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The chemical coherence of natural spent fuel at the Oklo nuclear reactors

David B. Curtis

New Mexico, USA, March 1985

SVENSK KÄRNBRÄNSLEHANTERING AB
SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO

BOX 5864 S-102 48 STOCKHOLM
TEL 08-67 95 40 TELEX 13108-SKB

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THE CHEMICAL COHERENCE OF NATURAL SPENT FUEL AT THE OKLO NUCLEAR REACTORS

David B. Curtis

Santa Fe, New Mexico 87501

ABSTRACT

Uraniferous rocks in the Oklo mine contain the wastes of natural fission reactors, which were critical two billion years ago. Interment of these natural wastes is analogous to the storage of man-made spent reactor fuel for much longer times than are required for the radioactive elements to decay to innocuous levels. The natural nuclear products were formed <u>in-situ</u> within the grains of the mineral uraninite, the primary host for the natural wastes. Grains of uraninite are dispersed in a clay matrix and these phyllitic rocks are enclosed in sandstone. Uraninite has been remarkably stable during the extreme length of time that has passed since nuclear criticality. More than 90% of the fuel has remained in the spatial configuration that it had during criticality. Many nuclear products, including the actinides and the rare earth elements, have also largely remained in place. The stability of these elements can probably be attributed to their containment within in the stable uraninite host. Other nuclear products have not been effectively contained in the rocks of the reactors. These elements include technetium, the alkali and the alkaline earth elements. Their loss manifests their incompatibility within the uraninite host. They were probably excluded from this mineral in response to the extreme conditions produced during nuclear criticality. Many of the nuclear products removed from their site of production have been contained within the peripheral sandstone. This geologic environment provided effective containment of many of the reactor products. Massive deficiencies of lead represent a serious failure to contain a radioactive decay product within the geologic environment of the sandstones that comprise the Oklo ores.

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1 INTRODUCTION

Fossils of natural nuclear reactors exist as discrete lenses of highly uraniferous rock at the Oklo uranium mines in the Republic of Gabon in equatorial Africa. The reactors were critical, perhaps intermittently, for a few hundred thousand years about two billion years ago. In many respects these natural reactors resembled man-made nuclear power reactors. Uranium-235 fissioned producing residues that were similar to the highly radioactive wastes from modern reactors. The interment of these natural wastes is analogous to the storage of unprocessed spent reactor fuel in a geologic repository for a period of time that is extreme compared to that required for its safe containment.

Isotope analyses of samples from the natural reactors, combined with a knowledge of reactor physics, have been used to quantitatively inventory the elemental constituents of the reactor fossils. The extent of the chemical coherence of the reactor products reflects complex relationships between natural materials and their hydrologic, thermal, mechanical and chemical environment over the last two billion years. An understanding of these relationships should provide relevant information for the design and evaluation of man-made repositories.

2 THE OKLO REACTOR FOSSILS AS A WASTE REPOSITORY ANALOGUE

2.1 WASTE FORM

Unprocessed spent fuel is the waste form most directly comparable to the natural reactor residues. Spent fuel from light water reactors is uranium dioxide, slightly enriched in ^{235}U. It contains less than 1 500 ppm of impurities. Uranium dioxide is in the form of cylindrical sintered pellets with dimensions of a few cm. Pellets are comprised of micron-sized grains which approach 95% of their theoretical density. These pellets are contained in a sealed zircaloy cladding to make the fuel rods. Thermal energy produced by fission, combined with the low thermal conductivity of UO_2, produces a steep temperature gradient from the center to the surface of the rods. Centerline temperatures are typically 1 200°C - 1 500°C, gradually decreasing to 600°C at the fuel surface and then sharply decreasing to 200°C at the inner surface of the cladding (1). Extreme temperatures and temperature gradients induce a variety of chemical, physical, and mechanical changes in the fuel. In response to tensile forces, the pellets develop cracks probably early in their operational lifetime. Individual UO_2 grains become more dense, achieving 96-97% of their theoretial density (~ 10.3 g/cm^3), and grow to sizes between 6 and 10 microns. The lattice structure of pellets subjected to typical operating temperatures above 500°C are remarkably stable; x-ray diffraction lines from the fuel are not broadened after such a thermal operating history. The absence of lattice defects is attributed to the increased mobility of incompatible fission products at high temperatures. Fuel rods exposed to extended operating temperatures below 400°C contain lattice defects, probably caused by the retention of incompatible fission products within the UO_2.

Gaseous fission products coalesce, forming bubbles that accumulate at grain boundaries, lattice defects, and cracks. Gases migrate through interconnected pores and accumulate in open spaces within the fuel can. Many gaseous fission products are produced in copious quantities because of their high yields. During a typical fuel rod lifetime the volume of gas will be roughly ten times the volume of UO_2. The large specific volume of these gaseous products can cause mechanical defects in spent fuel elements. If the cladding remains intact, typically 10% of the gas will be released from the fuel prior to the end of operational life. Less volatile, incompatible, fission products migrate to, and accumulate in, lattice defects, grain boundaries and cracks where they form distinct phases. Many well-characterized, crystalline phases have been documented (2); some are mixtures of fuel and fission products, others consist exclusively of fission products, and still others consist of mixtures of fission products and elements from the cladding materials. Molybdenum, palladium, tellurium, ruthenium, and barium are often the main constituents of these phases. Technetium, rhodium, tin, antimony, strontium, and cesium are found as minor components. The exact nature of such phases will vary with the operating history and physical-chemical character of the spent fuel.

The fuel of the Oklo reactors was uranium dioxide, UO_2, in the form of the cubic crystalline mineral uraninite. At the time of criticality the fuel was about 3% ^{235}U. The mineral is chemically identical to, but physically distinct from, pitchblende, the principal uranium-bearing mineral in Oklo ores. There is an exclusive relationship between uraninite and regions that sustained nuclear criticality. Pitchblende recrystallized to uraninite in response to the increased temperatures produced by the nuclear reactions (3). Uraninite occurs as well formed cubic crystals between 1 and 200 µm in size (4, 5), larger than the grains of UO_2 in spent fuel. There might be a small lattice contraction resulting from a slight oxidation of uranium (6). Uraninite contains a few percent radiogenic lead and thorium, titanium, vanadium, iron, manganese, calcium, silicon and selected rare earth elements at concentrations between 0.01% and 1% (7).

The total energy production at Oklo is estimated to have been 1.65×10^4 MW-years (8). Fission was sustained for 10^5 to 10^6 years at power levels less than a few hundred KW, two to three orders of magnitude less than those of commercial power reactors. Heat dissipation was less of a problem in the low power natural reactors than in the high power man-made reactors. Consequently, temperatures in the natural uraninite were probably lower than those in the UO_2 pellets. The thermal history of the materials has important consequences with respect to the physical, chemical and mechanical properties of spent fuel. It probably determines the degree of fission product retention within the uraninite grains, the nature of phases formed by fission products released from their host phase, and the extent of radiation induced damage sustained by the crystalline lattice. Temperatures within the reactor zone during criticality were estimated to have been between 400°C and 600°C (9, 10, 11). These were registered outside the uraninite grains and may not apply to the interior regions of the fuel bearing minerals during operation.

Uraninite grains from the Oklo reactor zones contain high densities of crystallites produced by radiation (12). The recrystallization from pitchblende to uraninite would have eradicated these features. Their existence indicates that the phase transformation occurred early in the operating history of the reactors. Temperatures were not high enough to anneal the crystallites from uraninite. Individual grains of UO_2 in the commercial spent fuel do not have comparable damage features, presumably because of grain growth and restructuring, at operating temperatures above 1 000°C.

