always located at the top of the oldest formation of this series, which is essentially a sandstone conglomerate.[8] The argillaceous fraction of the Francevillian sediment has been dated by K-Ar and Rb-Sr methods with results that center on an age of 1.8 x $10^9$ years.[9] A somewhat greater age, ∿ 2 x $10^9$ years, is derived from U-Pb analyses and from mass balance calculations that take into account the total fission products, the observed neutron fluences, and the $^{235}$U depletion.[10,11]

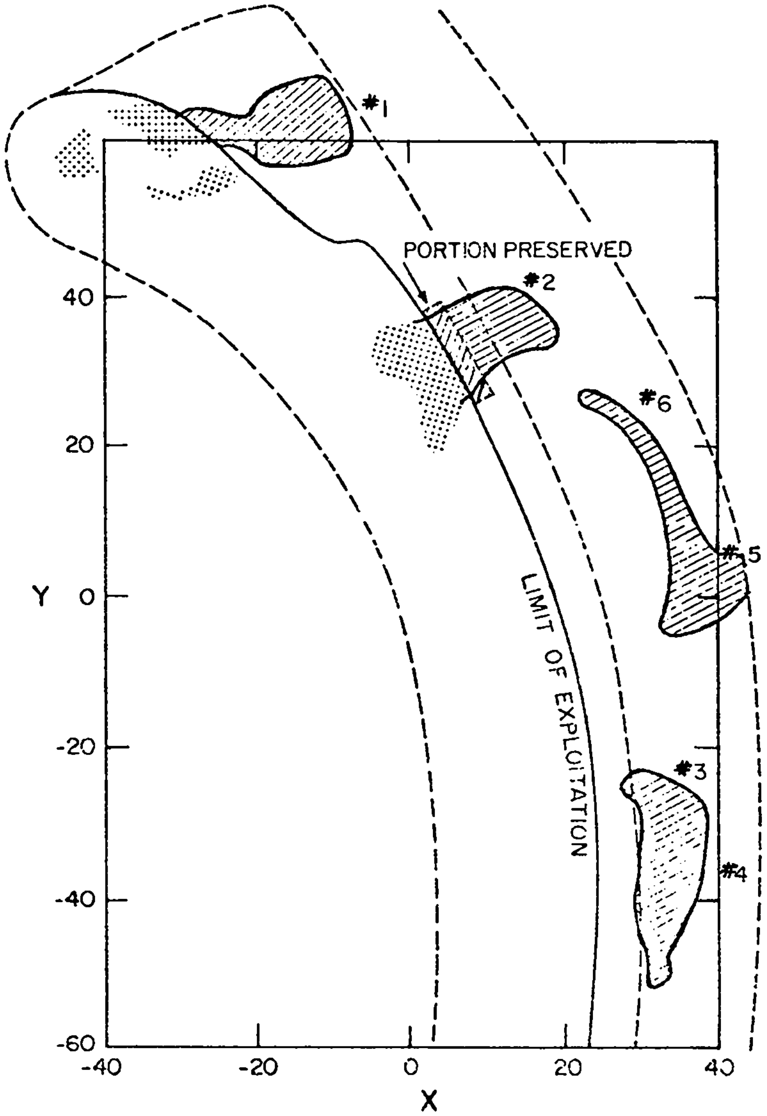
Within the Oklo deposit, the commonest Oklo ore is a black, highly silicified sandstone with $UO_2$ content in the range 0.4-0.6%, rarely exceeding 1%. The uranium generally occurs in a reduced form as pitchblende, where it is associated with organic materials and abundant sulfides (pyrite and galena). The second type of ore is a black unsilicified sandstone with little or no organic material. The uranium content is in the range 5-25%. It is in this rich ore that the reactor zones formed. Within these zones the uranium occurs as crystalline uraninite, and the surrounding matrix has been almost completely desilicified. Usually these pockets of rich ore occur in strongly tectonized zones in regions of microfractures that appear to correspond to major planes of shear.[8]

## E. Some Major Features of the Reactors

The reactor zones occur within irregular lenticular ore pockets with major dimensions of 20-30 m on a side and thicknesses of 0.5-1 m (Fig. 2). The reactor began to operate 2 x $10^9$ years ago when the $^{235}$U/$^{238}$U ratio was 0.037, more than five times the present value (0.0072). The duration of the period of criticality was several hundred thousand years, possibly as long as 8 x $10^5$ years.[12] During this period, approximately 6 tonnes of uranium were fissioned, out

Fig. 2

Reactor zones in the northern extremity of the Oklo quarry. The grid is in meters.



of the $\sim$ 800 tonnes of uranium involved in the reactor zones, and nearly 3 tonnes of $^{239}$Pu were made by neutron capture in $^{238}$U.[4]

