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Investigations of the Oklo Natural Fission Reactor

July 1975—June 1976

Compiled by

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INVESTIGATIONS OF THE OKLO NATURAL FISSION REACTOR: JULY 1975 THROUGH JUNE 1976

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ABSTRACT

This document reports on activities of the Oklo natural fission reactor program. During FY 76, studies have been directed toward (1) further characterization of the reactor, including operation, radionuclide production and dispersion, and ore paragenesis, (2) theoretical prediction of the geochemical behavior of reactor products, (3) search for evidence for other natural fission reactors, and (4) supportive analytical measurements and procedures development. These investigations are conducted by personnel at the Los Alamos Scientific Laboratory, the Allied Chemical Idaho National Engineer Laboratory, and the Department of Geology of the University of New Mexico and are in conjunction with the ERDA program for geologic isolation of nuclear fuel cycle wastes.

I. INTRODUCTION

The successful isolation of reactor products from the biosphere is a necessary adjunct to further adoption of nuclear power generation. Since certain radioactive waste products remain hazardous to some extent for hundreds of thousands or even millions of years, a very long-term perspective is necessary for addressing waste isolation. The concept of radioactive waste containment by geologic disposal is one of the most attractive options currently being considered by official and private parties. To help evaluate this option, we are fortunate to have available for study a unique natural experiment in geologic containment of reactor product wastes, the natural Oklo fission reactor.

We know now that the Oklo reactor system sustained criticality for a duration of perhaps 0.6 m.y. at a time approximately 1.8 b.y. ago. An estimated 6 tons of ^{235}U underwent fission, about 2 tons of ^{235}U were derived from precursor ^{239}Pu produced in the reactor. A small percentage of the total fission (<10%) resulted from ^{239}Pu that fissioned before it decayed and from fast-neutron induced fission of ^{238}U. [See for example IAEA (1975) or Cowan (1976) for reviews on the Oklo phenomenon.] Of the several tons of reactor products "emplaced" at Oklo, the majority have remained in situ. In general, the higher valence state elements, e.g., the actinides and lanthanides, were nearly quantitatively retained, whereas elements with less complex chemistries, such as Xe, I, Mo, Sr, Rb, etc., were almost completely removed.

A major objective of the Oklo program is to determine quantitatively the retention/migration behavior of the reactor products in the regions of formation and in the surrounding regions of migration. Further, geochemical and geophysical factors responsible for the observed behavior are to be identified. In order to characterize the behavior of the reactor products, it is necessary to know the operating characteristics of the Oklo system. Reactor and neutronics modeling studies can in principle elucidate not only "source terms" for reactor products but important physical constraints for the period of criticality. Furthermore, ore paragenesis and metallogenesis studies are important tools by which the Oklo geochemical environment can be determined. Mineralogy and petrography further establish temperature, pressure, and solution chemical conditions which the Oklo reactor products have experienced.

The geochemical behavior of many reactor products is not well known, particularly for non-ideal conditions routinely encountered in real geological settings. Hence, it is necessary to develop a theoretical basis for understanding the behavior of fission product and actinide elements. Migration/stabilization observations for Oklo can then be used to test predictions for the same system. In addition, it is expected that extrapolation of migration/stabilization models to other geologic settings can be made, thereby providing valuable data in assessing potential disposal sites for contemporary nuclear wastes.

It is suspected that the Oklo natural reactor system was not unique in the earth's history. Consequently, search for other such natural occurrences is an important corollary to these studies. If another fossilized Precambrian reactor is discovered, it would provide additional invaluable information on migration/stabilization behavior on yet another geologic environment. Predicted radionuclide behavior could then be calibrated with a second set of data. Evidence for a dispersed Precambrian reactor (as opposed to a fossilized system as at Oklo) may be found by characterizing worldwide variations on the $^{235}U/^{238}U$ isotopic ratio. Subtle uranium isotopic variations observed to date may indicate some combination of two factors: (1) an isotopic chromatographic effect may occur in the uranium geochemical cycle of continued reduction, mobilization, and redistribution. Isotopic effects on the reaction kinetics of such repeated cycles could give rise to at least localized uranium isotopic anomalies; (2) the dispersion of a natural fission reactor(s) by geochemical and geophysical phenomena could alter natural isotopic ratios on a continental scale. By investigating these two factors, a better understanding of the phenomenology of Precambrian fission reactors could be attained, thus permitting a probabilistic evaluation of the efficacy of natural and artificial geologic isolation of reactor wastes.

II. OKLO REACTOR CHARACTERIZATION

A. Reactor Model Calculations

The data for Bi and Th on Oklo ore samples, plus Ru isotopic results from INEL, and our previously determined Nd isotopic ratios, Nd/U, and U isotopics were incorporated into a calculation which allowed for self-shielding of ^{238}U. This calculation was carried out with cross sections from report BNL-325 as one set and, alternatively, with σ_{Th} = 266 barns for ^{143}Nd (INEL) for a second set, with 1.75 b.y. as the zero time and 0.6 m.y. as the duration. As expected, with the BNL value of 325 b for ^{143}Nd we found a discrepancy of approximately +20% for the Nd/U ratios, while use of either a 266-barn value or a zero time of 2 b.y. produced close agreement. The resonance fluence was based on ^{146}Nd/^{145}Nd, and ^{238}U fissions on a combination of ^{150}Nd/(^{143}Nd + ^{144}Nd) and ^{104}Ru/(^{101}Ru + ^{102}Ru). An overall good fit to our data (except for Nd/U) was obtained with either ^{143}Nd cross section. We also fitted the same data reported by Frejacques et al. (1975) for nearby samples; the Bi/U and Th/U fit better with the BNL value of 325 barns. The samples considered came from Zone 2, Cut P', and Core SC-36, on both sides of a clay-filled joint. Interesting results are that ^{239}Pu fission contributed 3-4% and ^{238}U fission 3-5%, capture in ^{238}U was reduced by factors of 4-10 by the resonance self-shielding effect, and the Bi and the Bi and Th daughters of ^{237}Np and ^{236}U appear to have been retained in this region. These results, plus a review of the Gabon Conference, were presented at an ACS meeting in New York (Bryant et al., 1975).

B. Reactor Zone 3 Analyses

Several samples were obtained from corings which were believed to be on the outer edges of reactor Zone 3. The location of Zone 3 is shown in Fig. 1 and the locations of the core samples in Fig. 2. Five samples were analyzed from core SC-55 and one each from SC-53, 54, 56, and 57.

Weighed fractions of the "as received" samples were leached for several hours in a mixture of boiling quartz-distilled 8M HCl and 1.5M HNO_3. After leaching, the sample solutions were filtered into tared quartz flasks and weighed. Weighed aliquots were removed and concentration and isotopic measurements made for U, Mo, Zr, Ru, Nd, and Sm.

1. U and fission density. The measured U concentration, ^{235}U abundance, and fission density are given in Table I. In most cases, it is apparent that the samples were from a relatively uranium-rich portion of Zone 3, rather than

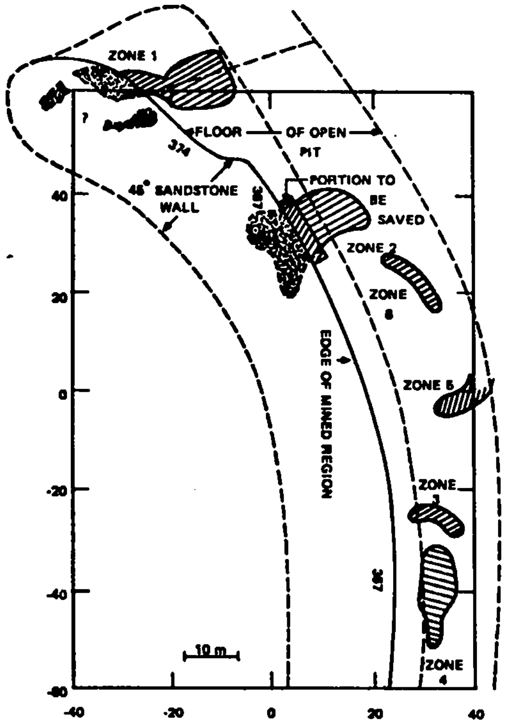

Fig. 1.
Aerial view of the reactor locations at Oklo. The bed containing the uranium dips steeply to the east and north.

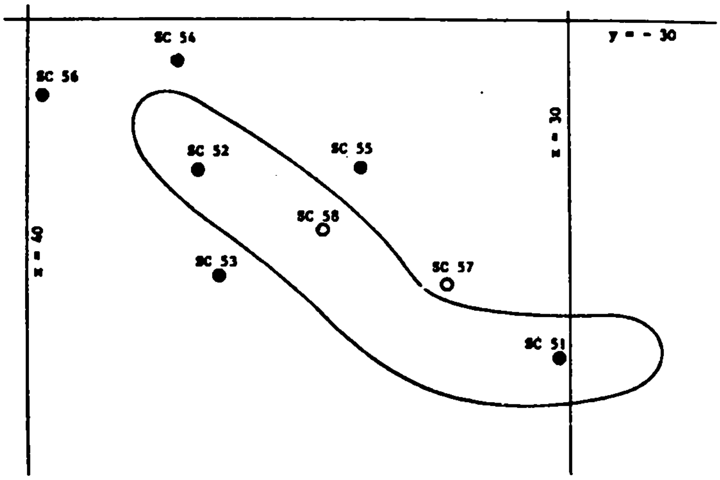

Fig. 2.
Diagram of reactor zone 3 showing locations for drill holes.

from the edges as desired, indicating that the area of the ore zone was not well known at the time of sampling. In general, the fission density for Zone 3 samples was approximately 10 times less than that observed in the center of Zone 2 (Maeck et al., 1975).

Some interesting observations are noted in the SC-55 series of samples. In particular, we note the decrease in ^{235}U content with depth and the very high fission density (fissions/atom U_T) associated with the uranium-poor 1864 sample at the edge of the zone. A similar observation (Maeck et al., 1975) was noted at the boundary of the SC-36 samples from Zone 2. We observe a high fission-product Nd content relative to uranium. We believe this is the result of some loss of U from the interface of the rich ore body and the surrounding material. Additional studies at the edges of the reactor zones are required to more fully establish the relative stability of the uranium and the fission products at Oklo.

TABLE I. URANIUM AND FISSION DATA FOR OKLO SAMPLES ZONE 3

Sample	Depth(m)	%U_T	% ^{235}U	Fissions/g Ore[a] ($x10^{19}$)	Fissions Atom U_T
SC-53-1763	19.3	36.42	0.7215	0.019	0.0002
SC-54-1876	19.5	5.98	0.7201	0.006	0.0004
SC-55-1844	13.9	27.48	0.6918	0.196	0.0028
SC-55-1852	14.3	49.27	0.6856	0.377	0.0030
SC-55-1856	14.5	21.96	0.6842	0.200	0.0036
SC-55-1860	14.7	12.63	0.6792	0.109	0.0034
SC-55-1864	14.9	3.03	0.6747	0.054	0.0070
SC-56-1877	22.3	47.91	0.6967	0.345	0.0028
SC-57-2223	11.4	31.96	0.6988	0.156	0.0019

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[a] Based on a ^{235}U thermal fission yield of 0.0169 for ^{148}Nd.

TABLE II. NEODYMIUM DATA FOR OKLO ZONE 3 SAMPLES

	Atoms/g Ore			Atom Ratios		
Sample	FP	Nat.	% Nat.	144/143	146/145	$\frac{150}{144+143}$
SC-53-1763	4.98E16	8.02E17	94	1.336	1.182	0.0444
SC-54-1876	1.32E16	7.96E16	86	0.986	0.716	0.0450
SC-55-1844	4.12E17	4.52E17	52	0.962	0.760	0.0565
SC-55-1852	7.92E17	5.21E17	40	0.967	0.763	0.0567
SC-55-1856	4.18E17	4.02E17	49	0.981	0.764	0.0574
SC-55-1860	2.30E17	2.82E17	55	0.987	0.757	0.0562
SC-55-1864	1.14E17	2.57E17	69	1.037	0.769	0.0565
SC-56-1877	7.17E17	2.51E17	26	0.964	0.770	0.0581
SC-57-2223	3.35E17	5.10E17	60	0.973	0.751	0.0509
- - - - - - - - - - - - - - -						
^{235}U thermal fission				0.913	0.759	0.0566

2. Fission products. The measured atoms/gram of ore for fission product and natural Nd are given in Table II. Also given are selected isotopic ratios of the fission product component. Although the natural Nd component has been subtracted from the data given in Table II, corrections have not yet been applied for the effect of neutron capture on the natural Nd which was present at the time of criticality. This probably accounts for the variability of the isotopic ratios shown in Table II, especially for samples SC-53-1763, SC-54-1876, SC-55-1864, and SC-57-2223, all of which have a high natural component.

Specific Ru isotopic ratios for Zone 3 samples are given in Table III. The measured concentrations of fission product and natural ruthenium are presented for comparison in Table IV. Of particular significance is the ratio of ^{99}Ru (^{101}Ru + ^{102}Ru). The high variability in this value is believed to result from the selective migration of 2.1x10^5 yr ^{99}Tc. Similar Tc movement was observed (Maeck et al., 1975) in the samples from Zone 2.

In some cases (e.g., SC-56-1877) the (101+102)/104 ratio is lower than that for pure U thermal fission. This could result from ^{239}Pu thermal or ^{238}U fast fission. At this time, however, we do not believe that sufficient data and information are available to make this conclusion. Additional studies in this area are warranted.

TABLE III. RUTHENIUM ISOTOPIC RATIOS FOR OKLO ZONE 3 SAMPLES

Sample	$\frac{99}{101+102}$	$\frac{101}{102}$	$\frac{101+102}{104}$
SC-53-1763	0.5846	1.200	4.632
SC-54-1876	0.7015	1.186	4.838
SC-55-1844	0.7045	1.211	4.997
SC-55-1852	0.5668	1.202	5.000
SC-55-1856	0.6635	1.222	5.143
SC-55-1860	0.6067	1.194	4.965
SC-55-1864	0.6694	1.194	4.965
SC-56-1877	0.5614	1.185	4.769
SC-57-2223	0.5320	1.201	4.976
^{235}U thermal FY	0.6630	1.202	5.065

TABLE IV. FISSION PRODUCT AND NATURAL ABUNDANCE CONCENTRATIONS OF SEVERAL ELEMENTS ANALYZED FROM OKLO ZONE 3 SAMPLES

	Atoms/g Ore							
	Mo		Zr		Ru		Sm	
Sample	FP	Nat.	FP	Nat.	FP	Nat.	FP	Nat.
SC-53-1763	<2%	1.09E18	NM[a]	NM	1.54E16	<2%	<5%	1.14E17
SC-54-1876	NM	NM	NM	NM	7.96E15	<2%	2.50E15	9.58E15
SC-55-1844	9.04E16	2.49E17	5.69E16	2.91E18	4.13E17	<2%	7.51E16	5.19E16
SC-55-1852	2.85E17	4.16E17	7.88E17	8.24E18	6.30E17	<2%	1.37E17	7.12E16
SC-55-1856	1.24E17	1.61E17	NM	NM	2.63E17	<2%	6.75E16	5.36E16
SC-55-1860	7.75E16	1.01E17	<2%	4.34E18	1.69E17	<2%	3.71E16	4.44E16
SC-55-1864	1.91E16	2.88E16	<2%	5.52E18	6.96E16	<2%	2.11E16	2,90E16
SC-56-1877	1.78E17	5.09E17	3.61E17	4.15E18	5.89E17	<1%	1.25E17	3.71E16
SC-57-2223	1.12E17	9.63E16	<2%	7.13E18	3.16E17	<1%	6.53E16	6.48E16

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[a] Not measured as of this date.