The integrated fission density in the Oklo reactor fuel was comparable to that in modern fuels (about 10^{19} fissions/g). At the end of criticality the concentrations of conserved nuclear products were comparable in the fuel of two reactor types. Because of differences in the power levels, the <u>rate</u> of nuclide production was orders of magnitude less in the natural reactor. Consequently, for extended periods of time the concentrations of conserved products were significantly less in the natural materials than they are in the synthetic ones. Elements expelled from UO_2 hosts by temperature sensitive processes were presumably more effectively mobilized in the high temperature environment of man-made reactors than in the lower temperature natural ones. It is difficult to speculate whether the relative rates of production and loss in the fuel of the two systems were sufficiently comparable to have produced comparable concentrations of mobile nuclear products within the nuclear fuel. It is thus difficult to speculate whether transport processes driven by chemical gradients might have been comparable in the two systems.

Many nuclear products expelled from synthetic fuels form crystalline phases at the interstices and in the voids of spent fuels (2). Despite observations using a variety of microtechniques, there are no references to the existence of similar phases in the Oklo rocks. There is a micron-sized spatial correspondence between uranium, neodymium and palladium (5), suggesting that uraninite is the host phase for these elements. The fission products yttrium, zirconium and ruthenium are observed in fissures adjacent to uraninite and must have formed new mineralogical associations since the time of criticality.

2.2 THE WASTE PACAKGE

Isolation of radioactive wastes in geologic storage will rely on a conservative philosophy of containment commonly called the multiple barrier concept. Such an approach relies on a series of engineered and natural barriers, each selected to isolate the waste, or some component of the waste for a sufficient period of time to allow the radioactive nuclides to decay below some predetermined level. Engineered barriers will consist of the waste form itself, and various cannisters, overpack and backfill each included for a specific purpose. Except for the spent fuel waste form that was just discussed, the nuclear fuel residue at Oklo is not comparable to waste packages that are being considered for man-made repositories.

In the rocks at Oklo individual grains of uraninite are dispersed and intimately mixed with constituent minerals. Although uraninite comprises as much as 60% of the mass of the rocks, the high density mineral only makes up 10-20% of the volume (13). Uraninite crystals are dispersed in clay minerals or, in certain massive samples, clay minerals occur as islands within clusters of uraninite (4). The clay minerals are mainly chlorite and illite (13).

The natural reactor fossils might be viewed as an extreme example of a violated spent fuel repository. Finely divided uraninite is dispersed in the rocks, maximizing the exposure of waste containing materials to the natural environment.

2.3 THE NEAR FIELD ENVIRONMENT

Duguid (14) defines the near field as "that volume of host rock in which internal (waste and repository) driving forces are dominant over natural forces. The near field phenomena include chemical interactions of the waste, the components of the waste package, and the host rock; the response of the host rock and its fluid to the thermal loading supplied by the waste ... The chemical interactions among the waste, the components of the waste package, and the host rock, including the water it contains, are controlled to a large extent by the temperature of the near field environment." The Oklo reactors are an analogue of a highly stressed near field environment.

The site where the natural reactors were critical and the site where their wastes are contained are identical on a microscale. There is nothing comparable in the proposed disposition of commercial high level wastes. Conditions generated during the period of reactor operation at Oklo were extreme compared to any that are likely to result from the disposal of man-made wastes in a geologic environment. The thermal loading of the rocks that housed the reactors at Oklo is estimated to have been 50 W/m^2 (15), two to five times greater than that estimated for waste respositories (16). Within a few meters of the site of criticality temperatures were between 400°C and 600°C (9, 10, 11). The rocks sustained 10^{19} fissions/g and neutron fluences of 10^{20} - 10^{21} neutrons/cm^2. Decaying fission products produced about 10^{28} beta-gamma emitting disintegrations during the lifetime of the reactor. The decay of plutonium produced 10^7 alpha particles per gram of rock per minute during the peak of reactor criticality. At the time of criticality the uraniferous rocks were buried at depths between 3 and 5 km and sustained pressure around 1 kilobar (9).

To compound the effects of this period, aqueous fluids were convectively circulating through the rocks of the reactor. Water was required to sustain the fission reactors. These fluids remain as inclusions in the reactor zone rocks (9). This period of extreme radiation and hydrothermal convection lasted for 10^5 - 10^6 years. The extreme conditions produced lenses that are unique in their mineralogy and lithology: Compared to the surrounding sandstone, the gangue of the reactor zone is deficient in quartz. This deficiency is attributed to the mineral´s increased solubility in hot aqueous fluids (3). The phyllitic residue forms a series of aureoles in and around the reactor zones each defined by unique mineral assemblages consisting predominantly of chemical and physical variants of illite and chlorite (13). The mineralogy and lithology of the reactors and their aureoles are a direct result of elevated temperatures, intense radiation and circulating fluids produced by the nuclear reactions. The aueroles are thought to manifest a thermal gradient away from the zones of reaction.

Compared to any conditions foreseen for man-made repositories the chemical and physical environment of the natural reactors during criticality was extreme in its intensity and its duration.

3 METHODS OF EXAMINING THE COHERENCE OF NATURAL REACTOR PRODUCTS

3.1 INTRODUCTION

Isotopes of elements representing nearly a third of the periodic table were created and destroyed in-situ by the nuclear reactions at Oklo. Many elements were produced in quantities comparable to, or in excess of, their primordial ("natural") counterparts. Some of the nuclear products such as technetium and plutonium are virtually non-existent in the natural environment. Their concentrations in the rocks of the reactors were comparable to many common trace elements!

3.2 COMPOSITION OF THE REACTOR FOSSILS

Nuclear products now in the reactors are stable, or exceptionally long-lived, isotopes of naturally occurring elements. The problem is to distinguish reactor products from their natural chemical counterparts. Abundances of nuclear products are usually determined by isotope dilution mass spectrometry. Some elements contain isotopes that were unaffected by the nuclear processes. Since the relative abundance of isotopes in most natural elements is constant, a measure of the abundance of one of these shielded isotopes is effectively a measure of the abundance of all the natural isotopes of the element. Excesses of the unshielded isotopes are the nuclear components. The distinction between the two components is unambiguous in such cases.

The ability to discriminate between natural and fission components becomes more ambiguous when there are no shielded isotopes. If each component contains the same isotopes in different proportions, the distinction between the two may be made by assuming that the isotopic composition of each is known and calculating the proportions required to produce the observed isotopic abundance. The isotopic composition of the natural component is usually well defined; however that of the nuclear product is often dependent on a variety of reactor operating parameters and thus the result is often uncertain.

The worst situation is that in which the isotopic composition of the natural component and that of the nuclear one are identical. This is the case for elements with a single stable isotope such as thorium and cesium. The abundance of these nuclear products can only be estimated from enrichments relative to an assumed natural abundance. Estimates of natural abundances in the reactors are usually based upon the analysis of similar rocks that did not sustain criticality. These estimated abundances of the nuclear components are speculative.

Stable nuclear products are the end result of a series of processes involving the isotopes of a variety of chemical elements. In most cases the precursors of the stable end products are nuclides with short half-lives relative to the rate of any natural process that might change the composition of the rocks. However, a few of the interceding radioactive nuclides have sufficiently long half-lives that they existed as distinct chemical species long enough to have been significantly affected by the natural environment. In such cases the isotopic abundance of the stable end product is a manifestation of the effects of natural processes on the radioactive precursor. Inferences about the stability of radioactive ^{239}Pu and ^{99}Tc are drawn from measurements of the isotopic abundances of the daughters, ^{235}U and ^{99}Ru respectively.

3.3 CHEMICAL COHERENCE OF THE REACTOR PRODUCTS

Despite the extreme length of time that has passed and the fleeting nature of the event, the results of isotope analyses, interpreted within the framework of reactor physics, provide the means to reconstruct the operational history of the reactors. In so doing the absolute and relative abundances of nuclides produced and destroyed in the rocks can be evaluated, i.e. <u>Details of the composition of discrete volumes of rock can be reconstructed as they were two billion years ago</u>. Comparisons between the abundances of nuclear products at that time and those in the rocks today provide quantitative estimtes of the gains and losses of specific elements during a period of time representing nearly half the age of the earth. Such estimates are uncertain to the extent of the uncertainty of the assumptions used in the reactor operating models (for example see 15, 17).