The amount of energy produced was 5 x $10^{11}$ megajoules (1.65 x $10^4$ MWy). The power density was only of the order of $10^{-4}$ W/cm$^3$ but, due to the absence of strong, long-range convection and the low thermal conductivity of the surrounding rock, the operating temperature of the reactor zones increased to about 200°C above ambient. Weber[13] and Gauthier-Lafaye[8] have shown that the depth of the deposit during the period of operation was in the range 3000-5000 m. Naudet[12] calculated that the reactor reactivity would decrease at these depths when the reactor temperatures neared 350 to 400°C, because the density of water, a neutron moderator, changes dramatically near its critical temperature. Hot spots may have existed at a higher temperature. Vidale[14] found small regions that appeared to have reached temperatures on the order of 650°C. Openshaw[15] found, from a study of inclusions, apparent temperatures of 450-600°C and pressures of 1000 bars. At the 1977 meeting, Gauthier-Lafaye[8] stated that the diagenesis of uranium, which apparently involved an interaction with oxidizing fluids, implies the reactor zones may have formed after the time of maximum burial of the sediments, i.e., during an uplift episode of the basin. The reactors, then, may have operated at depths less than 3000 m.

## F. Retention of Reactor Products

Determination of the relative mobilities of the reactor products in the Oklo geochemical and geophysical environment has been a chief concern of this program. Until recently most of the Oklo samples which were made available to us for analysis had been collected from within the reactor zones rather than peripherally. When the fraction of an element retained in the reactor is high, it is difficult to determine the amount lost by difference. In such cases it is more appropriate to refer to measurements of product retention, rather than loss. Table I, taken from a paper presented at a 1976 American Chemical Society Symposium on Actinides in the Environment,[16] summarizes what was known concerning the relative retention of 24 elements in the reactor zones at that time.

Additional work on retention was described at the Paris meeting. More detailed analyses by Ruffenach[11] for Nd, Sm, Eu, and Gd show that the Nd remained immobile in the center of the reactor (> 95% retained). However ∿ 10% of the Gd appears to have been mobilized. Migration of the rare earths was limited to < 80 cm from the center of the reactor.

Cowan[17] reviewed the various steps involved in the migration of reactor products at Oklo and concluded that, for most of the product elements, volume diffusion from extremely insoluble crystalline grains of uraninite was the most probable rate-limiting step.

TABLE I

MIGRATION OF FISSION PRODUCTS AND ACTINIDES IN THE "ZONE 2" REACTOR AT THE OKLO MINE

| Element | Migration Behavior |
|---|---|
| Kr | Measurable traces, 0.01 to 1% remaining |
| Rb | Measurable traces, less than 1% remaining |
| Sr | Measurable traces, less than 10% remaining |
| $^{90}$Sr (Now $^{90}$Zr) | Small migration, most decayed in place |
| Zr | Redistributed, mostly in place |
| Nb | Mostly retained |
| Mo | ∿ 90% missing |
| $^{99}$Tc (Now $^{99}$Ru) | Redistributed, migrated as Tc |
| Ru | Large fraction retained, redistributed |
| Pd, Ag | Mostly retained |
| Cd | ∿ 90% missing |
| Te | Mostly retained |
| I | Mostly gone |
| Xe | Measurable traces, 0.01 to 1% remaining |
| Cs | Measurable traces (as Ba), mostly missing |
| Ba | Obscured by natural but mostly gone |
| Ce, Nd, Sm, Gd | Very little migration |
| Pb | Redistributed, ∿ 2/3 missing from core |
| $^{232}$Th($^{236}$U,$^{240}$Pu) | Mostly retained |
| $^{209}$Bi($^{237}$Np,$^{241}$Pu) | Mostly retained |
| $^{235}$U($^{239}$Pu) | No $^{239}$Pu separation from $^{238}$U |
| U | Probably no major migration, some redistribution |

Diffusion losses of the least mobile elements from uraninite were less than $5 \times 10^{-10}$ (fraction of the element) per year and, for the most mobile elements, on the order of $10^{-6}$ per year.

The hypothesis that losses from the uraninite grains are limited by volume diffusion is based on the following observations.

1. Losses of uranium from the rich ore zones now appear to total less than 10% of the uranium, based on the acceptance of a

reactor age of 2 x $10^9$ years. This implies an average rate of loss of < 5 x $10^{-11}$ per year.

2. Sharp differences in the $^{235}U/^{238}U$ ratios in the depleted zones have been preserved within adjacent samples. For example, factors of two in depletion of mass 235 are observed over a distance of 5 cm.

3. The $^{235}U/^{238}U$ ratio in large single grains is a constant across the grain, with no measurable skin effects. Had the grains been in contact with a liquid phase including dissolved uranium, isotopic exchange could have resulted in observable skin effects. The observation of such effects would have tended to negate the hypothesis.