TABLE V. FISSION PRODUCT STABILITY FOR OKLO ZONE 3 SAMPLES

	Fissions/g Ore x10^{19}					Fission Product Ratios			
Sample	Nd[a]	Ru[b]	Mo[c]	Zr[d]	Sm[e]	Ru/Nd	Mo/Nd	Zr/Nd	Sm/Nd
SC-53-1763	0.0196	0.0092	f	f	g	0.47	---	---	---
SC-54-1876	0.0059	0.0045	f	f	0.0065	0.76	---	---	1.10
SC-55-1844	0.195	0.234	0.0369	0.0187[g]	0.203	1.20	0.19	0.10	1.04
SC-55-1852	0.375	0.386	0.116	0.322	0.370	1.03	0.31	0.86	0.99
SC-55-1856	0.198	0.153	0.0405	f	0.182	0.77	0.20	---	0.92
SC-55-1860	0.109	0.101	0.0316	f	0.100	0.93	0.29	---	0.92
SC-55-1864	0.0537	0.0402	0.0071	g	0.0570	0.75	0.13	---	1.06
SC-56-1877	0.343	0.360	0.0727	0.118[g]	0.337	1.05	0.21	0.34	0.98
SC-57-2223	0.156	0.197	0.0455	g	0.176	1.26	0.29	---	1.13

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[a] Based on ^{148}Nd and thermal FY of 0.0169 (^{235}U).

[b] Based on sum of 101+102 Ru and thermal FY of 0.0924 (^{235}U).

[c] Based on sum of 95+97+98+100 Mo and thermal FY of 0.2451 (^{235}U).

[d] Based on sum of 90+91+92+94+96 Zr and thermal FY of 0.3047 (^{235}U).

[e] Based on sum of 147, 149, 152, 154, Sm and thermal FY of 0.03706 (^{235}U).

[f] Not measured at this time.

[g] Not reliable because of poor FP analysis resulting from massive natural background.

The measured Mo fission product and natural components of the Zone 3 samples are given in Table IV. When compared to the measured quantity of Nd, all samples show a deficiency in Mo (Table V). The fact that a similar Mo deficiency was observed (Maeck et al., 1975) for the samples from Zone 2 indicates that the conditions for Mo migration were probably not localized, and that a similar environment existed for the two reactor zones even though the flux levels and fission densities for the two reactor zones were quite different.

Because the fission density in Zone 3 was ≈ 10 times less than in Zone 2, the abundance of fission product Zr was small relative to the natural component (Table IV). Thus, highly reliable Zr fission product data were difficult to obtain. Two samples (Table V) showed a Zr deficiency with respect to Nd. Partial movement of Zr also was observed for samples from Zone 2.

C. Oklo Paragenesis

The uranium ores of the Colorado Plateau, which formed some 115 to 140 m.y. ago, have been compared to the low grade (U_3O_8 = 0.2%) ore in sandstone-rich layers at the Oklo Mine and elsewhere in the 1 800 m.y. old Francevillien Series in Gabon. Further, Weber (in IAEA, 1975) has pointed out that the uranium deposits of the Oklo Mine may have formed near the Eh(oxidation potential)-pH fence which separates reduced and oxidized sulfur species. Thus at Oklo, most of the uranium ore is found in the reduced sulfur-stable zone where pyrite (FeS_2) occurs, but some uranium is found where primary hematite (Fe_2O_3) plus (SO_4^{2-}) are stable. Similarly, the high-grade ore at Oklo, while it occurs as very rich (to 75% U_3O_8 in places) uraninite (UO_2) in an irregularly mixed shale-conglomerate sequence infilled into a fracture zone surrounded by the lower grade ore, probably formed at Eh-pH, temperature, and pressure conditions close to those for the low grade ore. If the data for the Colorado Plateau uranium deposits are compared to both the low-grade and high-grade ore at Oklo, then the following geochemical conditions are implied: Eh from -0.2 to -0.4 V, pH from 6 to 8.5, T less than 100°C, P less than 300 bars. With respect to Oklo, low-Eh conditions are necessary to account for the presence of both organic carbon and reduced sulfur; the pH range must be above 6 else native sulfur might be a stable phase and none is observed. Below pH = 8.5 authigenic magnetite (Fe_3O_4) should not be present and it isn't. Low temperatures are necessary as evidenced by the preservation of organic carbon, the retention of radiogenic ^{40}Ar in illite, and the fact that illite occurs as the low-temperature, low-pressure 1Md polytype. Pressure due to lithostatic load must also have been low else 1M or $2M_1$ illite would be found in abundance and this is not the case.

Although the paragenesis of the Oklo ores is not well understood at present, it is important that this be rigorously determined as the retention of fissiogenic elements can only be discussed in quantitative terms,once more precise Eh, pH, T, and P estimates are available. At present one can state that during the reactor lifetime, and for some tens of millions of years after, conditions were reducing but possibly close to the oxidized:reduced sulfur Eh-pH boundary, and the pH was about 7 ± 1 else carbonate minerals would have been removed (for lower pH's) or the assemblage magnetite-pyrite would have been noted (for pH above 8.5). Further, if high T and P conditions greater than those for a burial of 3 ± 1 km occurred, then organic carbon, i.e., fossil algae, would probably have been destroyed and 1Md illite would have been transformed to 1M or $2M_1$ varieties which would, in turn, yield K-Ar dates less than 1.8 b.y. That Rb-Sr, K-Ar, and corrected U-Pb dates are all 1.8 b.y. attests to the post-formational stability of the Oklo deposit and the surrounding rocks.

Having thus set limits on these conditions of formation and preservation of the uranium ore and gangue minerals, one can then address the more important problem of reactor product retention and migration at Oklo.

D. Alkali and Alkaline Earth Element Behavior

Although work is under way to determine Eh-pH diagrams for ^{235}U fissiogenic elements and for transuranic elements, only comments on alkali and alkaline earth elements (and for plutonium later) will be made here. Specifically, studies of Rb, Sr, and Ba isotopic systematics have been conducted, and some comments about Cs retentivity can be made as well. There is abundant evidence (IAEA 1975) that alkali and alkaline earth elements have migrated to a large degree from host uraninite grains. However, amounts of fissiogenic Rb, Sr, Ba, and, by inference, Cs are still present in the rocks at Oklo although masked by large quantities of the normal elements. This is important because of the ease with which the alkali and alkaline earth elements migrate in nature. There are no stable sulfides of Rb, Cs, Sr, or Ba in natural environments. Hence, under reducing conditions one would predict migration of these elements (emplaced by fission) at the postulated Oklo Eh-pH conditions. Under slightly oxidizing conditions, i.e., hematite field, barite ($BaSO_4$) and celestite ($SrSO_4$) might be stable. Further, as clay minerals are abundant near or in the high-grade ore, then all of the above elements may be fixed to some degree in these minerals by surface adsorption or by cation exchange.

It is known that the total amounts of Rb, Sr, and Cs (but not Ba) are less than the amounts predicted by fission yield calculations based on knowledge of total U and percent ^{235}U remaining in uraninite-rich samples. In addition the fissiogenic Rb, Sr, and Ba noted has in part been from readily dissolved fractions and not from the insoluble minerals left after leaching experiments; hence, migration out of the ore grains has occurred, but to what degree is uncertain. The migration was probably localized.

Barium studies are of interest because both ^{135}Ba and ^{137}Ba are slightly enriched, and both form from fissiogenic ^{135}Cs and ^{137}Cs, respectively, with very different half-lives. Because these enrichments are noted, it is safe to assume that some fissiogenic ^{138}Ba and ^{133}Cs are present; the former, unfortunately, is predicted to be present in amounts below the limits of analytical uncertainty, and the latter cannot be resolved from normal ^{133}Cs (the only stable Cs isotope). Work is presently under way using milligram amounts of very pure, hand-picked uraninite from which nanogram quantities of Rb, Sr, and Ba can be extracted and their isotopic compositions determined. This will allow more accurate determination of the amounts of fissiogenic Rb, Sr, and Ba still locked within the uraninite as opposed to that which is known to be highly diluted with the normal element component of the gangue. Finally, attempts at "dating" the Oklo ores by the Rb-Sr method have been unsuccessful; the observed scatter of isotope ratio data suggests that addition of normal Rb and Sr occurred after 900 m.y. ago. (This age is the K-Ar date of a dolerite dike which cuts the Oklo deposit). Also, if K-Ar study of youngest generation kaolinite is accurate, then the Rb-Sr systematics may have been disturbed in the last 10 m.y. or so.

The stability of fissiogenic Ba (retained as barite and perhaps by clay mineral adsorption) yields information on the behavior of radium. If Ra had escaped from the uranium ore, it would have been even more effectively scavenged and retained either in sulfates (in the hematite stable Eh-pH range) or adsorbed preferentially to Ba in the reducing (pyrite stable) zone. While of limited application to Oklo, Ra migration would be negligible from this overall, reducing shale environment. Radium behavior is, of course, important in radioactive disposal site selection studies.

E. Plutonium Retention

Frejacques et al. (1975) have demonstrated the formation of ^{239}Pu, ^{240}Pu and ^{241}Pu from uranium at Oklo. Plutonium-239 decay led to formation of radiogenic ^{235}U which is relatively easy to document in zones of highest uranium concentration where one would logically expect most ^{235}U depletion due to fission. Most of the ^{239}Pu returned to ^{235}U during the duration of the reaction which is about 0.6 m.y. Much smaller quantities of ^{240}Pu and ^{241}Pu produced in the reactor are also believed to have remained in place. Inherent in these observations is the stability of Pu in the host uranium ore. In nature, Pu(IV) and U(IV) behave in almost identical fashion. Their ionic radii are similar, and their tetrahydroxides are extremely insoluble. At high temperatures UO_2 and PuO_2 form a nearly ideal solid solution, and similar behavior at low temperatures is to be expected. Consequently, when Pu is produced from U by neutron capture under reducing conditions such as are probable for Oklo, it is easily incorporated into the uraninite structure. More importantly, under slightly more oxidizing conditions (e.g., in going from the pyrite-stable to the hematite-stable Eh-pH range) Pu as PuO_2 or possibly $Pu(OH)_4$ is still stable whereas U(IV) may be oxidized to U(VI) and removed as soluble uranyldicarbonate ion (UDC). Since the Oklo ores are carbonate-rich (dolomite, magnesite, and siderite are present), then migration of U as UDC is likely. This may account for the post-900 m.y. migration of U in the Oklo pit noted by Chauvet (1975), although the U has probably been derived originally from the low-grade ore. For Pu, however, Pu-carbonate complexes do not fall in the Eh-pH stability range for water (at 25°C and 1 bar), and it is significant that whereas the UDC ion possesses two bonded water molecules ($UO_2(CO_3)_2.2H_2O)^{2-}$) the PuDC ion ($PuO_2(CO_3)_2{}^{2-}$) does not, thus indicating the latter to be stable only under high P_{CO_2} conditions in water-deficient environments. There is no reason to suspect that the P_{CO_2} was extremely high at Oklo despite an abundance of total dissolved CO_2 (now present as carbonate minerals), otherwise the siderite ($FeCO_3$) field would totally obliterate the pyrite field. Further, although Pu^{4+} ion disproportionates into Pu^{3+} and $PuO_2{}^{+}$, this occurs only at very low pH values (less than 2), and even then about two-thirds of the total dissolved Pu is still as Pu^{4+}. Hence, over the range of Eh-pH, T and P conditions at Oklo, Pu should have remained in place, and it is noteworthy that this is precisely what is observed. This fact is well documented as Pu retention is calculated to be approximately 100% over a period comparable to the duration of reactor operation. It must, however, be emphasized that the Pu retention at Oklo, probably due to PuO_2 stability, cannot be extrapolated to surface conditions where Pu spillage has occurred in present-day repositories and where Pu as Pu-organic complexes, aqueous species containing Pu(V, VI), and Pu-sorption on colloidal particles must be considered. Nevertheless, the point is made that in a potential burial site in shale under reducing conditions, Pu should be retained even if spillage should occur.

III. OTHER NATURAL REACTORS

A. Geologic Criteria

The discovery of the Oklo natural reactor system has prompted the question: was Oklo unique? The single occurrence of a natural reactor in the earth's history seems unlikely. Geochemical conditions during the middle Proterozoic, between about 1 and 2 billions years ago, were such that formation of very rich uranium deposits was favored on a global scale. Prior to this period, the earth's atmosphere was chemically reducing, e.g., surficial iron tended to the ferrous rather than ferric oxidation state. During the Archean Era and the lower Proterozoic, uranium was not chemically concentrated.

Significant uranium assemblages did occur, however, by placer processes, the so-called quartz pebble conglomerate detrital ore formations. With the advent of procaryotic life forms in the lower Proterozoic, significant oxygen appeared in both the hydrosphere and the atmosphere. During the middle Proterozoic, the appearance of eucaryota accelerated the general oxygenation, eventually causing oxidation of cratonic sediments and massifs. During this transitional period of the earth's chemistry, trace uranium, principally as the tetravalent UO_2 in detrital and crystaline rocks, was oxidized to the hexavalent state and subsequently incorporated into geochemically mobile uranyl complexes. The uranium was then able to migrate and chemically concentrate in sedimentary and metasedimentary terrains. Decaying proterozoa were commonly syngenetic to such terrains and created a chemically reducing environment where the uranium could be reduced to stable uraninite or pitchblende. As part of the uranium geochemical cycle of repeated concentration, mobilization, and redeposition, vein-type uranium deposits were formed in permeable regions of various host formations such as brecciated unconformities or fault zones; the important criterion for vein formation apparently being the existence of structural traps for massive emplacement. The Oklo reactors occurred in such an argillaceous seam of high-grade secondary mineralization within the brecciated primary ore of a stratiform host rock.

The geochemical condition of prolonged and intense weathering, which was in part responsible for the Oklo ore formation, was general during the middle Proterozoic and has apparently only been duplicated one other time during the earth's history, i.e., during the Permian period. The formation of rare, massive uranium mineralization (of thousands of cubic meters with grades of tens-of-percent to nearly 100% uraninite) is almost exclusively limited to this time window of the middle Proterozoic. Indeed, recent uranium exploration activities are heavily weighted in regions of Proterozoic emplacement.

Thus it seems logical that Oklo was not unique but perhaps one of several such occurrences. This supposition is circumstantially supported by the fact that if only one natural reactor existed, then the probability of it being discovered must be vanishingly small. It should be emphasized, however, that a high probability of several (or even many) natural Proterozoic reactors does not mean that chances are good for finding a second Oklo. Indeterminate factors such as geochemical and physical dissemination are important considerations in assessing the probability of other reactors.

Evidence for other natural reactors may be found in undisturbed Proterozoic ore deposits, as at Oklo, or in more recently deposited formations which exhibit slight depletions in fissionable ^{235}U relative to ^{238}U. Initial activities are directed toward surveying rich Proterozoic deposits. These old deposits existed at a time when the $^{235}U/^{238}U$ ratio was high enough to sustain a chain-reacting critical mass under the proper conditions of concentration, thickness, and water moderation.

In specifying the requirements for a natural reactor, we have chosen the least constraining conditions. We have assumed (1) that nature would have optimized the water/uranium ratio (water is an essential ingredient in almost any plausible natural reactor) and (2) that the effects of neutron poisons would have been no greater than those observed at Oklo. These criteria will undoubtedly include some deposits which never became critical but should minimize the possibility of missing a fossil reactor.