Direct comparisons between the relative abundances of fission products and their relative fission yields often provide fairly accurate estimates of the extent of fractionation between elements. In many cases such estimates are independent of the details of reactor operation and thus independent of uncertainties in the models. This is particularly true for high yield fission products such as neodymium and ruthenium. The rate of production of fission products formed in small yields, such as cadmium, is dependent upon the proportion of fission sustained by each fissile nuclide. Thus knowledge of this aspect of reactor operation is required to evaluate the stability of these elements. Fission product neodymium is often assumed to be stable in the rocks and absolute gains or losses of other fission products are evaluated by comparison with this rare earth element (for example see 18).

Less rigorous methods had been used to evaluate the stability of certain elements within the natural reactors. These usually involve spatial distributions of reactor products. Spatial variations of the isotopic composition and abundance of uranium provide evidence of the remarkable stability of this element in the reactors. Nuclear reaction theory was used to show a functional relationship between the variations of these two properties (for example, 19). Redistribution of uranium on the scale of a few cm would have obliterated these relationships. Conversely, the presence of reactor products in rocks that did not sustain nuclear criticality is evidence for the movement of elements out of the zones of reaction (20). Spatial relationships of reactor products provide qualitative evidence of the stability or instability of specific elements. Quantitative estimates based upon such evidence are subject to considerable uncertainty.

4 A CHEMICAL INVENTORY OF THE OKLO REACTORS

4.1 DRILL CORE SC-36

Literally thousands of analyses have been done on samples from the reactor zones. One of the most extensive set of results is from drill core SC-36, a complete section through reactor zone 2. Because of the availability of these results and because the spatial relationship between samples is well characterized, the discussion will focus on the reactor products in this section of reactor zone 2.

The reactor zones lie in thin strata of sedimentary rock. In the Oklo mine these strata are dipping to the northeast at a 45° angle. Zones of reaction can generally be characterized as thin disks lying in the plane of the dipping strata. Coring SC-36 was taken perpendicular to a horizontal outcrop located roughly a meter above the dipping section of reactor zone 2. The core extracted approximately a meter of mineralized sandstone above the reactor zone, another meter of argillaceous uraninite representing a compact section of the reactor zone and about a meter of mineralized sandstone below the region of criticality. The center section of the core sustained extreme nuclear activity, rock immediately above and below sustained little or none. The spatial distribution of nuclear products within the reactor zone provides the means to assess the mobilization and redistribution of elements. Because of the sharply defined boundary at the zone of criticality, nuclear products mobilized out of the reactor and into the peripheral rocks should be very "visible".

4.2 URANIUM

The minor isotope ^{235}U was the principal nuclear fuel in the Oklo reactors (21). It is in the rocks as the mineral uraninite, the crystalline oxide of tetravalent uranium. There is abundant evidence that the mineral has not been significantly altered chemically or physically since a time soon after the reactors became critical. The uraninite grains, as they are found in the rocks today, were the original host phases for the nuclear products. Any redistribution of products must have been initiated by their release from this mineral. Its physio-chemical stability is of prime concern to an examination of the stability of reactor products.

Normal uranium, that which has sustained no nuclear reactions, contains 0.725% ^{235}U and 99.275% ^{238}U. Prior to the discovery of the Oklo reactors, no natural uranium was thought to have an isotopic composition that is measurably different from this value. The center of reactor zone 2 contains uranium that is 0.41% ^{235}U: nearly half of the isotope was consumed by nuclear reactions. The remarkable degree of preservation of the reactors is inferred from systematic variations of the uranium concentration with the isotopic abundance of ^{235}U. Such variations along the length of core SC-36 are shown in Figure 1. The heart of the reactor zone is 70 cm long extending from 1.5 m to 2.2 m from the top of the core. The remains of the critical section are characterized by extreme enrichments of uranium and extreme deficiencies of ^{235}U. From the upper border to the center, $^{235}U/^{238}U$ decreases regularly as the uranium content increases. In the center portion variations in the maximum abundance correlate with changes in $^{235}U/^{238}U$. For instance, the sample at 1.6 m contains 58% uranium and $^{235}U/^{238}U$ is 0.5241%. Only 15 cm away the rocks contain 37% uranium and $^{235}U/^{238}U$ is 0.4087%. A sample from 25 cm deeper in the core, contains 58% uranium and $^{235}U/^{238}U$ is 0.5705%. At the lower edge, at about 2.2 meters, $^{235}U/^{238}U$ decreases sharply in correlation with a precipitous decrease in the uranium abundance. At greater depths the ratio increases regularly as the abundance decreases.

Such variations and covariations between the abundance of the element and the isotopic abundance of ^{235}U are observed along many traverses of the reactor zones (19). They result from shifts in the relative rates of destruction and production of ^{235}U produced by changes in both the absolute abundance of uranium and the relative abundances of uranium and water, the principal neutron moderator. Uranium-235 is destroyed primarily by fission and produced indirectly through a series of shorter-lived nuclides by neutron capture of ^{238}U. Neutronic models reproduce variations such as those shown in Figure 1 in great detail. Both the isotope and element abundance of uranium have maintained a detailed record of the spatial distribution of the nuclear reactions for two billion years. Even the redistribution of relatively small quantities of uranium over distances of several cm would have eradicated such fine details.

The $^{235}U/^{238}U$ is invariant on a scale where the neutron flux should be homogeneous. The average $^{235}U/^{238}U$ in three separated samples of uraninite in a sample from the heart of reactor zone 2 is 0.4027% ± 0.013 (22). The average isotopic ratio in three

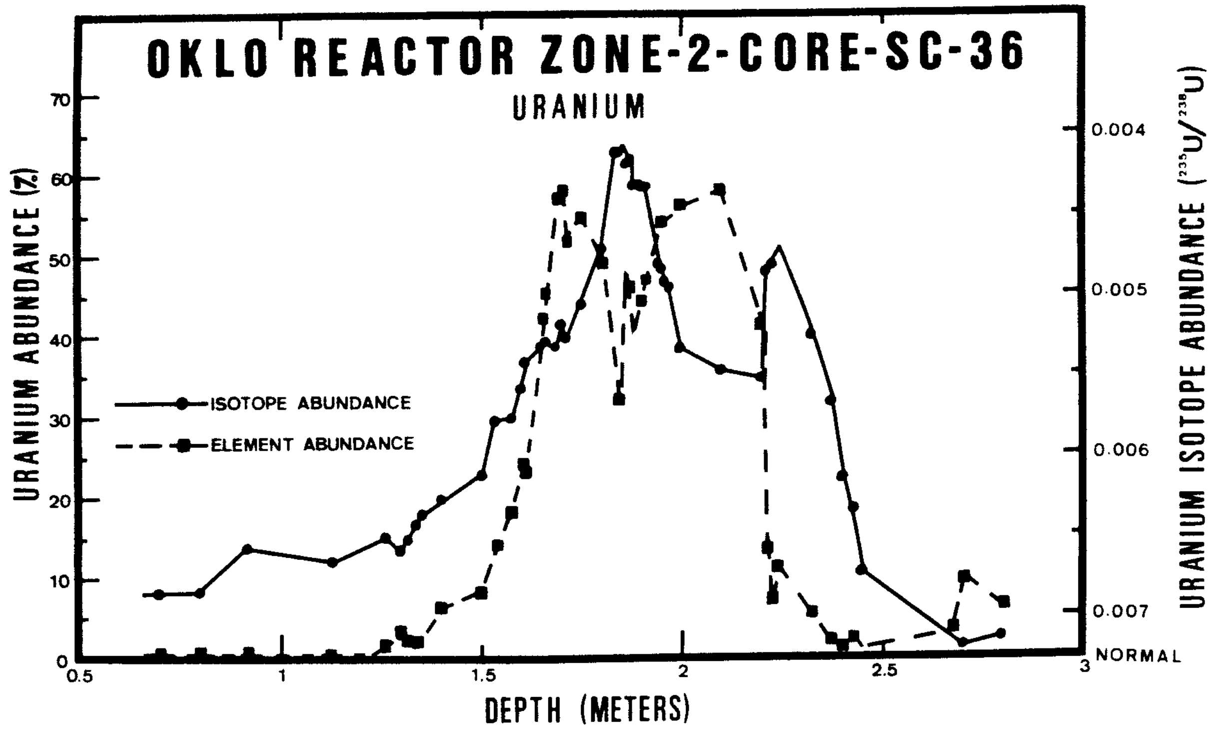

Figure 1. Two curves showing variations in the uranium abundance and $^{235}U/^{238}U$ ratio as a function of depth in core SC-36. At the borders of reactor zone 2 the two parameters correlate, while in the heart of the reactor zone they anti-correlate. Such variations can be quantitatively described by neutronic models suggesting that the properties are a "map" of relative changes in the rates of production and destruction of ^{235}U partially controlled by changes in the absolute abundances of uranium (25).

uranium poor clay separates from the same sample is 0.422% ± 0.012 imperceptibly different from that in uraninite. Contamination of the clays with small quantities of uranium of different isotopic composition would produce large isotopic shifts. The absence of such shifts suggests that the sample contains little uranium from nearby rocks.