These observations suggest that the uraninite grains have retained their original structures and uranium composition. In such a case the reactor products, to the extent that they are initially deposited in the grains, can be dissolved away only after diffusion to the surface of the grain. There is a further body of evidence with respect to the loss of radiogenic lead from uranium ores that suggests the operation of a similar diffusion mechanism.

## G. Geochemistry of Element Migration at Oklo

A number of studies in the U.S. effort have helped to characterize the geochemical processes that influence reactor product migration or retention at the Oklo site. These include studies to ascertain the temperature of the rocks at the site of the operating reactor and in its immediate vicinity, consideration of the oxidation-reduction conditions at the reactor site, and investigations of the times after their formation when elements began to disperse.

Temperature is one of the important parameters affecting overall element migration. Both the magnitude of the operating reactor's temperature and the thermal gradient to the surrounding rocks are important. A temperature of ∿ 650°C in restricted areas of an operating reactor was inferred by Vidale[14] from observations of mineral assemblages and textural relationships. This observation is consistent with reactor temperatures in excess of 400°C estimated by Holliger[18] from rare earth nucleonics and by Openshaw[15] from fluid inclusion studies. In the region up to 4 m beyond a reactor border, Vidale[14] found indications of temperatures at least as great as 400°C. Beyond this region, Brookins[19] concludes from the mineral association pitchblende + organic matter + quartz + Mg chlorite + 1Md illite that the ambient temperature must not have exceeded ∿ 150°C. A detailed delineation of the thermal halo around the reactors remains to be done.

To help understand element migration, Brookins[19] correlated information from Eh-pH diagrams with the empirical retention data reported by Bryant[16] (see Table I). The basis for the prediction of migration through the use of Eh-pH diagrams is the determination of the likelihood that an element will form either a stable solid phase or an aqueous species that might be easily transported. Brookins predicted the migration behavior of 20 elements under conditions where uraninite is stable. The predictions are in reasonable agreement with the empirical data for Y, Nb, Ru, Pd, Ag, Te, rare earth elements, Bi, Np, and Pu, which did not move significantly, and for Mo and Cd, which did migrate. Pb was predicted to be immobile, whereas significant migration was observed.

The mechanism by which reactor products become available for transport is another concern of this work. Cowan[17] concluded that 5 to 10% of the products formed in uraninite grains escape by fission recoil. Additional release occurs by volume diffusion, which is generally slow. Estimates of release can be made from the following considerations. The effective diffusion coefficient, $D/a^2$, may have been as high as $10^{-6}$ $y^{-1}$ for the most volatile elements, when the reactor was operating. In that case, most of the volatile fission products would have diffused out of the uraninite. For the lighter rare earth elements, Th, Pu, Am, and Cm, the values of $D/a^2$ are $\leq 5 \times 10^{-12}$ $y^{-1}$. Such small values imply that the overall transport rates of these elements are determined by diffusion from the initial matrix, rather than by subsequent geochemical transport mechanisms. Other elements, such as Sr, Mo, and Ba, are inferred to have values of $D/a^2$ of $\sim 10^{-10}$ $y^{-1}$, intermediate between the two cases just cited. Approximately 85% of the reactor products with these intermediate $D/a^2$ values could have diffused out of the uraninite during the

$\sim 2 \times 10^9$ years that have elapsed since the natural reactors operated. One should note, however, that the longest half-life for radiostrontium, for example, is 29 years for $^{90}$Sr. Therefore, the maximum time during which strontium could be considered a radiological hazard is $\sim$ 500 years. During the 500 years after formation of strontium in a reactor, one can calculate that 0.08% of the element could diffuse out of the grain, but inclusion of the radioactive decay of $^{90}$Sr to stable $^{90}$Zr decreases the fraction of $^{90}$Sr calculated to be found outside the grain to $\sim 5 \times 10^{-9}$ of the original $^{90}$Sr formed.

The times when reactor-produced elements have separated from one another in their geological environment are of interest in this program to help infer the conditions that result in such separations. Information about separation times can be obtained from measurements of certain isotopic abundances. For example, measurement of $^{99}$Ru together with an additional fissiogenic ruthenium isotope ($^{101}$Ru, $^{102}$Ru, or $^{104}$Ru) can indicate whether the long-lived $^{99}$Tc ($t_{\frac{1}{2}}$ = $2.13 \times 10^5$ y) migrated with respect to ruthenium before it decayed to $^{99}$Ru. The relative ruthenium abundances were measured in samples collected near the peripheries of the Oklo reactor zones. The $^{99}$Ru abundances show depletion relative to other fissiogenic ruthenium isotopes in some rock samples and enrichment in others. Thus, movement of Tc relative to Ru appears to have taken place during the operating periods of the natural fission reactors, or within $10^6$ years thereafter. Occasionally, fissiogenic ruthenium is observed to be enriched with respect to natural ruthenium. All of the ruthenium isotopic data, taken together, could indicate the direction along which products were transported from the reactor zones.