The criteria are summarized in Fig. 3 in terms of age of the deposit and the average concentration in a "thick" seam. The solid line divides the field of average uranium concentration vs age into two regions. The points on the line are the lowest critical concentration for an "infinite" size deposit at a particular time in the past. The concentrations are given as of "now", i.e., a correction for radioactive decay of ^{238}U has been included. At any point above the line there is a finite thickness and area of deposit which could go critical under the appropriate conditions. The dashed curve represents a more optimistic case in which the iron found in the Oklo gangue is assumed to be missing. For practical purposes any deposit which lies above the dashed curve deserves analysis if the seam thickness approaches a meter. A deposit which falls above the solid line is a prime candidate for thicknesses substantially less than a meter. The further above the line a deposit falls the thinner it can be, and the more poisons it can have and still have sustained a reaction.

The sensitivity to water is depicted in Fig. 4 where the ^{235}U enrichment required for criticality at constant total uranium concentration is given as a function of the hydrogen-to-uranium ratio. It is assumed that the hydrogen is present as water and that gangue neutron poisons are similar to those found in Oklo samples. Thus, for a large 45% U_3O_8 assemblage with a H/U ratio of 10 to 1, the uranium must have been about 1.8% ^{235}U for criticality. This percent enrichment corresponds to a time 1.1 b.y. ago. If such a formation did go critical, the fissiogenic heat would drive off water (either by boiling or thermal expansion) thus reducing the H/U ratio to the optimum of about 6 to 1 indicated in Fig. 4. Driving off too much water, on the other hand, would tend to reduce the power level thereby permitting water to circulate back into the system, again achieving the optimum H/U ratio. (The water of crystalization of the host rock determines the lower limit for the H/U ratio.) The power level of the Oklo reactor may well have been dynamically controlled by this process. But indeterminant changes in ore concentration, configuration and gangue constraints during criticality would have produced a more complicated operation.

Some rough rules of thumb, derived from the above considerations, are listed below. The average uranium concentration should be obtained only over regions containing 5% or more uranium. In general, samples should come from the highest concentration regions and be identified by age, seam thickness, approximate sample location, and immediately adjoining material. Normally, ten grams of ore sample would be sufficient for planned analyses.

POSSIBLE NATURAL REACTOR SITES

Age (m.y.)	Requirements
0-400	No interest as primary reactor sites
400-800	Relatively pure uranium oxide, massive form (0.5-1 m on side)
800-1200	~0.25-m-thick seam relatively pure oxide; ~0.5 m thick 40% oxide (~1 m thick if high iron)
1200-1600	15-30% oxide, 0.5 m thick (~1 m thick if high iron)
1600-2000	10% oxide, 0.5 m thick (~1 m thick if high iron)
2000-2400	5% oxide, >0.5 m thick
2400	5% oxide, ~0.5 m thick. Although uranium >3000 m.y. old is not described in the literature, we can specify, at 4000 m.y., a lower limit critical size for a relatively pure uranium oxide sphere of ~0.1 m in radius.

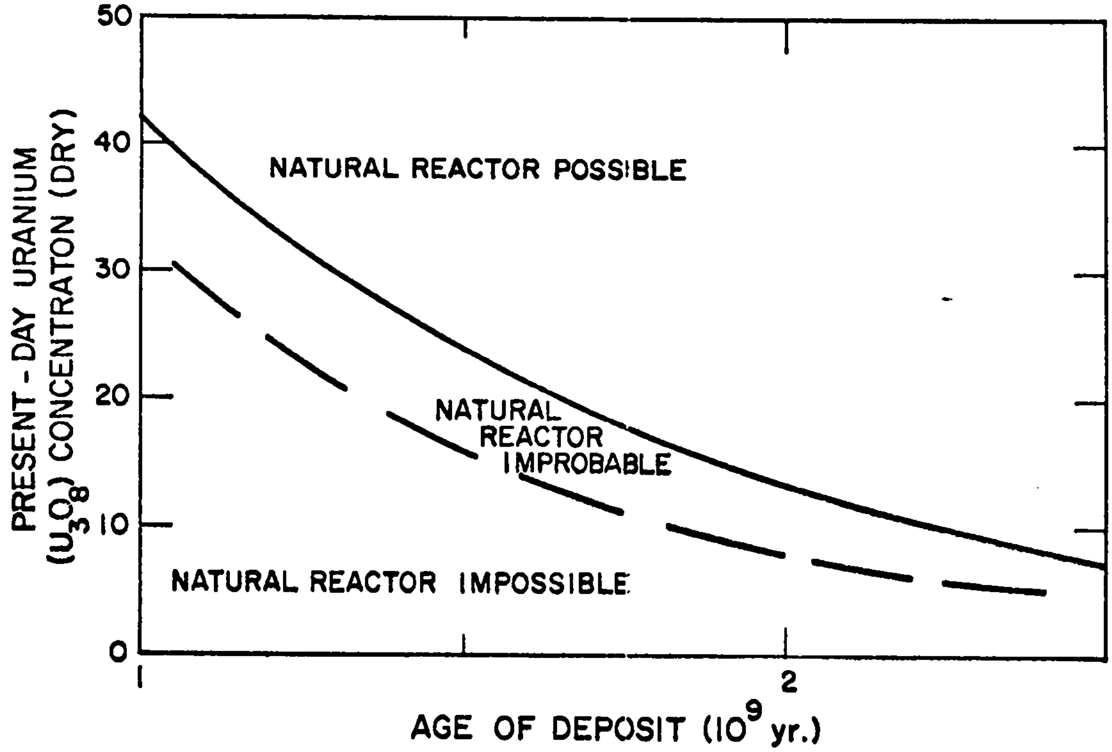

Fig. 3.
Minimum uranium concentration requirements for criticality in an Oklo-like environment expressed as a function of the age of the deposit.

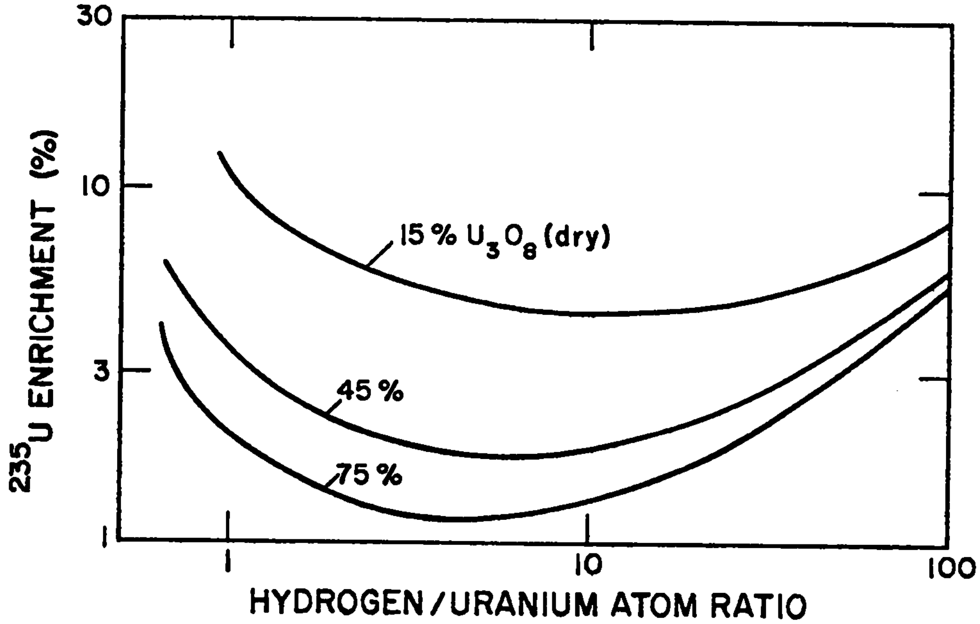

Fig. 4.
Minimum enrichment required for a critical configuration composed of U_3O_8, water, and Oklo-type gangue as a function of the hydrogen-to-uranium-atom ratio.

B. Field Investigations

Initial search activities for other natural reactors have been devoted to the Precambrian shields of northern Canada and northern Australia. The Canadian Shield has been a region of uranium production for over 30 years. More recent exploration activities confirm its economic importance as a major source of uranium. The rich deposits of interest (Beaverlodge, Rabbit Lake, Cluff Lake, and Key Lake) are found along the perimeter of the Athabasca Sandstone formation or in the Beaverlodge district. Most of the ores in this area are structurally-controlled, authigenic vein-type uraninite deposits, and the aforementioned deposits reportedly have lenses of massive uraninite (e.g., 50% U_3O_8 or greater) with volumes larger than a cubic meter. The ores are generally younger than their host formations, but dates of mineral emplacement are not always well known. The Cluff Lake ore body has been tentatively dated at 1.1 b.y. which is similar to the 1.1 to 1.2 b.y. date given for Rabbit Lake. The Key Lake deposit is presumably of similar age. Initial age of mineralization for the Beaverlodge deposits, however, is given as 1780 m.y., comparable to the mined-out Port Radium deposit of the Canadian NWT and to the Oklo mineralization.

Formal contacts have been made with appropriate officials for obtaining permission for either conducting field measurements or collecting samples at the Canadian ore bodies under consideration. The Canadian Ministry of Energy, Mines and Resources has been apprised of our program, and we are working in conjunction with people in the Canadian Geological Survey, Environment Canada, the Atomic Energy of Canada Limited, and the Saskatchewan Geological Survey. Our fossil reactor search activities are conducted bilaterally pursuant to Canadian regulations and interests. Approval has been obtained from four major uranium exploration and development companies operating in northern Saskatchewan: the French based Amok Ltee., who are developing the Cluff Lake ore deposit; the German owned Uranerz Exploration and Mining Ltd., developing Key Lake; Gulf Minerals Canada Ltd., who operate the Rabbit Lake mine; and the Crown Corporation Eldorado Nuclear Ltd. of the Ace-Fay mine and exploration activities in the Beaverlodge district.

During late summer of '76, reconnaissance trips were made to northern Saskatchewan in order to gain specific information on the ore formations, mine models, sample and core libraries, and logistics of an actual field analysis mission. During the fall, it is anticipated that a field expedition can be coordinated for purposes of identifying possible fossil reactors. Samples will be analyzed for $^{235}U/^{238}U$ isotopic anomalies with the interrogative fission detection system described elsewhere in this report.

Recent uranium discoveries in the Northern Territory of Australia are likely candidates for fossil reactors. The ore deposits of the Precambrian Pine Creek geosyncline near Darwin (namely Narbarlek, Jabiluka, Ranger, El Sharana and Koongarra) are important new economic discoveries. Uranium mineralization of the Pine Creek geosyncline occurs in sedimentary and metasedimentary terrain which has been compared to the Francevillien formation at Oklo. The age of the host rock is about 1.8 b.y. Although dates of ore emplacement are not generally known, they are thought to be middle Proterozoic. Efforts to gain access to the Australian NT uranium ore bodies for investigative purposes are in initial states. Communications with the Department of Natural Resources (Australian) and the Australian Atomic Energy Commission have been established, and authority for field investigations has been requested from Pancontinental Mining Ltd. and Poseidon Ltd. During late summer '76, Dr. G. A. Cowan of LASL made the necessary personal contacts with Australian Government and mining officials and reconnoitered the uranium ore deposits of the Northern Territory. It is anticipated that further sampling and analysis missions will occur in 1977.

Other Precambrian shield uranium ore formations are, of course, important. The large Congo Craton, of which the Francevillien formation is a part, may host evidence for another fossil reactor. By analogy, the San Francisco Craton of eastern Brazil is an important possibility. Indeed, at the time of the Oklo criticality, the San Francisco and Congo Cratons were united in what was then central Gondwanaland. It is reasoned that the Brazilian terrains would have experienced geochemical conditions similar to those responsible for Oklo. Our investigations do not yet include these locations.

C. U Ore Survey

In order to survey the possibility of the occurrence of other obvious fossil reactors in other parts of the world, 33 ore samples from known rich uranium deposits were obtained by LASL from the Harvard Geology Library. The predominant sources of these samples were Canada, Africa, and Australia. The samples analyzed, the $^{235}U/^{238}U$ isotopic ratio, and the measured U concentration are given in Table VI. Concurrent with these analyses, 11 natural U

TABLE VI. U ANALYSIS OF SELECTED RICH ORES

Sample		Location	wt. % U	at. % ^{235}U
3.1	Pitchblend	No. Territory, Aust.	66.7	0.7196
3.2	U-ore	Eldorado Mine, Canada	45.1	0.7173
3.4	Pitchblend	Great Bear Lake, Canada	12.9	0.7188
3.5	Pitchblend	Great Bear Lake, Canada	39.3	0.7191
3.6	Uraninite	Athabaska Mines, Canada	39.8	0.7220
3.10	Pitchblend	Martin Lake, Canada	32.6	0.7196
3.14	Uraninite	Chinkolowbe, Congo	74.5	0.7184
3.15	Pitchblend	Great Bear Lake, Canada	22.0	0.7202
3.17	Pitchblend	Adelaide River, Aust.	0.1	0.7210
3.18	Davidite	Portugese E. Africa	7.4	0.7221
3.19	Pitchblend	Great Bear Lake, Canada	20.8	0.7199
3.20	Uraninite	Hardisty Lake, Canada	30.2	0.7209
3.24	Thucolite	Besner Mine, Ontario	1.4	0.7176
3.25	Pitchblend	Beaverlodge, Canada	29.1	0.7218
3.26	Uraninite	Wilberforce, Canada	34.6	0.7186
3.27	Uraninite	Wilberforce, Canada	56.2	0.7086
3.28	U-ore	Nunn Lake, Canada	46.8	0.7220
3.30	Pitchblend	Great Bear Lake, Canada	28.5	0.7181
3.38	Uraninite	Algoma Dist. Canada	36.3	0.7169
3.42	Uraninite	No. Territory, Aust.	70.7	0.7184
3.43	Uraninite	Pled des Nouts, Canada	16.6	0.7201
3.44	Uraninite	Chinkolowbe, Congo	70.3	0.7166
3.46	Becquerelite	Katanga, Congo	37.8	0.7202
3.47	Uraninite	Rio Grande de Norte, Brazil	60.2	0.7173
3.48	U-ore	So. Australia	2.2	0.7224
3.49	Uraninite	Transvaal	38.7	0.7192
3.52	Uraninite	So. Africa	45.4	0.7186
3.55	Uraninite	Kasolo, Katanga	69.5	0.7192
3.59	Pitchblend	Kasolo, Katanga	69.4	0.7202
3.61	Uraninite	Wilberforce, Canada	58.1	0.7155
3.62	Uraninite	Gordonia, SW Africa	58.7	0.7205
3.63	U-ore	Great Bear Lake, Canada	46.7	0.7205
3.65	Uraninite	Theano Pt. Area, Canada	55.8	0.7200
	NBS standards (n=11)		$\bar{x}$	0.7192
			σ	0.0013

standards were also processed. While the magnitude of the standard deviation for the 30 field samples exceeded that of the control standards (0.18%), no value exceeded the 3σ limit. Although the precision of these measurements is not sufficient to eliminate the possibility that some of these samples represented other fossil reactors, it is certain that no obvious fossil fission reactors of the Oklo type were represented.