Similar conclusions are drawn from measurements of $^{235}U/^{238}U$ on 10 μ spots in four grains of uraninite from the same sample (23). The average of 27 analyses of three grains is $^{235}U/^{238}U$ = 0.522 ± 0.004%. In the fourth grain, the average of the analyses of 14 separate spots is $^{235}U/^{238}U$ = 0.500 ± 0.006%. There is no observable uranium isotopic heterogeneity or zoning in these grains as there would be if uranium were transported from another region and precipitated on the surface of the mineral.

Uranium within the core has suffered no observable redistribution and little of the element has been transported into the reactor zone and retained.

There is, however, evidence that small quantities of uranium have been removed from the reactor zones and redeposited in the nearby rock (20). The spatial distribution of uranium and uranium isotope abundances in SC-36 demonstrates the evidence for such redistribution: At the bottom of the reactor zone the relative abundance of ^{235}U increases steadily until it attains the normal isotopic composition (about 2.4 m deep). A very small deficiency of ^{235}U appears in sample 1905, 20 cm further away from the heart of the core. This suggests an erratic contamination of normal uranium with the reactor fuel. Samples overlying the reactor zone in SC-36 show a different distribution of uranium isotopic abundances. The ^{235}U isotopic abundance increases regularly as a function of distance from the heart of the reactor zone for about 30 cm but then defines a 60 cm plateau with ^{235}U/^{238}U $\cong$0.65%, significantly less than normal. Through this plateau the uranium abundance is less than 1%, a concentration too small to have sustained criticality. Naudet (20) suggests that uranium in this section originated in the reactor zone. It was transported into the rocks at the roof and redeposited. Naudet (8) believes that there has been a general redistribution of small quantities of uranium from the reactors into a few meters of host rock. Curtis and Gancarz (24) estimate that about 10% of the uranium in the reactor zones is contained within these contaminated aureoles.

4.3 PLUTONIUM

Plutonium-239 was produced in copious quantities by neutron capture by ^{238}U and the subsequent decay of short-lived radioactive products. This isotope of plutonium has a half-life of 2.4 x 10^4 years, an order of magnitude less than the estimated duration of criticality. Plutonium abundances increased after the initiation of criticality until the rate of production equaled the rate of decay. Its concentration during this time of nuclear equilibrium was about 300 ppm (24). After criticality ^{239}Pu disappeared at a rate controlled by its half-life: Plutonium was an abundant trace element during criticality. Although small portions of the nuclide fissioned, most of it decayed by alpha emission to repopulate the principal nuclear fuel, ^{235}U.

Because its half-life is short relative to the time that has passed since the reactors were funtional, ^{239}Pu no longer exists in the rocks. However, the geochemical stability of plutonium can be deduced from the isotopic abundance of ^{235}U. Some portion of this isotope is "fossil" ^{239}Pu. If plutonium and uranium had been fractionated during the brief duration that ^{239}Pu existed in the geologic environment, the measurable result would be shifts in $^{235}U/^{238}U$. Those samples that were enriched in plutonium related to uranium would have a larger ratio and those that were depleted in plutonium would have a smaller ratio than they would have had if they had been a closed system with respect to these two elements. This isotopic ratio can and does vary in the reactors as a result of variations of physical parameters. The difficulty in studying the chemical stability of plutonium is distinguishing between isotopic shifts due to physical parameters and those due to chemical ones. Previous arguments, based upon variations in $^{235}U/^{238}U$, that support the geochemical stability of uranium also support the stability of plutonium. Little plutonium was removed from the Oklo reactors or redistributed within them.

4.4 THORIUM

The long-lived nuclide ^{232}Th was produced principally by neutron capture by ^{235}U and the subsequent decay of the product, ^{236}U. Secondarily ^{232}Th is produced by neutron capture of ^{232}Pu and the decay of its products. Thorium-232 is the only stable isotope of this element: It is impossible to unambiguously distinguish the nuclear product from the natural background. Figure 2 shows that the abundance of ^{232}Th in the heart of reactor zone 2 is more than an order of magnitude greater than it is in the rocks immediately adjacent to the zone of criticality (with the exception of the anomalous sample 1901). Spatial variations of thorium abundances (Figure 2) mimic those of the uranium abundance and the ^{235}U isotopic abundance (Figure 1). This covariation suggests that thorium also manifests spatial variations in its rate of production. If thorium had been geochemically active in the last 2 x 10^9 years such detail could only have been maintained by the unlikely circumstance of proportional gains and/or losses throughout the core. The distribution of thorium shown in Figure 2 is plausibly attributed to the geochemical stability of the element in the Oklo environment. Thorium abundances are in reasonable agreement with those calculated from the reconstruction of the reactor operating history (25).

Because of its lack of isotopic uniqueness, the displacement of the nuclear product thorium cannot be distinguished from natural thorium in rocks surrounding the region of criticality. For instance, sample 1901, located 2.7 m into the core, 50 cm from the edge of the reactor zone, contains an extraordinary quantity of thorium. However, it cannot be determined whether this is a naturally thorium-rich rock or an exceptionally effective trap for a mobilized nuclear component. (The same sample also contains an extreme quantity of natural neodymium.) The evidence suggests that thorium has not been displaced from its site of production.