Information about element redistribution during the last 5000 years can be obtained from quantitative assays for $^{238}$U, $^{230}$Th, and $^{226}$Ra. The ratios of $^{238}$U/$^{226}$Ra in two Oklo samples show a 10% deficiency of uranium relative to radium, which suggests a possible recent relative redistribution. Measurements of $^{230}$Th on Oklo samples would help to decide which element is moving relative to the others. Finally, the U-Pb data summarized in detail in the following section suggest extensive loss of Pb relative to U. These data are insufficient to yield information about the time of the loss, but additional data, in principle, will elucidate the time of the U-Pb redistribution.

## H. Dating Techniques

Isotopic age determination techniques have been applied to Oklo samples in an attempt to delineate the chronology of this uranium ore deposit. These efforts, which include U-Nd and U-Pb techniques, have been directed principally toward determining both the primary age of the uranium ore deposit and the length of time during which portions of the ore body were natural fission reactors. The U-Pb data indicate a primary age of the ore deposit of $2.05 \times 10^9$ years, in contrast to an age of $\sim 1.8 \times 10^9$ years reported by other workers.[20] The younger age may be an artifact - a consequence of continuous diffusion of Pb from uraninite grains and subsequent removal from the ore deposit. For the length of time that the natural reactors operated, Hagemann[21] calculated a duration of $6 \times 10^5$ years, based on Ru, Pd, Nd, Sm, and Gd data. However, the measured data do not provide very sensitive indicators of this value.

Complete and critical discussions of the results just summarized are presented in papers by Cowan,[22] Bryant,[16] and Gancarz.[10]

Determining the precise times of mineralization of U ore deposits remains a difficult problem. In part, this is due to the fact that U ores typically are formed in multiple episodes, as indicated by petrographic data. The most common means of dating is with the U-Pb technique. In U ores, especially in young deposits, the intermediate U decay products are sufficiently mobile to have migrated with respect to one another. In addition, U ore bodies often contain clear evidence of the redistribution of Pb. These element redistribution processes can drastically alter U-Pb ages.

In the case of the Oklo U ore deposit, a precise age is especially important, because age is a critical parameter in modeling the nuclear processes that occurred while parts of the ore body functioned as fission reactors. Previously reported ages range from 1.75 to $2.05 \times 10^9$ years. In this time range the $^{235}$U abundance changes by 25%, and such a change has serious consequences for reactor models.

Ten samples of ore collected from the peripheries of the reactor zones were analyzed for U and Pb. The data are listed in Table II and plotted in Fig. 3. The concordia curve in Fig. 3 passes to the left of all the data. Thus, Pb has been lost relative to uranium. The average loss is 50%. The data shown in Fig. 3 can be used to define a straight line whose upper intersection with concordia is 2.05 x $10^9$ years and whose lower intersection is 0.375 x $10^9$ years. Such an analysis omits the effects of continuous volume diffusion, which appear to be significant (see Cowan[17]). When diffusion effects are included, following the conventions established by Tilton,[23] the result is the curve through the data shown in Fig. 3. The intersection of this curve with concordia indicates that the primary age for the formation of the ore deposit is 2.05 x $10^9$ years. This age