Unfortunately the lack of an observed depleted ^{235}U sample does not preclude the occurrence of a natural fission reactor for two reasons. First, it is possible that the reactor could have operated in a near breeder mode such that the amount of ^{239}Pu produced and decaying to ^{235}U is equal to the amount of ^{235}U fissioned. Second, it is possible that wide dispersion of a fossil reactor remains could be masked by the relatively large amount (1-3 ppm) of uranium which occurs in nearly all geologic specimens. To minimize the possibility of overlooking such cases, the measurement of selected fission product elements will be conducted; in particular, the isotopic measurement of Ru. This element is highly suited as a monitor for fossil reactor remains because the natural occurrence of Ru in the earth's crust is very small, being approximately one part in 10^9. Thus, the isotopic composition of naturally occurring Ru could be significantly altered if contaminated with fission product Ru whose isotopic composition is significantly different from that of natural. A large number of the rich ore samples listed in Table VII will be analyzed for Ru.

IV. ANALYTICAL DEVELOPMENTS

A. Bi and Th Procedures

Bismuth-209, the end product from decay of ^{237}Np and ^{241}Pu, and thorium-232, the long-lived decay product of ^{236}U, were of particular interest in the Oklo mine because of the light they could shed on neutronic and migration behavior of that environment. A simple cleanup procedure for bismuth has been developed which effectively eliminates any interference in quantitative determination with the atomic absorption spectrometer. The Bi is adsorbed on a short anion column from an HCl solution, washed first with concentrated HCl and then with diluted HCl to remove Fe, Pb, U. The Bi is eluted with 1 F H_2SO_4 and is ready for the spectrometer.

This procedure was applied to Oklo samples 1178, 1182, 1187, and 1421/5, with the following results: 113 ppm, 65 ppm, 121 ppm, and 1.2 ppm Bi, respectively. These results are in good qualitative agreement with less precise results obtained from arc-spark mass spectrometric analysis of Bi by the subcontracted Accu-Labs, thus giving us confidence in both Bi and Th results by them for twenty-two Oklo ore samples.

B. Ru Determinations

The average ruthenium content of the earth's crust is thought to be very low (≃1 ppb), but it is relatively abundant as a fission product. Therefore it is a potentially valuable indicator for fission processes in nature. We are developing a capability for Ru analyses via traced mass spectrometry, which will provide us with the amount of each isotope of Ru present in a sample, at a level of about 10 ng of Ru. The two facets of this procedure, i.e., preliminary separation and purification and the mass spectrometric analysis, are discussed separately.

1. Chemical separation. The first investigations were concerned with dissolving techniques on various ores without losing any volatile ruthenium oxide in the process. It was found that conc. HCl, conc. HNO_3, aqua regia (4 to 1), or H_2SO_4 could be used with boiling without losing Ru. Fuming HNO_3 volatilizes Ru as does fuming $HClO_4$. It was also found that Ru as an anion does not sorb on a cation column (Dowex 50 x 8, 100-200 mesh) in very dilute HCl (.01 M), whereas most other elements are held under these conditions. Ru can also be converted to a cation and as such will adsorb on a cation column. Washing with dilute HCl (0.5 M) will not move the ruthenium, but it can be quantitatively removed with 4 M HCl. The combination of using Ru as an anion and then as a cation constitutes a very effective decontamination procedure using only cation columns. However, it has not yet been satisfactorily demonstrated for actual geologic samples, even though the procedure worked well for tracer and carrier Ru.

So far, samples of three ores (3.63, 3.14, and 3.44)* have been prepared for mass spectrometry but results are not yet available. Oklo sample 404-4 (which has several hundred ppm Ru) was run several times, and the procedure was very satisfactory for isotopic analysis. However, samples with low Ru content (e.g., 0.1 ppm) may have interferences from contaminant species. Samples 3.14, 3.44, and 3.63 did not have ^{106}Ru added, but stable ^{96}Ru instead, so that the chemical yield will be measured by mass spectrometry rather than by radioactive tracer. The ^{96}Ru-spiked samples were run through two cation columns without changing the Ru to a cation in order to determine if this treatment is good enough for mass spectrometry purposes.

An alternate Ru chemical separation technique is currently being tested at INEL. The technique involves distillation of Ru as the tetroxide from

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*3.14 and 3.44 are pitchblende from Chinkalowbe, Katanga, Zaire, and 3.63 is an altered ore from Eldorado, Great Bear Lake, Canada.

sulfuric acid using sodium bismuthate as the oxidant. When using very clean glassware, 5 ng or less of Ru can be distilled. Ore interference in this method involves the presence of large quantities of Pb which precipitate as lead sulfate in the distillation flask resulting in excessive bumping. Improvements in the design of the distillation flask are being investigated. A final ruthenium separation procedure has not yet been selected pending completion of research activities at LASL and INEL.

2. Mass spectrometry. Our objective for ruthenium analysis was to develop a procedure capable of measuring the isotopic ratios of ruthenium isotopes relative to mass 99 with an accuracy of at least 0.5%. The procedure should permit measurement of samples as small as 10 ng of Ru.

Two problems had to be solved before precise measurements were possible. The first was the presence of high organic background from the prepared samples. It was found that heating to 250°C for 5 minutes in air during sample loading was sufficient to destroy the organics, provided no colloidal resin is washed through on the chemical separation. The second problem was caused by high molybdenum backgrounds in the Re filaments. Acid leaching, high-temperature bake-out, and the use of single-crystal zone refined rhenium all failed to produce the desired spectral purity. In addition, Pt, W, Ta, Pt-W, and Ir filaments were tested. Only iridium was found to be free of molybdenum contamination. However, the iridium was found to contain natural ruthenium contamination. It was determined that five leachings with hot fuming nitric acid would eliminate the surface ruthenium contamination. A ruthenium-free spectrum can be maintained up to temperatures of 1850°C. At this temperature ruthenium migrates to the surface from the interior. We are presently attempting to locate a source of high-purity iridium. Oak Ridge National Laboratory has material under assay now which may be completely ruthenium-free and is available to us if the assay confirms the absence of ruthenium.

We have measured one Oklo sample, No. 404, which was chemically separated by the LASL procedure outlined above. The measured and theoretically predicted values are as shown below. The predicted values represent fission yields corrected for neutron absorption affects. The measured values have not been corrected for a natural isotopic component which is known to be under 1% for each fissiogenic Ru isotope.

Ruthenium Isotope	Atom Percent Theoretical	Atom Percent Measured
99	34.0	32.2
100	.179	.119
101	28.3	28.5
102	24.2	25.5
104	11.7	12.5

These values suggest that some filament fractionation may be occurring. We have ordered pure ^{96}Ru and ^{104}Ru to prepare known standard mixtures for evaluating absolute measurements.

In collaboration with the Ru mass spectrometry studies being conducted at LASL, Ru mass spectrometric procedures are being developed at INEL. To date, several isotopic measurements have been obtained for Ru separated from rich U ores. The observed isotopic ratios represent neither natural Ru nor Ru from thermal-neutron fission of ^{235}U. The observed isotopic composition probably results from the poorly characterized spontaneous fission of ^{238}U. Studies are continuing to obtain reliable spectrometric measurements from 10-ng Ru samples; a major problem being interference by Mo which may result from the separation procedure and/or a mass spectrometer filament phenomenon.

C. Pd and Te Determinations

Because the isotopic composition of Pd produced by the thermal fission of ^{235}U and ^{239}Pu varies significantly from the fast fission of ^{238}U, the measurement of the isotopic composition of Pd may provide a means for the differentiation of the sources of fission. To date, no mass spectrometric measurement of fission product Pd by thermal ionization mass spectrometry has been reported. Investigations at INEL have shown that ng quantities of Pd can be measured by thermal ionization mass spectrometry using the silica gel technique. This technique involves drying a slurry of silica gel on the filament followed by the addition of the sample which is then dried. A drop of phosphoric acid is dried on the filament which forms a glass-type matrix containing the sample.

At low levels of Pd (< 50 ng) interfering peaks are observed. At this time the source is unknown, and a systematic study of the silica gel, phosphoric acid, and chemical separation procedure as sources of contamination is in progress. The separation method being investigated is solvent extraction using dimethyl glyoxime followed by an ion exchange cleanup step.

Initial measurement with 250 ng of Pd on the filament gave the isotopic composition shown below. Also given are the Chart of the Nuclide values.

	Pd Mass Numbers					
	102	104	105	106	108	110
INEL values	1.02	11.06	22.49	27.11	26.42	11.90
Chart values	1.0	11.0	22.2	27.3	26.7	11.8

Like Ru, Te is very rare in nature and may also serve as a monitor for fossil fission reactors. Using the silica gel technique < 50-ng quantities of Te have been measured using thermal ionization mass spectrometry. Development studies relative to the chemical separation technique and the mass spectrometric measurement are in progress at INEL.

D. Nd Cross Sections Significant parameters in the calculation of the neutron flux and age of the Oklo Phenomenon are the value for the ^{143}Nd and ^{145}Nd thermal and resonance capture cross sections. At the Oklo Conference, we reported a ^{143}Nd thermal cross section value which differed significantly (Maeck, et al., 1975) from other measurements. Because of the importance of this value, it was suggested that additional measurements were justified to resolve the discrepancy. Two techniques for measuring the ^{143}Nd and ^{145}Nd cross sections exist at INEL. One involves a reactivity measurement using a critical assembly and relatively large amounts ($\simeq$ 100 mg) of pure separate isotopes. Although this is a sensitive technique, it is not without problems. The major problems are the H_2O content of the specially prepared samples and the stoichiometry of the target material. It was felt that an extensive effort would be required to obtain an acceptable value using this technique.

It was concluded that the more conventional technique of irradiating separated isotopes in a thermal reactor, both bare and Cd-covered, would probably be the best approach. To aid in this work, we will enlist the help of the Physics Branch of INEL for the preparation of highly enriched samples of ^{143}Nd and ^{145}Nd using the mass separator. Microgram quantities of 99.99% enriched isotopes can be produced by this group as can flux monitoring standards.

E. U Studies

Because of the discovery of the natural reactors at Oklo we have a strong interest in the variability of uranium isotopic composition in nature. At a meeting held in Los Alamos, September '75, it was agreed that ore samples should be solicited from members of the geological community for the purposes of further studying the variability of $^{235}U/^{238}U$ in nature and possibly identifying another natural reactor site. We agreed to purify 5- to 10-g U samples for precision gas mass spectrometry at Oak Ridge and to carry out our own, less precise, surface ionization measurements on such samples. A number of ore samples have been received and our work with them is discussed below.

1. Precision mass spectrometry. Development has begun on a procedure capable of measuring the ^{235}U to ^{238}U ratio in natural uranium with a precision of 0.01 to 0.02%, relative. To accomplish this by thermal ionization mass spectrometry requires (1) improvement of the precision of the measuring circuit and (2) elimination of the error component due to filament fractionation.

The electron multiplier on the Avco instrument was replaced with a cubic suppression Faraday-cup collector to improve the precision of the measurement circuit. This collector provides a more reproducible geometry and better suppression of secondary electrons. A systems calibration was run using uranium isotopic standards. Over a range of 235/238 rations of 0.1 to 10 the system was linear with a 1σ precision of 0.105% relative. It is anticipated that this precision can be improved as filament loading techniques are more rigidly standardized.

A major portion of the remaining error component has been shown by W. Shields and others to be due to uncontrolled variation of the filament fractionation. To eliminate this error component we are preparing an internal normalization spike consisting of equal atom quantities of ^{233}U and ^{236}U. At the present time we have analyzed the ^{236}U starting material. It contains 0.15% ^{235}U which will have to be corrected out of the measured ratio. We are awaiting delivery of the high-purity ^{233}U from Oak Ridge. When the spike has been received and evaluated, an equal atom mixture will be prepared for addition to each sample. A large quantity of NBS-9502 has been dissolved and will be utilized after spiking to test the precision of the normalized measurement. A similar study will be conducted using the Teledyne instrument to determine the limits of the procedure on sub-microgram samples.

2. U ore samples. During the last year we have received 104 ore samples, 17 of them from Oklo and the remainder either as possible natural reactors or for investigation of small variations in the worldwide $^{235}U/^{238}U$ ratio. These samples were logged and the gamma specific activity was determined for most of them as a means of estimating the U content. Portions of 61 of the samples were ground; several batches for some where use was high. Of the non-Oklo ores, five were dissolved and 30 were leached for total U, $^{235}U/^{238}U$, and Ru analyses.

The first potential natural reactor sample received was from Cluff Lake (Saskatchewan, Canada), and portions of it were sent to INEL for U, Ru, Zr, and La analyses and to Accu-Labs for elemental analyses from Li to U via spark-source mass spectrometry. Several aliquots of this sample were dissolved, and the total U was determined to be 26.5% with a normal $^{235}U/^{238}U$ ratio as determined by mass spectroscopy. Uranium from a larger sample of this ore was sent to Oak Ridge for gas mass-spectrometry determination of the $^{235}U/^{238}U$ ratio. The observed result is 0.7109 wt %, which is normal.

The remainder of the non-Oklo samples which have been examined were almost entirely from those selected from the Harvard Museum collection. The selection includes 35 possible natural reactors and 32 ores for $^{235}U/^{238}U$ world surveys. Many of these ores have been photographed and aliquoted, and several have been reserved for further study. Portions of ground material from 33 possible nuclear reactors were sent to INEL for U analysis; recently larger portions of 12 of these were sent for Ru analyses. Aliquots of 16 of these same ores were sent to Accu-Labs for elemental analysis, Li to U, and determination of the $^{147}Sm/^{149}Sm$ and $^{151}Eu/^{153}Eu$ isotopic ratios. These ratios are sensitive to the presence of neutrons in the material because of the large neutron capture cross sections of ^{149}Sm and ^{151}Eu. Data received from both Accu-Labs and INEL do not appear to indicate another Oklo among these ores.

Thirty of the possible nuclear reactor ores have been leached by the procedure described below and are being analyzed for total U and $^{235}U/^{238}U$. To date, 17 uranium samples have been chemically separated and are awaiting mass-spec analysis. Final data have been obtained for one sample; a uraninite from Alligator Gorge in Australia was found to have a normal U isotopic ratio (within the $\approx 0.5\%$ accuracy of the system) and contain 75% U. When all of the reactor candidate ores have been processed, work will continue on the world survey ores using the more accurate "double spike" mass spectrometric U analysis method.

Since the standard dissolving procedure used in these studies is known to remove Ru, which is important in the search for natural reactors, it was necessary to develop the capability of dissolving the ores with essentially quantitative yields for Ru, U, etc. The procedure now in use is based on the INEL method of heating with a solution which is 8M HCl and 1.5M HNO_3. In most cases any remaining residue can be broken down by treatment with HF. A number of final residues have been checked for U, and the maximum found so far is less than 0.1%. The U content of a number of other residues is being measured. Examination of the behavior of Ru in this leach method has indicated no measurable Ru loss.

Since an element with such low natural abundance as Ru is of interest and since elements of possible interest cover the periodic table, it is desirable to minimize contamination during grinding of the ores. Possible sources of contamination include contamination from the grinding device itself, cross-contamination from samples ground in the same device, and contamination from other containers and handling devices. The mullite mortars and pestles which were originally used in these studies are no longer available. Alumina is not used because of high contamination and because the rough, porous surface gives cross contamination. Tungsten carbide is not used because of the Co binder which may be a source of Ru. The best materials appear to be agate and silicon carbide (which has no binder), and both materials are currently employed. The mortars and pestles are "dry cleaned" before use by first grinding and discarding a small portion of the material of interest. Metal grinding materials, screens, and scrapers are not used in the grinding process.