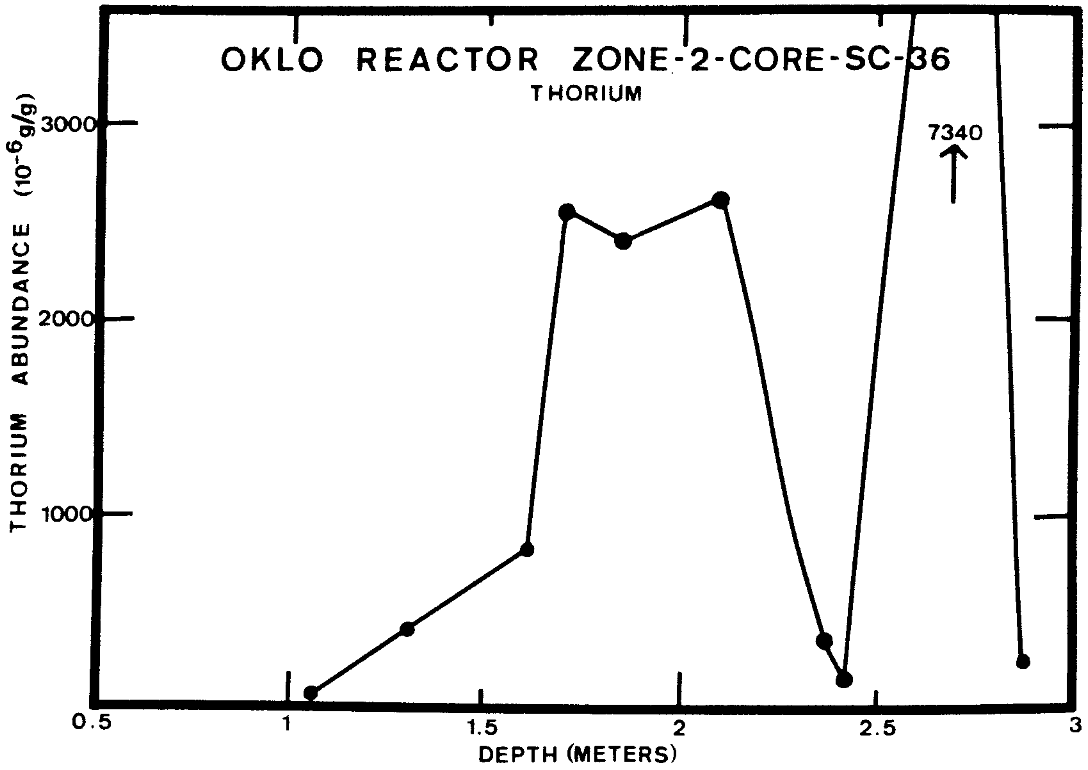

Figure 2. Spatial variations of ^{232}Th abundances in SC-36 are similar to those of uranium and ^{235}U/^{238}U suggesting that this element has also maintained a record of spatial changes in its rate of production. The extreme abundance of ^{232}Th in the sample 50 cm below the reactor zone is probably an enrichment of natural thorium rather than the nuclear product (25).

4.5 NEPTUNIUM, AMERICIUM, AND CURIUM

The transuranium elements neptunium, americium and curium were formed by nuclear reactions in the rocks of the reactors. Americium and curium were present in very small abundances. Their isotopes are short-lived relative to the time that has passed since criticality, and their stable products are not isotopically unique. Consequently, the geochemical stability of these two actinides cannot be assessed.

Neptunium-237 is a product of neutron capture by ^{236}U, which in turn is the product of neutron capture by ^{235}U. Neptunium-237 decays, with a half-life of 2x10^6 year, through a series of radionuclides to form the stable nuclide ^{209}Bi. Two other nuclear reactions produce lesser quantities of ^{209}Bi. As was the case with thorium, ^{209}Bi is the only stable isotope of this element and the nuclear product cannot be unambiguously distinguished from the natural background.

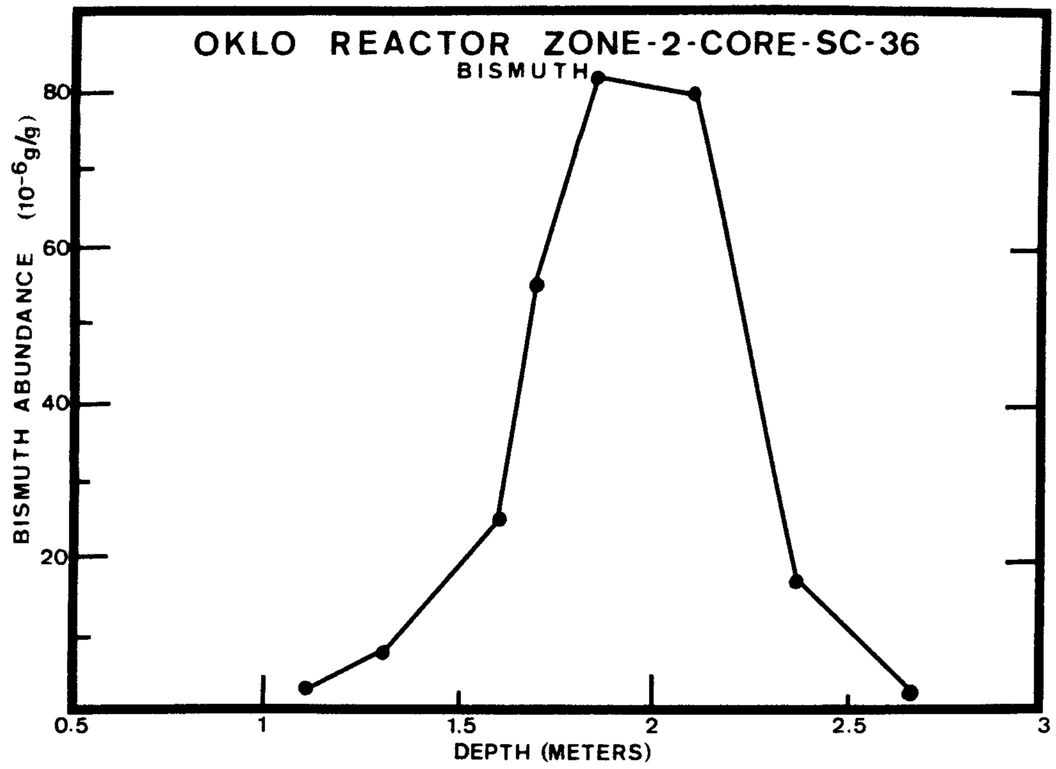

Figure 3. Within the reactor zone the presence of the nuclear product ^{209}Bi has enriched the rocks in this element. However, the spatial detail seen in the depth profile of other elements is missing for bismuth. The lack of such detail is probably due to redistribution and loss of bismuth in the reactor zone (25).

Bismuth abundances in SC-36 (Figure 3) show significant enrichments in the reactor zones. These enrichments are certainly the result of the nuclear reactions. Unlike thorium, the bismuth abundances do not mimic the changes in the uranium properties through the length of the core. This lack of covariation might be due to the redistribution of bismuth or its radioactive parent, ^{232}Np. The nuclear reactions produced twice as much bismuth as is now in these samples (25). Again, it is impossible to unambiguously associate these deficiencies with the loss of either the parent or the daughter. However, the extreme deficiencies of radiogenic lead (see discussion below) and the chemical similarities between bismuth and lead, suggest that deficiencies of ^{209}Bi are probably the result of losses of bismuth rather than the parent, neptunium.

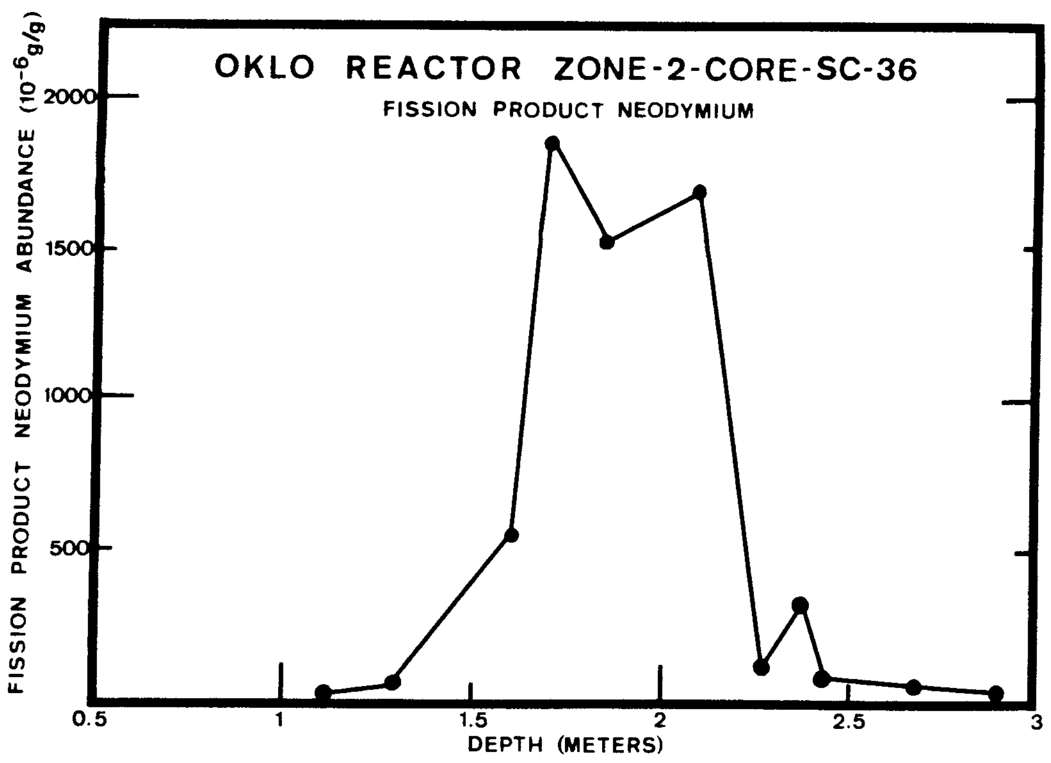

Figure 4. The depth profile of fission product neodymium shows the change in the rate of fission through reactor zone 2. As with other elements neodymium seems to have maintained its spatial distribution throughout the reactor zone suggesting that the element has been geochemically stable. (25)