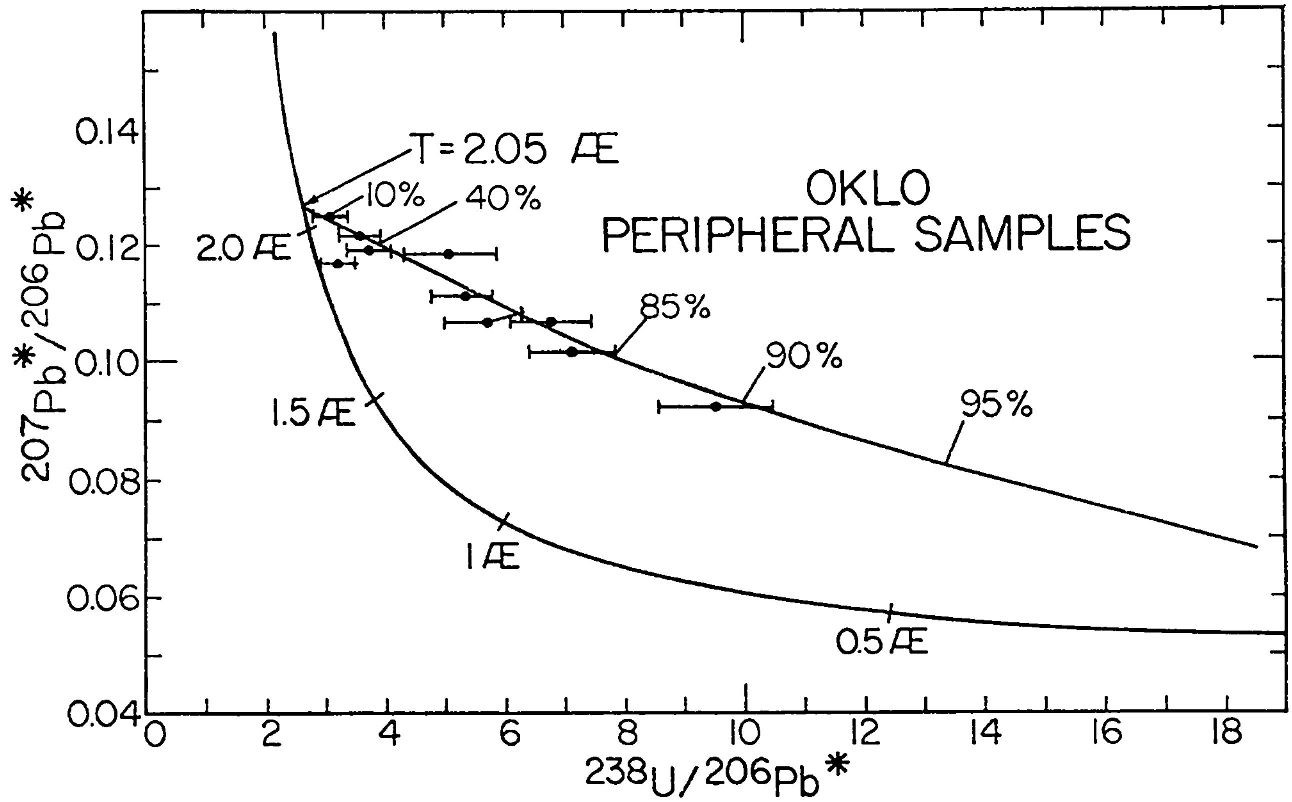


Fig. 3

Uranium and lead isotopic data for samples peripheral to the Oklo reactor zones. The curve through the data represents the continuous volume diffusion trajectory. The percentage figures indicate the $^{204}$Pb loss.

## TABLE II

## OKLO PERIPHERAL SAMPLES: U-Pb DATA

| Sample | | Wt% U | Wt% Pb | Pb/U | $^{238}U/^{235}U$ | $^{208}Pb/^{206}Pb$ | $^{207}Pb/^{206}Pb$ | $^{204}Pb/^{206}Pb$ |
|---|---|---|---|---|---|---|---|---|
| KN 270 | between zones 1 & 2 | 12.3 | 1.9 ± 0.2 | 0.14 | 138.1 | 0.00859 ± 1 | 0.10851 ± 4 | 0.000180 ± 1 |
| SCO 2252 | | ∿3.2 | 0.62 ± 0.06 | 0.19 | 137.9 | 0.01270 ± 1 | 0.12099 ± 2 | 0.000256 ± 1 |
| KN 258 | peripheral to zones 5 & 6 | ∿2.0 | 0.27 ± 0.03 | 0.14 | 128.0 | 0.00773 ± 12 | 0.10291 ± 5 | 0.000140 ± 3 |
| KN 266 | | 8.5 | 2.7 ± 0.3 | 0.32 | 137.8 | 0.00769 ± 2 | 0.12645 ± 3 | 0.000167 ± 3 |
| KN 244 | | 2.7 | 0.83 ± 0.08 | 0.31 | 137.8 | 0.00877 ± 1 | 0.1187 ± 2 | 0.000198 ± 1 |
| KN 255 | | 5.3 | 0.98 ± 0.10 | 0.18 | 137.9 | 0.01030 ± 1 | 0.11310 ± 6 | 0.000219 ± 2 |
| KN 268 | | ∿1.3 | 0.34 ± 0.03 | 0.26 | 138.0 | 0.01006 ± 1 | 0.12117 ± 3 | 0.000206 ± 1 |
| KN 224 | peripheral to zones 3 & 4 | 3.0 | 0.30 ± 0.03 | 0.10 | 138.1 | 0.00522 ± 1 | 0.09369 ± 2 | 0.000112 ± 1 |
| KN 236 | | 1.5 | 0.41 ± 0.04 | 0.27 | 138.9 | 0.01061 ± 1 | 0.12630 ± 2 | 0.000219 ± 1 |
| KN 241 | 15 m. so. zone 4 | 8.3 | 1.4 ± 0.2 | 0.19 | 137.9 | 0.00591 ± 3 | 0.10760 ± 3 | 0.000115 ± 1 |

is consistent with the age of 2 to 2.1 x $10^9$ years calculated for the reactor from the $^{143}$Nd-$^{144}$Nd abundances, the U abundances, and the recently remeasured value of 331 ± 8 barns[24] for the $^{143}$Nd thermal neutron capture cross section. An age of 1.8 x $10^9$ years was deduced by Lancelot[25] and by Devillers[20] from their U-Pb data. This younger age can be derived from the average $^{207}$Pb/$^{206}$Pb age, if one uses the value of 3.5 x $10^{-11}$ $y^{-1}$ for $D/a^2$ determined by Cowan[17] from his U-Pb mass balance calculations.