3. In-situ $^{235}U/^{238}U$ measurement system. In order to facilitate the search for other natural reactors we have begun development of a field instrument for measuring the ratio of $^{235}U/^{238}U$. It would be most desirable to measure the ratio on raw ore cores or samples, and preliminary trials indicate this may be feasible. As a backup, we are developing a procedure involving chemical purification of small amounts of uranium followed by γ-ray spectrometry.

It appeared that the ratio of ^{238}U to ^{235}U in rich ores could be determined with 10% accuracy by counting fission fragments from ores exposed to a neutron source. The measurement would involve first exposing the sample to an unmoderated source of neutrons and then to the same source moderated by adding water to the systems.

An apparatus was designed and built which accomplishes this measurement, and a series of foils of known $^{235}U/^{238}U$ content was used for calibration. The range of ratios used was from the natural abundance of 138:1 to a ^{235}U depleted ratio of almost 400:1. A straight line fit the data giving a line of calibration $Y = -0.0113\ X + 7.86$ where X is the $^{238}U/^{235}U$ ratio. A 10% measurement appears to be well within the capability of this instrument, certainly for the samples investigated so far. A 1-mg ^{252}Cf source is being purchased which will give ten times the fission-fragment count rate presently available. A statistically accurate $^{238}U/^{235}U$ ratio can then be obtained in 10 minutes with this source.

The same moderated/unmoderated technique was used for trials of a detection system based on counting delayed neutrons from fission. The sensitivity of this method was not as good as the fission counting instrument.

A simple uranium separation/purification procedure has been developed which permits gravimetric determination of total uranium and γ-ray spectrometric measurement of ^{235}U. The procedure involves uranium purification with an ion-exchange column, followed by precipitation of uranium as the hydroxyquinoline, weighing, and γ-ray counting. For samples containing about 10 mg of U, $^{235}U/^{238}U$ isotopic ratios of 2% precision can be determined for eight or more samples a day. The simple nature of the technique and the use of a single channel NaI (Tl) spectrometer are thought to be compatible with a field operation.

4. ^{226}Ra equilibrium studies. The degree of disequilibria of ^{226}Ra with its ^{230}Th, ^{234}U and ^{238}U parents in various uranium ores is of interest as a source of information on the long-term migration rates of ^{226}Ra and ^{230}Th relative to U. It would be expected that the behavior of ^{226}Ra would be somewhat similar to ^{90}Sr.

We have found it feasible to make such measurements with a Ge(Li) gamma-ray spectrometer, but samples must be preconditioned to contain the ^{222}Rn daughter of ^{226}Ra and then allowed to sit while the daughter chain grows into equilibrium.

5. ^{239}Pu equilibrium studies. In rich uranium ores, the neutrons from spontaneous fission of ^{238}U can (1) migrate from the region of interest, (2)

be absorbed by accessory elements, (3) induce ^{235}U fission, or (4) be absorbed by ^{238}U causing fission or more likely γ-ray emission. The latter reaction, $^{238}U(n,\gamma)$, yields β-unstable ^{239}U, ^{239}Np, and eventually $^{239}Pu(t_{\frac{1}{2}}=2.44\times10^{4}y)$. Given time periods on the order of >0.1 m.y., ^{239}Pu will come to some state of atomic equilibrium with ^{238}U. The equilibrium ratio will depend on the geometry of the ore formation and its richness with respect to other neutron absorbing/moderating elements. In the limit of a large ore body and a minimum of neutron absorbing elements, the $^{239}Pu/^{238}U$ atom ratio is approximately 5×10^{-12}, whereas values of 1 to 3×10^{-12} would be more typical for actual deposits.

A portion of the Cluff Lake ore (11 g) was analyzed for ^{239}Pu as a preliminary measurement to examine the feasibility of studying disequilibrium of plutonium in uranium ores. It was found to have an atomic ratio of about 6×10^{-13} $^{239}Pu/^{238}U$. Without knowing the deposit's geometry and accessory elements, it is impossible to extract quantitative information pertaining to the relative stabilities of plutonium vs uranium in this system. It would appear, however, that there is less Pu in the ore than would be expected. These measurements demonstrate the feasibility of Pu/U equilibrium measurements, and future activities will include the correlation of predicted versus measured Pu/U ratios for ore systems of known geochemistry. By this technique, demonstrated natural experiments of plutonium geologic isolation will be studied.

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PUBLICATIONS

For the period of this report, the following professional communications have been made for Oklo studies:

R. D. Walton and G. A. Cowan, "The Relevance of Nuclide Migration at Oklo to the Problem of Geologic Storage of Radioactive Waste," in The Oklo Phenomenon, IAEA-SM-204/1, 1975, pp. 499-507.

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APPENDIX A

OKLO PARAGENESIS

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I. LOW-GRADE ORE FORMATION

Weber (1969) and Weber et al. (1975) have pointed out the similarities between the uranium deposits of the Oklo mine, Gabon,and those of the Colorado Plateau, United States. Further, Weber (ibid.) has argued for formation of the Oklo ores in a primary "roll-type" fashion (i.e.,analogous to Wyoming or Texas deposits). Due to its extreme age of 1.8 billion years plus tectonic disturbances (i.e., tilting, folding, fracturing followed by localized uranium redistribution) it is impossible to speculate as to the geometry of the original mineralization. Indeed the entire "Couche 1" at Oklo appears to be mineralized in a disseminated fashion as opposed to either roll or lensoid zones of mineralization noted in Wyoming and New Mexico, respectively. The picture is complicated not only by the formation of the high-grade reactor ore at Oklo (which is treated separately in this report) but also by uranium redistribution since at least 900 m.y. ago (see Chauvet, 1975). As similar redistribution may have occurred prior to 900 m.y. ago, then possibly one is presently observing a system mineralized some 1.8 b.y. ago which has been undergoing redistribution, etc. since then. A further complication is that there is a paucity of data concerning the distribution of the elements molybdenum, selenium, vanadium, arsenic and their host phases at Oklo, while such information is more readily available for the Colorado Plateau deposits. Data for these elements and their host minerals are even more valuable in discussing the Wyoming-type deposits (see Cheney and Trammell, 1973) which can then in turn be extrapolated to somewhat older deposits in New Mexico (Brookins, 1976a). Without knowledge of the distribution of these minor phases, it is difficult to speculate on the Eh-pH conditions for formation of the deposits. However, the presence of organic carbon (i.e.,fossilized algae), dolomite,and clay minerals (especially illite and chlorite) makes some comparisons possible.

Weber (1969) and Pfiffelman (1975) mention volcanic detritus as a probable source of uranium for the mineralization at Oklo as opposed to derivation of the uranium from weathering of the granitic rocks bordering the Francevillien Basin. Certainly both could have contributed uranium to the system, but appreciable uranium can be more readily leached from fine-grained silicic volcanic detritus than from granitic detritus. For example, in the Grants Mineral Belt (Colorado Plateau) Brookins (1976b) mentions syngenetic Rb-Sr ages on volcanic-derived montmorillonite while granitic grains have retained their 1.3 to 1.4 b.y. age of formation. The relevance of this to Oklo is that it is probable that the low-grade mineralization may have occurred by a series of reactions involving minerals derived through the abundant fossil algae, and uranium leached from the volcanics or their derivatives (presumably as uranyldicarbonate ion (UDC) since the presence of dolomite attests to the high dissolved CO_2 content of the mineralizing solutions). Organic acids affect most rock-forming silicates but are especially effective in causing reactions involving montmorillonite destruction, less effective on detrital illite, and usually cause, rather than alter, chlorite to form. As an overall low Eh is likely, then a net reaction may be written:

$$\text{UDC} + \text{Montmorillonite} + [(\text{Al},\text{Fe});(\text{HA})] + (\text{HS}^-) \tag{A-1}$$
$$\text{uraninite} + \text{pyrite} + \text{illite} + \text{chlorite} + \text{C} + (\text{H}^+)\ .$$

Original humic acid (HA) linked to Fe(II,III), Al(III), or other cations in authigenic montmorillonite, reacts in the presence of (HS^-), although in theory no oxidant other than reduced C is necessary, resulting in the formation of the assemblage: uraninite (+ coffinite) + pyrite (plus other sulfides) + illite + chlorite + C + (H^+). The (H^+) produced is effectively buffered by the dolomite present. Further, siderite formation may scavenge Fe(II) before incorporation into pyrite.

Of special interest is that Weber et al. (1975) do not mention montmorillonite in their reports, yet this mineral almost certainly must have been produced by the weathering of volcanic detritus; the usual sequences:

volcanic detritus → "bentonite" → montmorillonite → 1Md illite (A-2) may well have occurred. Further, the dominance of 1Md of the illite polytypes is strange. For the 1.3 to 0.8 b.y. unmetamorphosed Belt Series in the United States the sequence:

$$1Md \rightarrow 1M \rightarrow 2M_1 \qquad (A-3)$$

as a function of burial is well documented (Maxwell and Hower, 1967). Possible explanations are: (1) The burial was so slight that, although montmorillonite was destroyed, 1Md illite did not undergo transformation to more ordered polytypes. This is consistent with the K-Ar work of Bonhomme et al. (1975) who have determined essentially concordant K-Ar and Rb-Sr dates on the 1Md illite. (2) This age agreement not only indicates a very low temperature (<150°C) due to burial beneath about 2 to 4 km of sediments, but postmineralizing solutions must have had minimal effect on the rocks otherwise cation exchange in a carbonate-rich environment would certainly cause age perturbations in the Rb-Sr systematics (Kulp and Engels, 1963) if not on the K-Ar dates. (3) It is conceivable that 1Md illite was formed from volcanic detritus directly without montmorillonite formation; the activity-activity, i.e. for log $[(Mg^{2+})/(H^+)^2]$ vs log $[(K^+)/(H^+)]$, diagrams of Helgeson et al. (1969) indicate that montmorillonite only appears in appreciable quantities at 1 atm pressure at T=60°C and higher temperatures. (4) Further, the abundance of organic acids may have promoted chlorite formation directly from montmorillonite, i.e., the log $[(K^+)/(H^+)]$ values may have fallen below the illite stability field during early diagenesis. (5) Finally, montmorillonite originally present may have been altered to 1Md illite and both to chlorite in the first 100 m.y. years or so of the Oklo deposit, so that little if any evidence for original montmorillonite now exists.

Although the above arguments pose more questions than answers they suffice to emphasize the importance of closer examination of the clay minerals plus cogenetic minerals in non-uraniferous, low-organic carbon rocks of the Francevillien Series. Further, kaolinite formation in relatively recent times may have destroyed all of the montmorillonite left, then illite and some chlorite. This speculation is applicable to the high-grade ore where kaolinite is more abundant (e.g., lower log $[(Mg^{2+})/(H^+)^2]$ and $[(K^+)/(H^+)]$ ratios due to lower pH). This hypothesis can readily be tested by examination of rocks from outside the mineralized areas although this has not yet been done.

II. SIGNIFICANCE OF CARBONATE MINERALS

Carbonate minerals, especially dolomite ($CaMg(CO_3)_2$), are abundant in the Francevillien Series (Weber et al., 1975). Dolomite, magnesite ($MgCO_3$), and siderite ($FeCO_3$) have been reported from the reactor zone ores and elsewhere by Geffroy et al. (1975). The importance of the carbonate minerals is: (1) A relatively high amount of dissolved CO_2 is indicated. (2) Mg-rich solutions are indicated. (3) Relatively low total dissolved sulfur is indicated.

A. Dolomite. Berner (1971) has pointed out that dolomite is common in ancient sedimentary rocks but, with the exception of dolomitization accompanying evaporite formation, precipitation of dolomite from modern sea water has not been demonstrated. This is difficult to understand because modern sea water is supersaturated with respect to dolomite; Berner (1971), for example, points out that for the reaction:

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2\ CO_3^{2-}\ , \qquad \text{(A-4)}$$

that the solubility product is 10^{-17} while the ion activity product for modern sea water is 10^{-15}. Further, dolomite is more stable in sea water than calcite (Berner, ibid.). For the Francevillien Series it is possible (if not probable) that, due to a higher total dissolved amount of CO_2 (in turn partly controlled by lower oxygen in the atmosphere at 1.8 b.y. ago) that the degree of supersaturation was even greater such that dolomite precipitation was facilitated. This in turn implies a greater stability field for dolomite but not necessarily a drastic shift in pH from the modern sea water value of 8.4. Von der Borsch (1975) has further pointed out that dolomite stability is greater under conditions of both higher Mg^{2+}/Ca^{2+} ratios than that for modern sea water and higher pH values.

B. Magnesite. Magnesite at Oklo, especially in the reactor zones, poses some interesting constraints on mineral paragenesis at Oklo. First, the amount of Mg^{2+} in solutions accompanying magnesite formation must be relatively high so that a hypothetical reaction such as:

$$CaMg(CO_3)_2 + Mg^{2+} = 2\ MgCO_3 + Ca^{2+} \qquad \text{(A-5)}$$

will proceed to the right. For this reaction, ΔG^{o}_{R} = 3.2 kcal, which is extremely small; hence any accompanying reaction(s) or other factors could easily cause this reaction to take place with dolomite formation. As Deer et al. (1962) point out, however, the presence of magnesite alone is usually sufficient to indicate a high amount of dissolved Mg^{2+}. Mg-chlorite is common at Oklo and this has been used to infer alkaline conditions for such Mg-chlorite associated with sedimentary uranium deposits (Kendall, 1971; Brookins, 1976a). Further, at pH = 10 magnesite will dissolve to form brucite ($Mg(OH)_2$), although the kinetics of this reaction are not known. Brucite is common only in metamorphic rocks as most $Mg(OH)_2$-complexes in sedimentary rocks occur in clay minerals such as montmorillonite and mixed layer clay minerals (i.e., illite-montmorillonite, illite-chlorite, chlorite-montmorillonite). A final complexity of the magnesite at Oklo is that it has not been unequivocally demonstrated that magnesite is a primary phase, i.e., it may have formed from dolomite at some later time. Geffory et al. (1975) infer magnesite formation at about the time of uranium mineralization, so even if magnesite formation is secondary it must have formed close to 1.8 b.y. ago.

C. Siderite. Siderite is relatively rare in sedimentary rocks, primarily because the conditions under which it is stable are not often encountered in nature. A combination of low Eh, low total dissolved S, and high pH are favorable for siderite formation (Garrels and Christ, 1965; Berner, 1971). Berner (ibid.) points out that siderite is not observed forming in modern sediments as some SO_4^{2-} is always present which limits the amount of H_2S or HS^- and indirectly controls the nature of iron bearing species, for example hematite or goethite in the sulfate-stable field and pyrite or one or more of its precursors in the reduced-sulfur stable field. Hence low total sulfur (ΣS as H_2S-HS^- -S^{2-}) and high total dissolved CO_2 favor siderite formation. The presence of both dolomite and magnesite attests to the abundance of high total dissolved CO_2, and the absence of native sulfur and many common accessory sulfides to low total dissolved sulfur. Further, Weber et al. (1975) suggest that some hematite may be primary but that, over all, conditions for the uranium mineralization at Oklo were in the reduced sulfur stability field. Collectively these factors suggest that conditions were favorable for siderite formation. Further, with reference to Garrels and Christ (1975; Fig. 7.21), siderite is stable over the pH range of 6 to 10.8 for an activity of dissolved ferrous iron of 10^{-6}.

When waters are low in sulfate ion and contain organic matter, such as at Oklo, then anaerobic decay processes result in low Eh and high total dissolved CO_2 but low total dissolved reduced sulfur. Not all barium is present in barite but appreciable quantities are present in other minerals, e.g., adsorbed on clay minerals, etc. Siderite is a common mineral found associated with coal beds or other accumulations of organic matter, and is thus to be expected at Oklo.