4.6 NEODYMIUM

Isotopes of neodymium are among the most abundant fission products. Six of the seven stable isotopes are produced by fission. The single shielded isotope, ^{142}Nd, provides the means to unambiguously distinguish between the natural and fission produced constituents of this element. Figure 4 shows the variation of the abundance of fission product neodymium, as a function of depth in SC-36. Nuclear fission increased the neodymium concentration of rocks within the reactor zone by factors up to 30. Spatial variations of the abundance of fission product neodymium through SC-36 (Figure 4) are similar to variations in the abundances of uranium and ^{235}U/^{238}U (Figure 1). As with thorium, neodymium has maintained a "map" of its production rate in the reactor zone and has probably been geochemically stable for the last two billion years. This conclusion is reinforced by the reconstruction of the nuclear operating history using the uranium and neodymium isotopic composition of samples from the heart of the reactor zone (15). The data yields a reasonable and consistent set of reactor operating parameters. Such consistency could result only if neodymium has not been redistributed *within the reactor zone*. The consistency of the results of the model calculations does not exclude the possibility that neodymium has been removed from the reactor zone since the end of criticality. Curtis *et al*. (15) concluded that 10% to 30% of the fissiogenic neodymium has been removed from the rocks. Using the same data, Ruffenach (25) estimated that little of the rare earth element has been lost from the samples. This inconsistency in the conclusions of two sets of investigators emphasizes the magnitude of the uncertainties of these methods. Model predictions of gains and losses are probably uncertain to at least 20%. Estimates of the proportion of fissiogenic neodymium remaining in the samples are presented in Table 1. These are the larger estimated losses from Curtis *et al*. (15), and thus represent lower limits on the actual proportions of neodymium retained in these rocks.

Table 1

			Fraction of Element Remaining					
Sample No.	$^{235}U/^{238}U(x10^3)$	U (%)	Nd	Ru	^{99}Ru	Zr	Pd	Te
Zone 2								
SC-36 1892	6.71	0.28	0.82	0.2	0.24			
SC-36 1402	6.65	2.73		0.32				
SC-36 1408/4	5.45	23.3	0.72	1.2	1.09			
SC-36 1410/3	5.27	57.8	0.78	0.90	0.70			
SC-36 1413/3	4.10	37.2	0.89	0.61	0.49			
SC-36 1418	5.74	57.9	0.79	0.81	0.60			
SC-36 1421/5	5.30	9.01		0.46	0.53	0.81		
SC-36 1424/5	6.34	1.66	3.38	0.07	0.074			
SC-36 1425/5			1.80	0.11	0.11			
SC-36 1897/5	6.93	1.83						
SC-36 1901	7.25	9.48	$2x10^5$	0.03	0.03			
2L 401/3	3.98	33.0	0.84	0.86	0.81	1.25		
2L 404/3	5.62	61.0	0.78	0.62	0.58	0.90		
2P 433/3		59.0					0.95	1.05
2´P´ 1177	5.32	63.8	0.90	0.57	0.46	0.80		
2´P´ 1179	5.04	55.7	0.75	0.59	0.47	0.94		
2´P´ 1181	3.06	21.4	0.98	1.16	1.10	1.44		
2´P´ 1184	3.77	25.4	0.91	0.96	0.80	1.52		
2´P´ 1187	4.27	48.5	0.90	0.75	0.70	1.22		
KN-50 321	5.6	13						
KN-50 323	4.7	9						
Zone 1								
SC-61 1498	5.52	48						1.0
Zone 3								
SC-52 1470	6.63	48						
SC-53 1763	7.19	31	2.04	0.384	0.338			1.16
SC-54 1876	7.18	6.6	1.09	0.71	0.55			
SC-55 1844M	6.90	27	0.964	1.13	1.22			
SC-55 1852M	6.86	47	1.03	1.00	0.854			
SC-55 1856	6.86	21	1.00	1.763	0.759			
SC-55 1860	6.85	12	1.00	0.911	0.83			
SC-55 1864	6.79	3.0	0.66	0.724	0.738			
SC-56 1877	6.93	48	1.13	1.03	0.88			
SC-57 2233	7.04	32	1.05	1.21	0.97			

Table 1 (cont)

Sample No.	**Fraction of Element Remaining** **Mo**	**Ag**	**Sn**	**Pb**	**Cd**	**Rb**	**Sr**	**Ba**	**Xe**
Zone 2									
SC-36 1892				0.91					
SC-36 1402				0.48					
SC-36 1408/4				0.43					
SC-36 1410/3				0.29					
SC-36 1413/3				0.34				<0.01	
SC-36 1418				0.29				<0.01	
SC-36 1421/5	0.09			0.68					
SC-36 1424/5									
SC-36 1425/5	0.04			0.98					
SC-36 1897/5									
SC-36 1901	0.06			0.41				<0.01	
2L 401/3	0.09					<0.01	<0.01	<0.01	<0.01
2L 404/3	0.09					<0.01	<0.01	<0.01	
2P 433/3		<0.23	0.53		2×10^{-3}				
2'P' 1177	0.15								
2'P' 1179	0.14								
2'P' 1181	0.14								
2'P' 1184	0.11								
2'P' 1187	0.11								
KN-50 321						<0.06	<0.08		0.01
KN-50 323						<0.09	<0.13		0.001
Zone 1									
SC-61		<0.45			2.10^{-3}				
Zone 3									
SC-52 1470		<0.50	0.42		5.10^{-3}				

Unambiguous evidence for the redistribution of neodymium is found in samples from the edges and periphery of reactor zone 2. These samples contain fission produced neodymium. However, the isotopic abundances of neodymium and uranium do not yield consistent solutions to calculations of nuclear operating parameters. The samples clearly violate assumptions implicit in those calculations: They have been chemically altered with respect to neodymium and/or uranium at some time since the reactors began to function. It is likely that reactor products in these samples were transported from the nearby reactor zone.

There has been little redistribution of neodymium within the heart of reactor zone 2. Small proportions have been removed and redeposited in rocks immediately adjacent to the zone of reaction.

4.7 RUTHENIUM

Four isotopes of ruthenium are produced by fission, ^{99}Ru, ^{101}Ru, ^{102}Ru and ^{104}Ru. There are three shielded isotopes of the ele-