## II. OKLO-RELATED STUDIES

### A. Search for Other Reactors

The existence of the Oklo natural fission reactor gives reason to believe that a search for natural fission reactors elsewhere might yield positive results. Such a search was undertaken through examination of uranium ore samples from Africa, Australia, and North and South America. Methods were developed to monitor currently producing uranium mills for indications of fossil fission reactors. An instrument was designed and constructed to permit nondestructive measurements of the ratio of $^{235}$U/$^{238}$U under field conditions, to aid in the search. To date, however, no positive indications of another natural fission reactor have been found.

The uranium ore samples collected for this search on the whole were restricted to those deposits that satisfied the following criteria, which are considered necessary for the formation of a natural fission reactor:

1. An age greater than 0.6 x $10^9$ years. The terrestrial $^{235}$U isotopic abundance prior to that time was 1% or greater.
2. Rich ore, preferably greater than 20% uranium.
3. A volume of 1 $m^3$ or more with a thickness at least 200 mm.

The majority of samples for this search came from northern Canada and northern Australia. There the geological conditions adjacent to exposures of the Precambrian continental shields appear to have favored the formation of rich, thick uranium ore bodies. The particular locations from which samples were obtained include Cluff Lake, Fay Mine, Key Lake, Port Radium, Rabbit Lake, Theano Point, and Wilberforce, Canada, and Jabiluka and Nabarlek, Australia. Additional samples for this search were obtained from Shinkolobwe and Kasola, Zaire; Gordonia, Southwest Africa; and Rio Grande do Norte, Brazil.

Evidence for the existence of a natural fission reactor was sought by measuring deviations from the normal isotopic abundances in the ratios of $^{235}U/^{238}U$, $^{143}Nd/^{142}Nd$, or $^{150}Sm/^{149}Sm$. These measurements were made with thermionic mass spectrometry techniques. Selected uranium isotopic analyses were performed with high-precision gas mass spectrometry techniques. The results, given by K. E. Apt,[26] together with recent duplicate analyses of gas mass spectrometry analyses, indicate no evidence for a new natural fission reactor.

The localized nature of the natural fission reactors at the Oklo site indicate that analyses of uranium ore samples from drill cores may provide too coarse a sampling grid for detection of a natural fission reactor outside of Oklo, even if one were present. However, uranium depleted in $^{235}U$ may also be detected during the uranium milling process. The effectiveness of two such sampling schemes is presented in a report written by K. E. Apt.[27]

An apparatus has been designed and constructed to measure the $^{235}U/^{238}U$ isotopic ratio at the site of uranium mining operations. The principle of operation depends on the differing fission rates induced in samples containing both $^{235}U$ and $^{238}U$ by moderated and by unmoderated neutrons from a $^{252}Cf$ source. This apparatus permits the measurement of the $^{235}U/^{238}U$ ratio with a relative error of a few percent. The use of this device in the field where a rich uranium deposit is being mined might aid in the rapid confirmation of a suspected fossil fission reactor before its destruction during the mining operations. This field instrument is described in a paper by J. P. Balagna.[28]

## B. Development of a U-Ru Dating Technique

Initial studies[29,30] have indicated that the measurement of ruthenium produced by the spontaneous fission of $^{238}U$ shows promise as a means of dating rich uranium ore deposits. The development of this technique requires the quantitative assay of ruthenium and the measurement of ruthenium isotopic abundances, both at the nanogram level. Obtaining sufficient sensitivity for high-precision mass spectrometric measurements with small samples has proven to be difficult. When a satisfactory technique is developed, the U-Ru ages will be compared with U-Pb ages that have been measured in the same samples.

The uranium ore samples that are being used for this development work are ones kindly provided by Amok, Ltd., from their Cluff Lake, Saskatchewan, deposit. The U-Pb dating results indicate a major episode of uranium mineralization occurred $1.05 \times 10^9$ years ago. At this measured age, the probability of the occurrence of a natural fission reactor is low, even though the uranium deposit at Cluff Lake is rich enough to have supported such a phenomenon.

## C. Radiogenic Equilibria of Th and Ra in U Ores

The measurement of the relative concentrations of U, Th, and Ra in uranium ores can yield information about the redistribution of these elements in their geochemical environments during the past thousands to hundreds of thousands of years. Measurements of $^{223}$Ra, $^{226}$Ra, $^{227}$Th, and $^{230}$Th have been made on fifteen uranium ore samples from various parts of the world. The calculation of the $^{230}$Th/$^{226}$Ra ratio assumes that the 18.7-d $^{227}$Th and its daughter 11.4-d $^{223}$Ra in the $^{235}$U decay chain are in equilibrium at the time of the Th and Ra measurements. In addition, the $^{238}$U/$^{226}$Ra ratios were measured for eighteen samples, including two from the Oklo site (see Sec. I.G.). The data for the initial set of experiments, including a brief description of the techniques, are given in the previous annual progress report in this series.[31] The recent data are given in Table III.