Of further interest is that calcite is stable relative to siderite via the reaction:

$$FeCO_3 + Ca^{2+} = CaCO_3 + Fe^{2+}, \qquad \text{(A-6)}$$

for which K = 0.05 according to Berner (1971). In sea water, iron is only 0.1 percent as abundant as Ca^{2+}, whereas for siderite to be stable the concentration of iron must be some five percent greater than that of calcite. In a situation similar to that at Oklo dolomite apparently removes most Ca^{2+} hence the Fe^{2+}/Ca^{2+} ratio must have been great enough for siderite to form.

In summary, dolomite, magnesite, and siderite are all observed at Oklo although it is not clear if three phase equilibria were established. It is more likely that dolomite-magnesite and dolomite-siderite pairs formed but that magnesite may have been separated from siderite. Regardless, it is noteworthy that these three carbonates suggest the following constraints on Oklo ore formation: (1) High pH. (2) Low Eh. (3) Solutions relatively rich in Mg^{2+} but impoverished in Ca^{2+}, i.e., Ca^{2+} preferentially incorporated in dolomite and some in uraninite relative to calcite. (4) Low total sulfur under reducing conditions. (5) Close association of carbonates with organic carbonaceous matter in the low-grade part of Couche 1 but not in the high-grade reactor zone ore. (6) A Fe^{2+}/Ca^{2+} ratio favorable for siderite formation.

Unfortunately, the data reported in IAEA (1975) are insufficient to properly quantify the genesis of the carbonate minerals at Oklo, yet it is probable that the data gathered since that symposium will allow the exact paragenetic sequence to be established in terms of pH, Eh, and other variables.

III. TEMPERATURE AND PRESSURE CONSTRAINTS OF HIGH GRADE ORE

Despite considerable research concerning the genesis of both the Oklo reactor zone ore and the surrounding lower grade ore, there exist many uncertainties concerning the probable temperature and pressure during the high-grade ore formation. (The reader is referred to the numerous articles in the IAEA Symposium 204, "The Oklo Phenomenon" concerning mineralogy, chemistry, tectonics, petrography, mineragraphy, etc.)

The simplistic model whereby high-grade ore resulted from dissolution of low-grade ore uranium which was then transported into and deposited in conglomeratic-shale infill in fractures of the mineralized "Couche 1" appears reasonable (see Chauvet, 1975). The fractures resulted from tectonic events soon after mineralization of Couche 1, which itself was mineralized very soon after sedimentation of the upper Francevillien (F_{1A}) Series. Hence one can justifiably argue for equal T and P conditions for mineralization of Couche 1 and the high-grade reactor zone ores. At least it is probably safe to state that the high-grade ore formed in shale forced downward into the fracture system from local sources. The drag folds and other structural evidence confirm the down-filling of the shale-conglomerate mixture into the fracture zone, although the rich uranium oxide of this zone commonly exhibits textures characteristic of deposition from solution.

It is first necessary to make some brief comparisons between the primary minerals in the low-grade ore in Couche 1 and the high-grade ore as follows:

	Low-Grade Ore	High-Grade Ore
1. Chlorite	Abundant; apparently associated with organic matter.	Abundant; may have been mechanically re-worked.
2. Organic C	Abundant.	Scarce.
3. Quartz	Abundant.	Scarce (note: very abundant at edges and between reactor zones.
4. Illite	$1M_d$ polytype abundant.	$2M_1$ polytype apparently abundant.
5. Sulfides	Common.	Common; some PbS with total Pb~206-Pb.
6. Dolomite	Common.	Present, but not abundant.
7. Magnesite	Rare (?).	Common.
8. Siderite	Abundance uncertain.	Abundance uncertain.
9. U minerals	Uraninite with rare coffinite; ore is low grade and disseminated in sandstone with shale partings and galls.	Uraninite with rare coffinite; ore is very high grade. No definite relationship to shale or sandstone noted; absence of quartz; carbon noted.

It is easier perhaps to make some general comments concerning the maximum temperature for the ore in Couche 1 before addressing the problem of T and P conditions in the high-grade ore. Breger (1974) has shown that coalified logs from the Colorado Plateau yield extractable organic carbon which is stable only to temperatures in the 100 to 125° range. Remembering the Colorado Plateau and Oklo similarities and because of the more simple structure for the Oklo algal-derived material, this seems to be a safe upper T limit based on organic carbon constraints. Furthermore, Hostetler and Garrels (1962), citing the work of Rafalsky (1958), note that UDC becomes unstable above 120°C but that between 25° and 120°C the stability of UDC is such that appreciable uranium can be transported by this complex. Certainly the works of Bullwinkel (1954) and Schmidt-Collerus (1969) document the existence and mobility of uranium as UDC between pH conditions of 6 to 10 (This range of pH is thought to be reasonable based on the paragenetic conditions for co-existing accessory minerals in the Colorado Plateau ores according to Brookins, 1976a; Lee, 1976). Hostetler and Garrels (1962), citing field evidence, argue for an approximate cover of two kilometers over the sedimentary rocks during their mineralization in the Colorado Plateau. Assuming a relatively high geothermal gradient of 30°C/km, then a reasonable temperature for ore formation is approximately 75°C. Additionally, Brookins (1976b) has argued that temperatures for clay mineral and organic acid reactions in the Ambrosia Lake district must fall near 60°C as montmorillonite is present, i.e., the montmorillonite field shrinks considerably at lower temperatures thus reducing the chances for montmorillonite to illite and/or chlorite types of reactions. Further, the agreement between the K-Ar and Rb-Sr dates is indicative of low T since the Oklo minerals were formed, otherwise the temperature sensitive K-Ar values would be greatly affected by T=150°C.

These various lines of evidence suggest that for the Oklo deposit the cover must have been relatively shallow at the time of mineralization of Couche 1; a depth in the 2-to 4-km range seems reasonable, with perhaps the 2-km range being more likely as the geothermal gradient may well have been closer to 20°C/km (a typical Precambrian value away from orogens) in the Francevillien Basin.

Maurette (1976), has argued for burial of the Oklo deposit to a depth of at least 5 km and a resultant temperature of near 375°C based on fission track studies in quartz from the reactor zones and from the edges of the zones.

Assuming a high surface value of 25°C,then the geothermal gradient would have to be 70°C/km to attain the 375°C value cited. This is unreasonable in view of the above comments. For cover as shallow as 1 km the lithostatic pressure would be approximately 300 atm and the hydrostatic pressure approximately 60 to 100 atm, hence a depth of 5 km and temperature of 375°C would put water above its critical point. Many minerals would be highly reactive at the critical point (e.g., sulfides, illite), yet there is no evidence for extreme chemical reactivity involving water as a critical phase. Thus, the temperature was probably below the critical point. Additionally, if the Oklo gangue were held at this temperature with water available (either from pore fluid or from hydrous phases) then prograde metamorphism to at least the greenschist facies would result. As the chlorite observed is of sedimentary origin and the other minerals present not representative of metamorphic sequences, then Maurette's (1976) temperature estimate appears to be too high. Fission track studies of quartz and phyllosilicates are very difficult to undertake; it would perhaps be more useful to study in detail the fission tracks in zircons from the outer rims of the reactor zones.

The problem of formation of low-grade ore at Oklo is addressed elsewhere in this report. The comparison between sandstone deposits of the Colorado Plateau and Oklo cannot be ignored. The difficulty is in lack of important data concerning minor elements concentrated in common accessory minerals of uranium deposits such as molybdenite, selenium species, pyrite-marcasite, vanadium-species relative to the uranium and carbon distribution. One can only infer that deposition of uranium occurred near the hematite-pyrite redox interface (Weber et al., 1975), and it is fruitless to speculate on roll versus tabular type of geometry for the ore. However, assuming there are many similarities between the Colorado Plateau and Oklo ores,then both the uranium mineralization and clay mineral paragenesis become important in terms of Eh-pH diagrams. Figs. A-1 and A-2 (from Brookins, 1976) show stability fields for uranium species (Fig. A-1) and aqueous species plus carbon (Fig. A-2). For uranium (VI) transported as UDC, the uraninite (or coffinite):UDC boundary is very near the hematite:pyrite boundary. If both boundaries should overlap then some U(VI) will be precipitated as S(II) if (HS^-) is oxidized to either S(O) (i.e., in pyrite) or to S(VI) (i.e., as sulfate ion as hematite is formed from pyrite). To a large degree the sulfur redox energetics of the system control

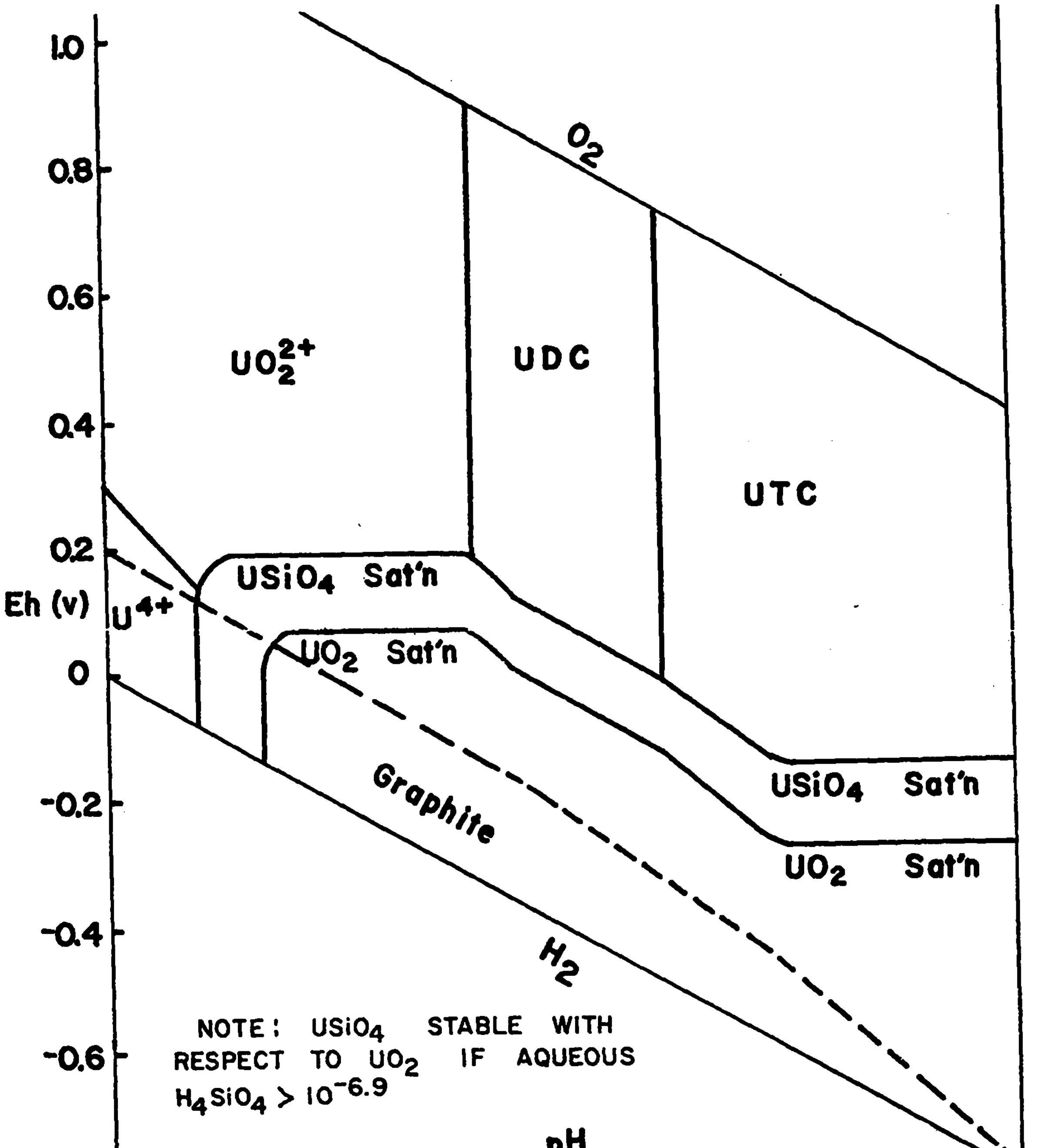

Fig. A-1.
Eh-pH diagram for the U-C-Si-H-O system at standard temperature and pressure. Graphite is used as the analog for organic carbon.

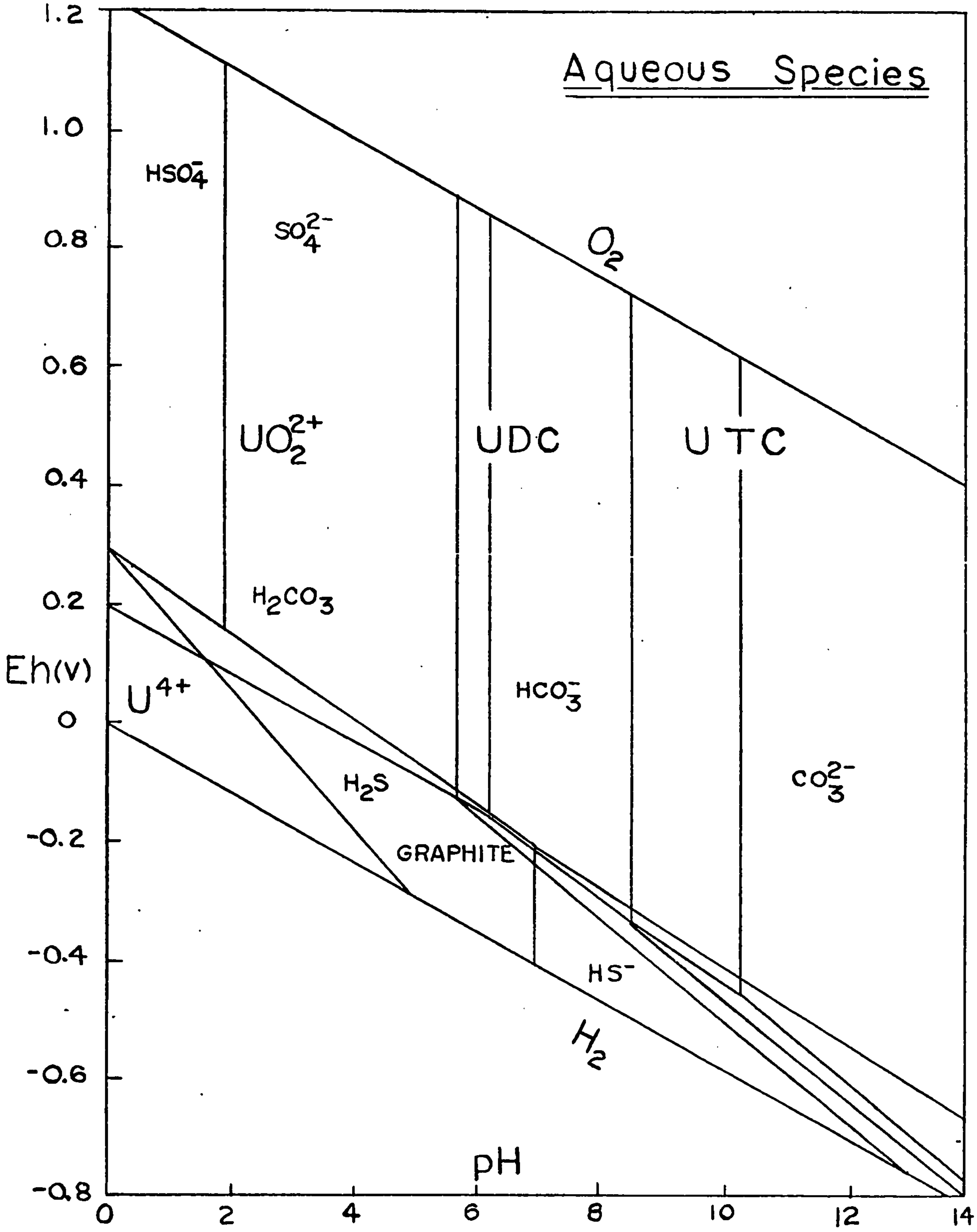

Fig. A-2.
Eh-pH diagram for the U-C-S-H-O system at standard temperature and pressure showing only aqueous species except for graphite.

the uranium precipitation. For more dilute solutions, however, or in case the activity of dissolved uranium is decreased as a function of ionic strength, then it is possible to carry uranium as UDC into the sulfide stability field before precipitation begins. In this case oxidation of S(II) to S(0) or C(0 or IV) will be energetically sufficient to cause U(IV) precipitation. For S species, oxidation of pyrite formation will be the consequence; for C species, (HCO_3^-) will result. For the low grade ore, penecontemporaneous formation of uraninite and pyrite, with associated illite (and/or chlorite) formation facilitated by organic acid reactions, is advocated. At the same time, organic carbon is fixed in the zones of active attack on silicates and in the areas of uranium mineralization. This is essentially the model advocated by Brookins (1973; 1976a,b, Brookins and Lee (1974) and Lee (1976) for the uranium deposits of the Grants Mineral Belt and appears reasonable for the Oklo deposit.