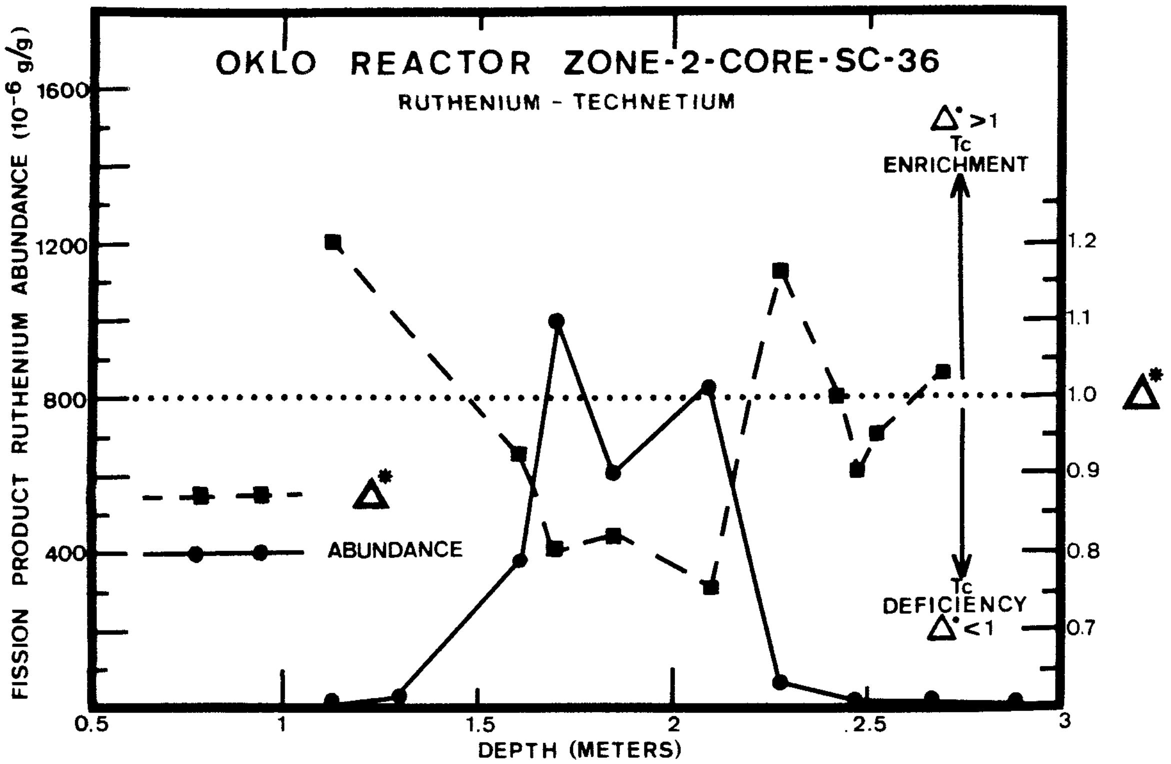

Figure 5. As with neodymium, ruthenium abundances provide a "map" of the rate of fission through the reactor zone suggesting that the element has been relatively stable. The parameter

$$\Delta^* = \frac{(^{99}\mathrm{Ru}/^{101+102}\mathrm{Ru})\mathrm{meas}}{(^{99}\mathrm{Ru}/^{101+102}\mathrm{Ru})\mathrm{F.Y.}}$$

measures the fractionation between ^{99}Tc from Ru during a period of 10^6 years after the beginning of criticality. Within the reactor zone $\Delta^* < 1$ indicating that technetium was preferentially lost from these rocks. In peripheral samples technetium has been both enriched and depleted relatiove to ruthenium. (25).

ment at masses 96, 98, and 100. These are unambiguous indicators of the presence of natural ruthenium. There is very little of the natural constituent relative to the fission product in the rocks of the reactor zones. Figure 5 shows the abundance of fission produced ruthenium as a function of depth in SC-36. Abundances of this nuclear product demonstrate the familiar variations as a function of depth: There are dramatic increases between about 1.5 and 2.25 meters and sharp variations in the center of the core that presumably track changes in the rate of production of the nuclides through the reactor zone. This depth profile suggests that ruthenium has been relatively inert since the beginning of nuclear criticality. Gains or losses from sample to sample have probably been small. Estimates of the fraction of ruthenium remaining in samples from SC-36 and other reactor zones are in Table 1. These values are the abundances of the fissiogenic ^{101}Ru + ^{102}Ru + ^{104}Ru relative to fissiogenic neodymium normalized to the fission yields of the same nuclides. Unity indicates no fractionation between ruthenium and neodymium, values greater than unity indicate enrichment and those less than unity indicate depletion of ruthenium relative to neodymium. The values do not show large variations from unity. If neodymium has been stable then the losses and gains of ruthenium have been small.

Samples from the periphery of zone 2 show regular deficiencies of ruthenium relative to neodymium. The abundance of fission product ruthenium in sample 1901, from 50 cm below zone 2, is only 3% of the neodymium. Ruthenium was not as effectively retained in the peripheral rocks as the rare earth element.

4.8 TECHNETIUM

The three heavy isotopes of fissiogenic ruthenium are produced instantaneously relative to the time scale of geologic processes that might have changed the composition of the rocks. However, the lightest isotopic fission product, ^{99}Ru, has a precurser, ^{99}Tc, with a half life of 2.13 x 10^5 years. The mean lifetime of ^{99}Tc is sufficiently long that the element existed in concentrations of μg/g for a period of about 10^6 years after the beginning of criticality. If natural processes fractionated ruthenium from technetium during that time, the result would be measurable as excesses or deficiencies of ^{99}Ru relative to the other fission produced isotopes. Such variations can be assessed by comparing the measured isotopic ratio, ^{99}Ru/^{101}Ru+^{102}Ru to the ratio of the fission yields of the same isotopes. Such a comparison is made by normalizing the measured ratio by the ratio of the fission yields. This ratio of ratios, characterized as Δ^*, is plotted as a function of core depth in Figure 5. If Δ^* is equal to unity, there was no fractionation of technetium and ruthenium. If Δ^* is greater than unity, the rock was enriched in technetium relative to ruthenium and if Δ^* is less than unity the sample was depleted in technetium. It is apparent from Figure 5 that the samples from the reactor zone, those that contain large abundances of the nuclear products, selectively lost technetium. Rocks from the periphery contain both excesses and deficiencies of technetium relative to ruthenium. Other samplings of reactor zones (Table 1) show a similar pattern: With two exceptions, rocks from reactor zones are deficient in ^{99}Ru while those from the periphery show variable enrichments and depletions. One sample taken a meter away from reactor zone 9 contains ruthenium that is about 95% ^{99}Ru (26). At one time this rock contained nearly 1 ppm of ^{99}Tc. Technetium was geochemically active during the million years period following the beginning of criticality.

4.9 ZIRCONIUM

There has been some redistribution of zirconium in the reactor zone relative to neodymium. A few analyses show small fractionations between the two elements (Table 1). Samples are both enriched and depleted in zirconium relative to neodymium.

4.10 MOLYBDENUM

Relative to neodymium, between 80% and 90% of the fission produced molybdenum has been lost from the reactor zones. The magnitude of these losses is quite uniform: In addition to the data presented in Table 1, recent analyses from reactor zone 9 show the loss of similar proportions. Rocks from the periphery of zone 2 and zone 9 contain fissiogenic molybdenum. Major proportions of molybdenum were lost from the reactor zones. However, its prevalence in peripheral rocks suggest that it was not transported over great distances.

4.11 PALLADIUM, TELLURIUM, SILVER, TIN AND CADMIUM

Abundances of these elements were measured to study the relative contributions of ^{235}U, ^{239}Pu and ^{238}U to the total number of fissions (21, 27, 28). Interpretations of the data with respect to the stability of these elements are complicated. Their production rates are highly dependent upon the nature of the fissioning nuclides. Values in Table 1 are estimates of absolute gains or losses rather than excesses or deficiencies relative to neodymium. Palladium and tellurium have been largely retained in the reactors. Less than 50% but more than 10% of the fission produced silver and tin remain. Cadmium has been quantitatively lost from the rocks. Within the detection limits fissiogenic silver could not be observed in the rocks around the reactors. Small abundances of fission product cadmium was detected in these rocks. The only peripheral sample in which palladium and tellurium were found was 300 meters away from the nearest known zone of criticality (28).

4.12 ALKALI AND ALKALINE EARTH ELEMENTS

Four alkali and alkaline earth elements: strontium, rubidium, barium and cesium are prominent fission products. Six samples from the reactor zones continued less of these elements (fissiogenic and natural) than were produced by fission (29, 30). Strontium, rubidium and barium in these and other samples contain extremely small proportions of the fissiogenic component (30, 31, 32, 33). Cesium has only one stable isotope and it is thus impossible to distinguish the fission product from the natural component. Most of the alkali and alkaline earth fission products have been lost from the rocks of the reactors.

4.13 NOBLE GASES

There have been a few analyses to determine the abundance and isotopic composition of krypton and xenon in the reactor zone (12, 34). Each gas contains significant proportions of their fission component. However, the abundances are too small to account for the quantities produced by the reactions. Most of these gaseous fission products are missing from the reactors.