For most of the samples, the measured ratios are close to those expected for radiogenic equilibrium. The inference then is that U, Th, and Ra have undergone little or no relative redistribution during the past thousands of years. However, some of the uranium ore samples were selected because they appeared to be more weathered than normal samples. The weathered samples were considered to be more likely to show U, Th, and Ra disequilibria than the normal samples. For the weathered samples, the measured $^{238}$U/$^{226}$Ra ratio averages 0.83 ($\sigma$ = 0.12). This result can be interpreted most easily as a loss of uranium relative to radium.

TABLE III

U-Th-Ra EQUILIBRIA MEASUREMENTS

| Sample | wt (U)/wt (ore), % | $^{238}$U dpm/$^{226}$Ra dpm | $^{230}$Th/$^{227}$Th | $^{226}$Ra/$^{223}$Ra | $^{230}$Th/$^{226}$Ra |
|---|---|---|---|---|---|
| 3.36-11 | 45.6 | 0.802 | 22.02 | 22.23 | 0.991 |
| 3.36-12 | 45.3 | 0.714 | 21.74 | 22.05 | 0.986 |
| 3.54-11 | 33.5 | 1.051 | 21.88 | 19.91 | 1.099 |
| 3.60-11* | 2.9 | 4.4 | 21.22 | 21.41 | 0.991 |
| 3.64-11* | 2.7 | 2.7 | 20.77 | 20.98 | 0.990 |
| 3.8 -11 | 62.1 | 0.726 | 21.72 | 20.54 | 1.057 |
| 3.8 -12 | 62.4 | 0.734 | 20.25<br>20.12 | 19.85<br>20.82 | 1.020<br>0.996 |
| 10.23-11 | 20.3 | 0.860 | 20.84 | 18.79 | 1.109 |
| 10.27-12 | 30.6 | 0.904 | 21.56 | 21.15 | 1.019 |

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*The uncertainties in these results are $\sim$ 30% or greater; the uncertainties for the remainder are 5 to 7%.

Two of the weathered samples, which were excluded from the averages given above, exhibit a $^{238}$U content that is 3 to 4 times greater than the equilibrium value with respect to the measured $^{230}$Th or $^{226}$Ra. These two samples apparently accreted large fractions of their present uranium recently without any accompanying decay-chain members. The two ores are from widely separated mines. One comes from La Sal Creek Canyon, Colorado; the other, from Johannes Schact, Wollendorf, Bavaria. The ores are carnotite and uraninite, respectively.

## III. RECOMMENDATIONS FOR FUTURE WORK

### A. Migration Measurements

The design of experiments that may lead to the reconstruction of the paleohydrology of the Oklo environment becomes possible with the availability of new samples from regions outside the fossil reactors. It will first be necessary to locate the early transport paths away from the reactor zones. These paths then will be examined to determine the relative transport distances of some of the reactor products. A relative scale of transport lengths for a number of reactor products will be very useful for calibration of laboratory transport measurements.

The most obvious tracer for the identification of transport paths is radiogenic lead. Although ∿ 70% of the radiogenic lead has been lost from the richest ore at Oklo, it is still not possible to say whether it left the lower grade ore deposit altogether or, if it did, in which directions it traveled. Naudet has suggested a set of measurements across an entire bed, which might provide an integral Pb/U ratio in the bed to help determine whether there has been a net loss of lead from the deposit. The results reported by Gauthier-Lafaye[8] for the Pb/U ratio in a number of samples with a uranium content < 3% indicates that at Oklo the very rich lenses of ore enriched the lower grade ore in lead, but the apparent migration distances have not been evaluated. Also, if lead has been retained in the ore deposit as a whole, the samples that are found to be enriched in radioactive lead should show abnormally high ratios of $^{207}Pb/^{206}Pb$ and yield apparent ages greater than two billion years. To date no such anomalies have been observed at any distance from the reactor zones.

It is desirable to examine all of the existing lead data, structural geology, and mineralogy to help identify transport paths. Additional lead analyses should be performed on samples that lie on probable transport paths and, wherever the lead content is significantly higher than the common lead background, isotope ratio analysis should be performed. The 207/206 ratio should indicate the period of time when the transport path was active and excess lead was deposited along the path.

Once early transport paths are identified, it may be possible to identify additional reactor products along these paths. The most mobile products are Kr, Rb, Mo, Tc, Cd, I, Xe, Cs, and Ba. On the basis of observed losses and low natural background of Ru in soil, it seems probable that $2.1 \times 10^5$ year $^{99}Tc$ would have produced a measurable enrichment in $^{99}Ru$ due to its mobility before it decayed to Ru. Anomalies in the $^{135}Ba/^{137}Ba$ ratio may have been produced due to the slow migration and decay of $2.3 \times 10^6$ year $^{135}Cs$. These elements should be examined in mineral fractions that could serve as collectors or remineralization loci.