IV. HIGH-GRADE ORE FORMATION

Consider now the consequence of fracturing Couche 1 due to tilting and uplift. Slightly oxygenated waters accompany the infilling of shale into the fracture zones at Eh-pH conditions not only below the hematite:pyrite boundary but possibly below the $C:(HCO_3^-)$ boundary. As these waters are from an already pyritiferous environment they may not be sufficiently oxidizing to reach the pyrite:hematite boundary but they can quite easily move from the organic carbon field to higher Eh conditions such that (HCO_3^-) is formed. If this is the case then uranium is remobilized, most probably as UDC. As the U(IV) is oxidized to U(VI) in UDC it is removed and C(0) is destroyed. With continued dissolution the uranium content of the aqueous solution is increased, hence the boundary between uraninite:UDC is also raised. There is no evidence for very high P_{O_2} conditions for subsequent uraninite precipitation within the hematite field. Instead it is likely that the uraninite:UDC boundary is raised to near the hematite:pyrite boundary at which point UDC is reduced as uraninite is formed because the sulfide-sulfate reaction predominates. In this model the kinetics are unknown but one can argue for rapid precipitation, possibly in void space, as the uranifierous solutions reach the environment of precipitation. The quartz content will be lower in these zones but its virtual absence is difficult to explain unless uranium precipitation occurred much faster than detrital infilling. Only fine grained shale constituents (i.e., phyllosilicates) should be transferred to the sites of deposition, and indeed this is what is observed. Further, as the UDC for the rich uraninite accretions was formed while C(0) was being oxidized then it would be unlikely and certainly unnecessary for carbon to be present since the precipitation occurrs well above the C:(HCO_3^-) boundary. Again, absence of carbon is common. Further, as the solutions are moving to a K-favorable environment (relative to the host Couche 1) a higher chlorite/illite ratio would be expected, and the illite should be more K-rich relative to illite in the lower grade parts of Couche 1. This, again, fits the observations except that the illite present has been identified as the $2M_1$ polytype as opposed to the $1M_d$ polytype in the low-grade rocks. This is not an easy situation to explain yet it is possible that, facilitated by the chemical activity of the solutions, the directional pressure in the fracture system is sufficient to cause the 1M to 2M polytype transition. It is perhaps no accident that the phyllosilicates are oriented in the reactor zones while this is not the case in the surrounding rocks. Additionally, quartz is more brecciated in the high grade zones relative to the more rounded quartz in Couche 1. The presence of magnesite indicates rather high pH conditions (certainly above 7), and the presence of pyrite (as well as other sulfides) indicates sulfide-field Eh-pH conditions. Yet Weber et al. (1975) point out that some primary hematite is present so one can argue for Eh-pH conditions near the hematite:pyrite boundary. If quartz were removed by dissolution then the activity of dissolved silica would increase significantly and coffinite might be the preferred U(IV) phase rather than uraninite. As this is not the case, then the indirect argument can be made that quartz was rare to begin with in the highest grade ores. The incremental filling was apparently due to uraninite precipitation. The absence of quartz and subsequent absence of increased activity of dissolved silica explains the absence of quartz overgrowths on the brecciated grains near the reactor zones.

The rate of nucleation of uraninite is uncertain, but there must have been sufficient uranium in solution to allow growth as space was made available. There may have been low pressure domains along such a fracture system, and perhaps this accounts for the rather systematic occurrence of the six reactor zones noted so far at Oklo.

An interesting consequence of this model is that water present during the uraninite formation need not necessarily be directly correlated with water of crystallization. The H/U ratio may have been controlled by the aqueous solution independent of the clay minerals. Another interesting aspect is that during the assumed oxidation of U(IV) and C(0) after initial low-grade mineralization in Couche 1, the UDC-rich solution should be relatively impoverished in elements such as vanadium, selenium and perhaps molybdenum. Vanadium would have been fixed in octahedral sites of clay minerals and retained in these sites as the ionic radii of V(III,IV) and V(V) are all close to 0.65 A. Selenium species should be unaffected by the oxidation of either U(IV) or C(0) as the $Se^o:(HSe^-)$ boundary is significantly higher than the $C:(HCO_3^-)$ boundary. Finally, molybdenum species may or may not have been affected by oxidation. The $MoS_2:(HMoO_8^-)$ or $MoS_2:(MoO_8^{2-})$ boundaries are close to the $C:(HCO_3^-)$ boundary and some Mo(IV) may well have been oxidized in this fashion. However, it is not necessary for Mo(VI) to be reduced to Mo(IV) in the high-grade ore contemporaneously with uraninite since Mo(VI) complexes are stable at the Eh-pH conditions along the pyrite:hematite boundary. Thus molybdenum may well be concentrated elsewhere. Interestingly enough Frejacques et al. (1975) and Walton and Cowan (1975) mention migration of molybdenum at Oklo. If the Eh conditions were high enough to prevent MoS_2 precipitation then it is conceivable that Mo produced by fission was removed as a Mo(VI) complex from the reactor zones. If this is the case then reduction of Mo(VI) to Mo(IV) would occur in local "sulfide traps" of lower Eh, higher pH. As these traps may be outside of the reactor zones then it is not surprising that the fate of remobilized molybdenum is unknown at present.

The relatively high abundances of the rare earth elements (REE) and barium in the reactor zones can be explained by transport of the REE as common carbonate-complexed ions and barium carried as Ba^{2+} until either adsorbed on clay minerals or locally precipitated as barite.

The abundance of a very young generation of kaolinite in the reactor ore makes it difficult to reconstruct pre-kaolinitization conditions. Slightly more acidic conditions are necessary and, as the chlorite/illite ratio is already high, then kaolinite formation should go hand-in-hand with destruction of illite. Hence alkali and alkaline earth elements will be removed as kaolinite forms.

APPENDIX B

GEOCHEMISTRY OF ALKALI AND ALKALINE EARTHS

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I. BEHAVIOR OF Ba, Sr, AND Ra

The thermochemical data for barium, strontium, and radium are presented in Table B-1. There exist large uncertainties for some of the data but, fortunately, the chemistry of these three elements in the natural environment is fairly simple.

Barium at the Oklo site is abundant; concentrations in excess of 1000 ppm are common and values as high as 4000 ppm have been reported. Branche et al. (1975) have summarized many chemical data for major constituents and the reader is referred to Walton and Cowan (1975) for some data on barium.

TABLE B-1. THERMOCHEMICAL DATA FOR Sr, Ba, AND Ra.

Species	ΔG_f^o	Ref.*	Species	ΔG_f^o	Ref.*
Ba^{2+}	- 134.00	1	Cs^+	- 67.41	3
$BaSO_4$	- 325.30	1	PO_4^{3-}	- 244.00	1
Sr^{2+}	- 133.20	1	$BaCO_3$	- 278.36	1
$SrSO_4$	- 319.83	1	$SrCO_3$	- 275.45	1
SO_4^{2-}	- 177.97	1	Cs_2O	- 65.6	3
HCO_3	- 140.26	1	K_2O	- 76.2	4
CO_3	- 126.17	1	KOH	- 89.5	3
BaF_2	- 274.50	2	CsOH	- 84.9	3
SrF_2	- 277.20	2	CsF	- 119.5	4
F^-	- 66.64	1	KF	- 127.4	4
H_2O	- 56.69	1	Ra^{2+}	- 134.5	4
K^+	- 67.70	1	$RaSO_4$	- 326.0	4

*References

1. Robie and Waldbaum (1968)
2. Wicks and Block (1968)
3. Garrels and Christ (1965)
4. Latimer (1961)

A. Chemistry. Barium, strontium, and radium exhibit similar behavior in low T and P aqueous environments. Their ionic radii are similar and they all occur most commonly as simple, non-complexed divalent ions in aqueous solutions in the pH range 3 to 11. The divalent ions are the only species stable over the entire range of Eh-pH encountered in the natural environment.

A compilation of the solubility product constants for the sulfates are as follows:

species	pK_{so}
$SrSO_4$	6.30
$BaSO_4$	9.50
$RaSO_4$	10.4

These data show that $SrSO_4$ is the most soluble and $RaSO_4$ less soluble by 10^4. Barium and radium show a very strong affinity for each other, much more so than strontium with either barium or radium. This is readily explained by the fact that strontium as Sr^{2+} has a smaller ionic radius than either Ba^{2+} or Ra^{2+} and may be incorporated into a Ca^{2+} site (especially if the coordination number of the site is 8 rather than 6). Consequently, Ba and Sr will most likely be concentrated in different phases. This is especially true if both (CO_3^{2-}) and (SO_4^{2-}) are available for scavenging of Sr^{2+} and Ba^{2+}. For the hypothetical reaction:

$$MSO_4 + (HCO_3^-) = MCO_3 + (SO_4^{2-}) + (H^+) \,, \qquad \text{(B-1)}$$

the $\Delta G_R^o = 13.6$ kcal for barium species, but only 7 kcal for strontium species. Phase equilibria studies show extensive solid solution between $SrCO_3$ and orthorhombic $CaCO_3$ but only limited solid solution between $BaCO_3$ and $SrCO_3$.

It is of further interest that the ion imagery studies of Havette et al. (1975) show that Ba and Sr are indeed commonly located in different sites in Oklo ores and gangue. The scavenging of Ra^{2+} by $BaSO_4$ (the mineral "radiobarite") is a well-known phenomenon. This is illustrated by the simple reaction:

$$BaSO_4 + 0.1\ Ra^{2+} = (Ba,Ra)SO_4 + 0.1\ Ba^{2+} \,, \qquad \text{(B-2)}$$

for which $\Delta G_R^o = -0.15$ kcal and $\log K = +0.11$. For a system with pre-existing

$BaSO_4$, Ra^{2+} removal by exchange is near total. If both Ba^{2+} and Ra^{2+} are introduced into solution at the same time then $RaSO_4$ will precipitate before $BaSO_4$. As SO_4^{2-} concentration will in all likelihood be greater than Ra^{2+}, then the removal of Ra^{2+} should be nearly 100% complete.

B. Oklo samples. At Oklo there is some uncertainty concerning whether or not the primary ores were precipitated near a sulfate:sulfide redox interface (Weber et al., 1975). The presence of pyrite and marcasite (both FeS_2) and probable primary hematite (Fe_2O_3) suggest that ore formation did indeed occur near or at the sulfate:sulfide Eh-pH fence. The greater abundance of pyrite and other sulfides and relatively small amounts of sulfate (some barite is reported but barium is found in non-sulfate minerals as well) suggest that a greater proportion of uranium precipitation occurred under reducing conditions, i.e., in the sulfide field. However, due to its extremely insoluble nature any barite formed near the hematite:pyrite fence should survive even with a drop of Eh into the sulfide field. Whether or not appreciable (SO_4^{2-}) would exist during, say, the lifetime of reactor zones is quite another story. The data for galena containing essentially only ^{206}Pb, and other data, suggest reactor operation under sulfide-stable conditions in which case the activity of (SO_4^{2-}) would be extremely low. Thus it is not surprising that barium is noted in clay mineral-rich parts of the gangue (Weber et al., 1975). Should Ra^{2+} be released from uraninite from Oklo samples it may well have (1) been scavenged by small amounts of barite, Eq.(B-2), (2) precipitated as $RaSO_4$ (unlikely), or (3) been affixed by ion exchange in K^+-sites in illitic clay minerals. As (3) may well account for the Ba present at Oklo, the exchange efficiency, which is proportional to ionic potential (Z/r), would predict that Ra^{2+} would effectively be removed from solution. Of note is that Ra^{2+} migration is apparently not a factor in the ^{238}U-^{206}Pb systematics even for disturbed (due to the fission processes) samples. As the samples become more and more oxidized, any Ra^{2+} released will be scavenged by sulfates or by clay minerals.

II. LIMITS OF FISSIOGENIC Rb AND Sr

Hagemann et al. (1974) estimate that less than ten percent of the Rb and/or Sr studied from Oklo reactor zone samples is fissiogenic; their results cannot, unfortunately, be further refined. Lancelot et al. (1975) report data which indicate the presence of an unspecified, but easily recognized, quantity of fissiogenic rubidium. Brookins et al. (1975) note the presence of fissiogenic

Rb, Sr, Ba, and Cs (determined by inference from ^{135}Ba and ^{137}Ba excess formed by decay from ^{135}Cs and ^{137}Cs, respectively). Their data cannot be used to estimate the amount of fissiogenic material retained relative to that originally produced, because the total U and ^{235}U contents were carried out on separate splits of samples which were not homogenized prior to splitting.

What can be done, though, is to comment on the percentage of fissiogenic Rb and Sr which is now present in the total amount of Rb and Sr for various Oklo samples. For Rb and Sr this is estimated by considering the hypothetical fission yields of ^{85}Rb, ^{87}Rb, and ^{88}Sr from the following data (from Meek and Rider, 1974) for an assumed fission mix of ^{235}U (93%), ^{238}U (3%), and ^{239}Pu (4%) (see Frejacques et al., 1975).

Fissiogenic Isotope	^{235}U Yield (%)	^{238}U Yield (%)	^{239}Pu Yield (%)	Mix (%)
^{85}Rb	1.31	1.06	0.56	1.27
^{87}Rb	2.55	1.76	0.96	2.46
^{88}Sr	3.62	2.06	1.37	3.48

Now for Rb, the measured isotopic (85/87) ratio is 2.470, which is close to values reported by Lancelot et al., 1975, and by Brookins et al., 1975, for some Oklo samples. The normal (85/87) ratio is 2.593, and the fissiogenic (85/87) ratio from the data tabulated above is 0.516. Thus, the percent of fissiogenic Rb present in a sample can be calculated from the standard equation:

$$\left.\frac{^{85}\mathrm{Rb}}{^{87}\mathrm{Rb}}\right._{m} = \frac{(0.7215\ N) + (0.340\ F)}{(0.2785\ N) + (0.660\ F)}\ , \tag{B-3}$$

where m designates the measured ratio (which can be determined with a precision of ± 0.5% (one sigma), 0.7215 N indicates the atomic fraction of ^{85}Rb in the normal element, 0.2785 N the atomic fraction of ^{87}Rb in the normal element, 0.340 F the atomic fraction of ^{85}Rb of the fissiogenic element, and 0.660 F the atomic fraction of ^{87}Rb of the fissiogenic element. Solving for F/N yields:

$$\frac{F}{N} = \frac{(0.7215) - (0.2785)\ (2.47)}{(0.660)\ (2.47) - (0.340)} = \frac{0.0336}{1.290}\ . \tag{B-4}$$

Hence 2.5% of the measured Rb was fissiogenic.