4.14 LEAD

Isotopes of lead are not the product of nuclear criticality. They are produced by radioactive decay; ^{206}Pb from ^{238}U, ^{207}Pb from ^{235}U and ^{208}Pb from ^{232}Th. A fourth isotope, ^{204}Pb, is not the product of radioactive decay; it is used to evaluate the abundance of primordial lead. These decay processes are not unique to Oklo; they are the basis for determining a chronology for many geologic events. The stable daughter accumulates and the radioactive parent disappears at a rate dictated by the decay constant of the parent. The length of time since a geologic system has been closed to the loss or gain of lead and uranium can be measured by determining the relative abundance of parent and daughter nuclides. The decay constant for these natural radionuclides is extremely small and thus current analytical techniques are not capable of distinguishing changes representing small durations of time. For instance, Gancarz (35) determined that the uranium enrichments found in the Oklo mine were formed 2.05 x 10^9 years ago. If the rocks containing uranium had been closed to the loss or gain of lead and uranium since that time, the measured ^{206}Pb/^{238}U today would be 0.3744 (excluding any primordial ^{206}Pb). If the time of ore formation and the initiation of nuclear criticality were simultaneous, and lead was totally removed from the rocks during a period of 5 x 10^5 years after criticality began, the measured ratio would be 0.3743, the two results differing by only 0.03%. In fact, ^{206}Pb/^{238}U in the Oklo ores are much smaller than either of the calculated ratios. Such values indicate extreme losses of lead relative to uranium either continuously or periodically in recent times compared to the time of ore formation and/or nuclear criticality. The fraction of radiogenic lead remaining in the rock is included in Table 1. Values in the table reflect the measured quantity of lead compared to the quantity that would have been produced in 2.05 x 10^9 years by the measured quantity of uranium. Although these values were determined in a different way than those given for the nuclear products, they convey the same meaning.

Samples throughout SC-36 have lost radiogenic lead. In some samples the losses are extreme representing as much as 74% of the ^{206}Pb produced in the rock (26). The largest relative and absolute abundances were lost from samples at the heart of the reactor. Two samples, one from the reactor zone border and one from the periphery show losses of only a few percent. None contain an excess of ^{206}Pb! Such results are not unique to this small sampling. Many ores samples have been analyzed for uranium and lead isotope abundances. Virtually every one is deficient in radiogenic lead (36). The losses are not confined to the rector zones: there has been a pervasive loss of lead from the uranium-rich rocks of the Oklo mine.

The loss of lead is important in considering conditions that have impacted the reactor zone since the time of nuclear criticality. Deficiencies of this element manifest the same type of processes that produced deficiencies of the nuclear products: lead was preferentially expelled from its host uraninite by a process in the solid state, and transported from the host rock by a mobile phase. Processes capable of mobilizing elements in these rocks existed long after the immediate impact of the nuclear reactions had subsided. Thus in considering the long term chemical stability of the nuclear products, conditions produced by the ambient geologic environment must be taken into account.

5 SUMMARY AND CONCLUSIONS

Deficiencies of nuclear products are common and excesses are rare within the fossils of the reactors. Since the time of criticality these rocks have suffered a net loss of many elements representing relatively large changes in their composition and involving the movement of substantial quantities of material over distances of at least a few meters. Rocks at the periphery of the fossil reactors contain small quantities of many of these nuclear products, representing net gains but relatively small changes in the composition of the rock. The localized nature of this redistribution suggests that it was the result of a local phenomenon, directly or indirectly induced by the nuclear reactions. In the jargon of the management of nuclear wastes, the redistribution of nuclear products was in response to the near field environment; an environment produced by the reactors themselves. Considerations of geochemical controls in the transport of nuclear products must take into account the extreme nature of these conditions.

More than 80% of the uranium, thorium, plutonium, neodymium, zirconium, palladium and tellurium remain in the rocks where they were produced. The nuclear products were formed and originally contained in uraninite. It is likely that the effective retention of these elements can be attributed to their compatibility with this mineral and its long-term chemical and physical stability.

It has been estimated that 10% of the uranium fuel, representing about 100 tons was removed from the reactors (24). In contrast, there is no evidence that uranium was transported into the reactor zones and retained there. In the context of ambient geologic conditions this is a surprising observation: Uraninite is the only important uranium-bearing mineral in the reactor zones. The uraniferous sandstone ores that host the reactors contain the uranium in pitchblende, a cryptocrystalline variant of tetravalent uranium dioxide. At 25°C and a pressure of one bar, pitchblende is more soluble than uraninite (23). If the relative solubilities of these two minerals can be extrapolated to higher temperatures, an aqueous phase moving from normal ore into the reactors would be supersaturated with respect to uraninite and precipitate isotopically-normal uranium. Fluids moving out of the reactors would be undersaturated with respect to pitchblende and isotopically-normal uranium would be preferentially dissolved from the host rocks. Within the ability to detect and interpret isotopic shifts in uranium this is the opposite of what has occurred at Oklo. Uraninite in the reactors appears to have been more soluble than pitchblende in the hosts. This apparent increase in uraninite solubility probably reflects differential conditions between the reactors and the host rock. Curtis and Gancarz (24) suggested that the radiolysis of water during reactor operation produced locally oxidizing conditions within the reactor zones. Curtis, *et al*. (15) considered the effects of increased temperature on the solubility of oxides of various reactor products. *The containment of many nuclear products in natural spent fuels depends directly on the chemical stability of the uranium dioxide host phase. Small portions of this phase were dissolved and removed from the natural reactors, probably in response to extreme conditions produced by the nuclear reactions*.

Uraninite was ineffective in containing many nuclear products. Between 20% and 90% of the ruthenium, technetium, molybdenum, silver and tin produced in the rocks has been lost from them. Virtually all of the cadmium, rubidium, strontium, barium and the noble gases are missing. These proportions are much greater than the proportions of uraninite that were dissolved. *These elements were lost from their host phase by processes other than simple dissolution*. By analogy with the loss of fission products from commercial reactor fuels, many of these elements may have been released by solid state diffusion or vapor phase transport. In commercial fuels such losses are a direct response to the extreme temperatures in the fuel during criticality. If the processes are analogous, the loss of these elements from the natural wastes is a direct response to localized conditions produced by the reactors themselves; conditions that were extreme compared to proposed spent fuel repositories.

In commercial reactor fuels, elements released from uraninite form new phases. The long-term stability of these phases will be a critical factor in the retention of the nuclear wastes. It is likely that similar phases were formed within the rocks of the natural reactors. It is the solubility of such minerals that controlled the retention of the elemental constituents once they were released from uraninite. A study of such phases is a critical, and neglected, aspect of the study of the natural nuclear waste as an analogue of a geologic repository for similar man--made wastes.

Rock adjacent to the reactor zone contain small quantities of many nuclear products. Uranium, neodymium, ruthenium, technetium, molybdenum, cadmium, barium, tellurium and palladium have been identified in peripheral rocks. These elements were transported, probably sporadically, over distances of a few meters in the last two billion years. The mineralized sandstones at Oklo appear to have provided remarkably effective containment of the products released from the natural waste package. Nothing is known of the processes that so effectively contained the released wastes. The information to address the nature of such processes at Oklo does not seem to be available.

Ores from throughout the Oklo mine, including the regions of criticality, are deficient in radiogenic lead. These deficiencies provide proof that elements do not require extreme conditions to be preferentially released from uraninite. Lead losses occurred long after nuclear criticality, under conditions imposed by the ambient geologic environment. Lead and uranium isotope abundances in Oklo ores can be quantitatively interpreted by a model of lead loss by continuous volume diffusion in solid uraninite (35, 37). Unlike many of the nuclear products, lead, once it was released from uraninite, was not retained locally.

Although lead itself is of little interest to the management of nuclear wastes, its loss at Oklo (and at other sites) provides an excellent example of the failure of geologic containment in a far field environment. The conditions of this failure are of interest so that they might be avoided in selecting a repository site.

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The Royal Institute of Technology
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