Transport paths identified by radiogenic lead deposition can be examined for possible deposition of mobile products made by spontaneous fission. As mentioned above, $^{99}$Ru and $^{135}$Ba isotopic anomalies may be found along such paths. Other possibly mobile products that should be looked for are 1600 year $^{226}$Ra, radioactive $^{99}$Tc, and anomalies in $^{135}$Cs/$^{133}$Cs.

## B. Other Natural Reactors

Continuing discoveries of Precambrian uranium along the edge of the ancient shields in Canada and Australia suggest that, sooner or later, new natural reactor sites will be found. Identification of such sites may not occur early enough to prevent their destruction by mining operations before isotopic anomalies are found that suggest their existence. Accurate dating of these deposits and further discussions with mining company officials and field geologists should increase the likelihood of early identification of new reactors.

The discovery and extensive study of one or more additional natural reactors should permit generalizations to be drawn concerning the mobilities of reactor products based on their behavior in more than one geological environment. At a minimum, reliable dates should be determined for rich Precambrian deposits, and a surveillance program, enlisting the active cooperation of field geologists engaged in mining the most promising deposits, should be instituted.

## C. Development of Mass Spectrometric Procedures

The development of mass spectrometric procedures to measure ruthenium from small samples is in progress (see Sec. II.B.). Additional development work is desirable for the mass spectrometric measurement of cesium, technetium, and palladium. Both cesium and technetium have been suggested for possible use in tracing hydrological flow regimes. The $2.3 \times 10^6$ year $^{135}$Cs and $2.13 \times 10^5$ year $^{99}$Tc would be measured both in rich ore samples and in samples taken at various distances and directions from the primary ore body. Calculations indicate that picogram sensitivities are desirable for these two elements. The measurement of palladium is useful for calculating the amount of $^{239}$Pu fission that occurred in the natural fission reactors. The mass spectrometric analysis of palladium does not have adequate sensitivity. Therefore, further development work is necessary.

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Activities of this program were conducted at (1) the Los Alamos Scientific Laboratory, Chemistry and Nuclear Chemistry Division, (2) the Allied Chemical Idaho National Engineering Laboratory, and (3) the University of New Mexico, Department of Geology. The contributors to this report are as follows:

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## PUBLICATIONS AND COMMUNICATIONS

An important objective is the dissemination of the results of this work and its relevance to nuclear waste disposal. During the period of this report, 12 papers have been accepted for publication, the abstracts for presentations given at two meetings have been published, and an additional 11 talks were given to audiences at universities, scientific laboratories, and scientific meetings.

The following papers from this work have been published or accepted for publication during the period of this annual report:

1. D. G. Brookins, "Predictions of Radioactive Element Behavior in Aqueous Systems from Eh-pH Diagrams," Geol. Soc. Amer. meeting abstracts 9, no. 7, p. 911-912 (1977).
2. D. G. Brookins, "Oklo Reactor Reanalyzed," Geotimes 23, p. 26-28 (1978).
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5. D. G. Brookins, "Eh-pH Diagrams for Elements from Z=40 to Z=52: Application to the Oklo Natural Reactor," Chem. Geol. in press.

The following nine papers were presented at the International Atomic Energy Agency's Meeting of Technical Experts on Natural Fission Reactors, Paris, December 19-21, 1977. All of these papers will be published in the proceedings of the meeting.

6. G. A. Cowan, "Migration Paths for Oklo Reactor Products and Applications to the Problem of Geological Storage of Nuclear Wastes," IAEA/TC/119/26.
7. W. J. Maeck, K. E. Apt, and G. A. Cowan,"A Possible Uranium-Ruthenium Method for the Measurement of Ore Age," IAEA/TC/119/32.
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Presentations concerning natural fission reactors and their relevance to radioactive waste disposal were made at the following meetings:

1. EG&G seminar, Idaho Falls, Idaho, October 1977.
2. University of Arkansas seminar, Fayetteville, Arkansas, November 1977.
3. University of Missouri seminar, Columbia, Missouri, November 1977.
4. American Chemical Society, South Central Missouri Section meeting, Rolla, Missouri, November 1977.
5. American Chemical Society, Quincy-Keokuk Section meeting, Quincy, Illinois, November 1977.
6. Kansas State University seminar, Manhattan, Kansas, November 1977.
7. American Nuclear Society meeting, Santa Fe, New Mexico, January 1978.
8. University of New Mexico colloquium, Albuquerque, New Mexico, February 1978.
9. American Association for the Advancement of Science, South Western area meeting, Albuquerque, New Mexico, April 1978.
10. Florida International University colloquium, Miami, Florida, April 1978.
11. Lawrence Livermore Laboratory colloquium, Livermore, California, June 1978.

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