Without knowing the original amount of fissiogenic Rb in the sample, it is impossible to say what percentage of total fissiogenic Rb the above ratio represents. From the work of Frejacques et al., (1975) and Maeck et al. (1975), the amount of fissiogenic Rb retained is probably less than one percent for some samples. The significance of the above calculation is that measurable fissiogenic Rb is still noted. If one were to assume loss of fissiogenic Rb by volume diffusion or some other continuous process over 1.8 b.y. and addition of significant amounts of normal Rb, then it is unlikely that any measurable amounts of fissiogenic Rb would be detected.

For Sr the situation is simpler in that only ^{88}Sr is affected by fission. The analogous equation for Sr isotopes is based on $^{86}\mathrm{Sr}/^{88}\mathrm{Sr} = 0.1194 \pm 0.0010$ (two sigma) for normal Sr, and the relation of fissiogenic ^{88}Sr to normal Sr is given by:

$$\frac{^{86}\mathrm{Sr}}{^{88}\mathrm{Sr}}_{m} = \frac{0.0986\ N}{0.8256\ N + F}\ . \tag{B-5}$$

The measured ratio ($^{86}\mathrm{Sr}/^{88}\mathrm{Sr}$) m is 0.1150, and this represents 3.1% fissiogenic Sr. This value, again, is only an indication of the amount of fissiogenic Sr in total Sr from a sample for which the exact amount of initial fissiogenic Sr is not unknown. The measurement attests to the presence of small but not insignificant amounts of fissiogenic Sr. The comments by Frejacques et al. (1975), Maeck et al. (1975), and Walton and Cowan (1975) indicate that most fissiogenic Sr has migrated, but this is with reference to total measured Sr compared to predicted fission Sr in the reactor zone. Nothing is said as to whether the fissiogenic Sr has been totally removed from the system, i.e., from entire reactor and barren zones. Systematic measurements of total U, ^{235}U, Rb, and Sr on reactor and peripheral zone samples would provide a better understanding of Rb and Sr migration behavior.

The fact that any measurable amount of fissiogenic Rb or Sr is present suggests that for purer uraninite mineral separates, there will be a greater probability of finding higher percentages of fissiogenic Rb and Sr. This is borne out by the fact that the two lowest $^{86}Sr/^{88}Sr$ ratios reported by Brookins et al. (1975) were from the purest mineral separates. At present this problem is being pursued using carefully hand-picked mg quantities of uraninite-rich samples (as opposed to one-gram samples in the original study) from which μg or ng amounts of Rb and Sr (plus Ba) will be extracted for isotopic study. This work is in progress and will be reported at a later date.

III. NEUTRON ABSORPTION EFFECTS ON Rb AND Sr

Lancelot et al. (1975) suggest that neutron absorption by Rb would, for 200 ppm Rb originally present in an Oklo reactor zone, lower the 85/87 ratio at 1.8 b.y. ago to 2.539, assuming a fluence of 6 x 10^{20} n/cm^2. This value is lowered to 2.383 if fission plus neutron absorption are considered. Unfortunately the amount of total uranium, the percent of ^{235}U depletion, and other important parameters were not given by Lancelot et al., so it is difficult to reproduce their figures. However, a more complete picture can be obtained by considering neutron capture effects on both Rb and Sr. The thermal capture cross sections for Rb and Sr isotopes (from Mughabghab and Garber, 1973) are given below:

Isotope	$\sigma_{(n,\gamma)}$ (barns)
^{85}Rb	0.46
^{87}Rb	0.12
^{84}Sr	0.81
^{86}Sr	0.84
^{87}Sr	16.0
^{88}Sr	5.8 (mb)

If neutron absorption is important in discussing variations in isotopic ratios for Rb and Sr, then ratios involving ^{87}Sr would be the most pronounced. During the reactor's lifetime at 1.8 b.y. ago, the $^{87}Sr/^{86}Sr$ ratio for an assumed abundance of 20 ppm Sr would be well below 0.710 (which is a likely value for undisturbed Francevillien rocks). Further, since Brookins et al. (1975) show Sr contents for 2'P' Oklo samples from 9 to 30 ppm while the Rb content varies from 30 to 90 ppm, then rather drastic $^{87}Sr/^{86}Sr$ variations relative to very slight ^{85}Rb/^{87}Rb depletions should result. As this is not the case, then neutron absorption does not appear to have been significant in causing destruction of either Rb or Sr isotopes.

The relevance of this is that one can treat the observed 85/87 ratio for Rb and 86/88 ratio for Sr as being due to a simple mixture of the normal elements with fission produced isotopes of ^{85}Rb, ^{87}Rb, and ^{88}Sr from the assumed mix of fissile ^{235}U (93%), ^{238}U (3%), and ^{239}Pu (4%).

A summary of Rb and Sr data are given below:

Sample	^{87}Sr/^{86}Sr	Rb (ppm)	Sr (ppm)	^{87}Rb/^{86}Sr	Source
1186A	0.7337	63.0	31.1	5.86	Brookins (unpub.)
1186B	0.7251	32.7	30.9	3.07	Brookins (unpub.)
1404/2	0.7749	49.2	8.9	16.11	Brookins (unpub.)
1404/1	0.7496	91.4	11.2	23.72	Brookins (unpub.)
KN50 2	0.731	17	30	1.65	Lancelot et al. (1975)
KN50 322	0.730	10	43	0.67	Lancelot et al. (1975)
KN50 322b	0.733	55	19	8.39	Lancelot et al. (1975)

The reference isochrons for the above data are shown in Fig. B-1; the apparent ages are 275 and 120 m.y. Collectively the data shown in Fig. B-1 argue for open-system conditions and especially for dilution of reactor zone ore with much younger Rb and Sr, although it cannot be stated whether the Rb and Sr were introduced episodically or continuously. Further, the samples used by Brookins (unpublished) are certainly not "whole rocks," and those studied by Lancelot et al. (1975) probably do not meet whole-rock criteria either. Hence, one cannot unravel the data in terms of possible post-1.8 b.y. metamorphic events. From the data of Bonhomme and Weber (1975), however, it is unlikely that any severe post-1.8 b.y. event has occurred, else the K-Ar ages reported would be severely lowered and this is not the case.

IV. Cs ADSORPTION ON CLAY MINERALS

Frejacques et al. (1975) and Walton and Cowan (1975) point out that, following the work of Hagemann et al. (1974), alkali and alkaline earth elements have migrated at Oklo. While this point seems well documented, it is important to note that Brookins et al. (1975) present data which indicate that ^{135}Cs, with a half-life of 2.3 million years, may have been preserved for

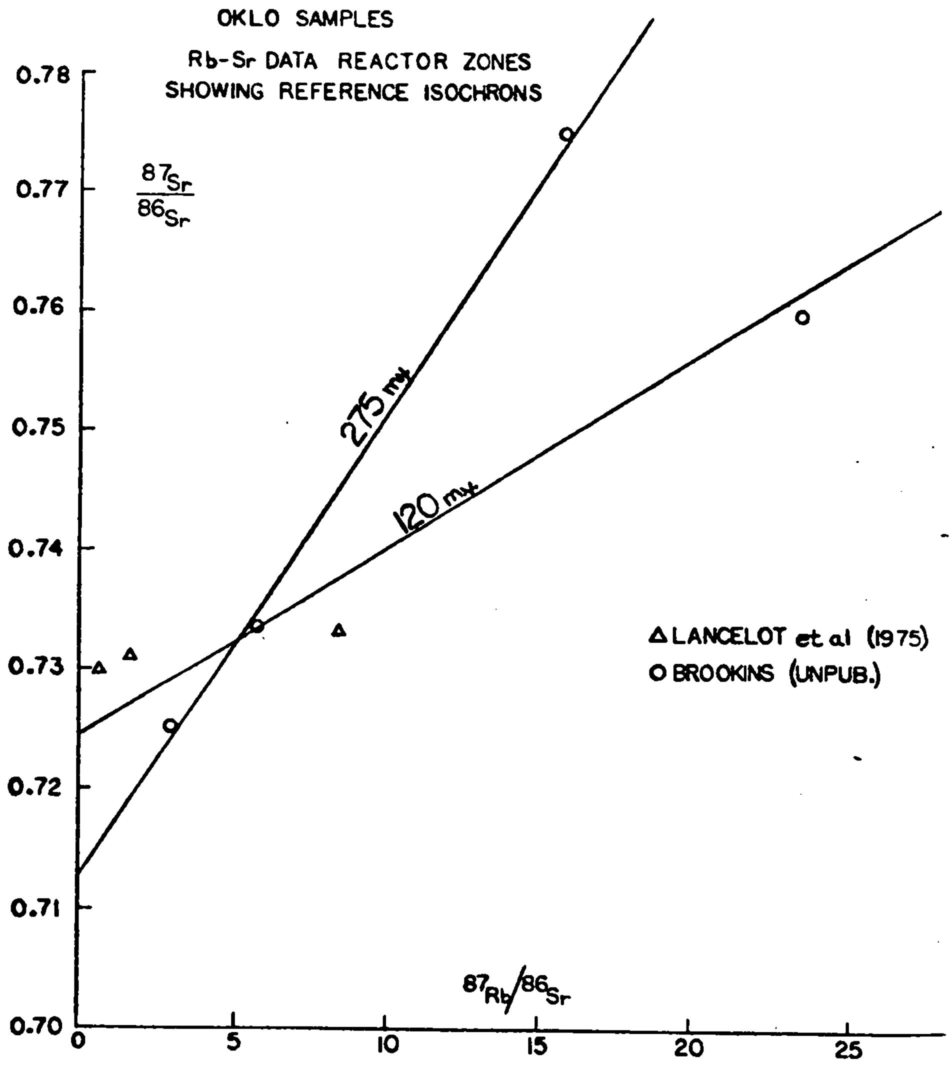

Fig. B-1.
Rubidium and strontium for Oklo reactor ore samples with reference isochrons.

roughly ten times that duration such that the stable ^{135}Ba formed was retained. There is a correlation between increasing ^{135}Ba/^{137}Ba and decreasing ^{85}Rb/^{87}Rb for four samples which attests to the retention of fissiogenic ^{135}Cs, ^{137}Cs, ^{85}Rb, and ^{87}Rb for approximately twenty-five million years. Further, if barium isotopes were fixed at the Oklo site then small amounts of ^{138}Ba may be assumed to have been retained as well; unfortunately the large amount of normal barium which has diluted the high-grade ore has so far prevented detection of $^{138}Ba_f$ although work is in progress on this matter. Similarly, $^{133}Cs_f$ can also be assumed to have remained in place for at least as long as ^{135}Cs and ^{137}Cs. Hence the problem is not whether or not cesium has migrated (the evidence is that it has), but rather how much has migrated and how far.

Important to this problem is the role of adsorption of large alkali metal and to a lesser degree divalent alkaline earth cations on clay minerals. It is well known that samples with low electronegativities and low ionic potentials (Z/r) tend to occur as the free ion and do not complex with anions. A common reaction involving just K^+ and Cs^+ is:

$$\text{Clay Mineral-K}_{\text{fixed}} + (Cs^+) = \text{Clay Mineral-Cs}_{\text{fixed}} + (K^+) , \qquad \text{(B-6)}$$

for which the ΔG_R^o must be negative from laboratory experimentation and observations in nature. Lowest K/Cs ratios are found in near-deltaic environments where this reaction has probably taken place. If one assumes that the ΔG_f^o for the clay minerals in Eq. (B-6) are both equal then the ΔG_R^o is controlled by the ΔG_f^o of the K^+ and Cs^+ ions; thus $\Delta G_R^o \simeq - 0.3$ kcal and pK $\simeq - 0.22$. In principal, the clay mineral will remove most Cs by ion exchange and/or adsorption-site exchange.

An important study by Kharaka and Berry (1973) indicates the following comments to be made with regard to ion exchange and related phenomena; all based on combined laboratory experiment and study of natural samples from different media:

(1) M^+ ions are retarded more than M^{2+} ions in seepage through relatively impervious, clay-mineral-rich substances.

(2) If one defines R = moles hyperfiltrate/moles effluent in pure solution, then for bentonitic clays, $R \geqslant 5$, and for shales $R \geqslant 2$; thus indicating the efficiency of large cation removal.

(3) Bentonitic clays are effective in removing (Cs^+), which is effectively fixed as (K^+) is removed.

(4) K-montmorillonitic clays may be better than other clays for Cs removal. Na-montmorillonitic clays, for example, may suffer structural collapse due to the very large differences in Cs^+ and Na^+ ionic radii relative to the lesser difference in ionic radii between Cs^+ and K^+.

(5) A "filtration rate" (FR) is defined as: FR = (concentration of species in input solution)/(concentration of species in effluent solution) and, in a plot of compaction pressure between 4 and 10 psi, experimental results show excellent membrane efficiency for removal of Cs and good membrane efficiency for removal of Rb, K and Ba.

(6) Further, a mixture of 10% illite and 90% montmorillonite-rich shale should retard (SO_4^{2-}) to a large extent. This is important as M^{2+} ions (e.g., Ba^{2+}, Ra^{2+}) replaced by (Cs^+) will then be more likely to be removed as insoluble sulfates as discussed earlier.

When cation exchange takes place under reducing conditions, such as at Oklo, then the exchange reactions are quite different than those reported by Kharaka and Berry (1973). In addition to redox-influenced aspects of the reactions, shales rather than clay mineral constituents may have to be considered (but see comment (2) above). It is probable that Cs migration at Oklo was not appreciable until relatively recent times, perhaps only in the last ten million years or so. Assuming a volume diffusion model as opposed to an episodic loss model, which is justified based on the low T and P constraints mentioned elsewhere in this report, cesium should have remained locally fixed near the original site of formation. This may be substantiated by further work between the reactor zones and on the edges of the zones; or even possibly near the 900-m.y.-old dolerite dike which has acted as a barrier for uranium migration in "Couche 1" (Chauvet, 1975). Evidence for Cs fixation may be found from ultra-low K/Cs ratios (less than 10) coupled with other supportive alkali and alkaline earth studies.

The gangue of the high-grade reactor ore was hardly expected to be efficient in preservation of mobile elements, yet several percent of fissiogenic Rb, Sr, and Cs were retained. This implies that (1) a shale could be a proper storage site for some radioactive waste and (2) shale partings in salt deposits may be beneficial rather than detrimental for storage of waste in salt deposits.

APPENDIX C

GEOCHEMISTRY OF PLUTONIUM

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Walton and Cowan (1975) and Frejacques et al. (1975) have pointed out that plutonium has largely remained in situ for the Oklo reactor zone ores; the latter investigators also point out that this is not only true for ^{239}Pu produced from ^{238}U but for ^{241}Pu and ^{240}Pu as well. It was found that ^{235}U, which resulted in part from ^{239}Pu decay, occurred in the same positions in the ore as did ^{238}U. A comparison of uranium and plutonium systematics will be made later; the prime purpose here is to comment on the immobility of plutonium at Oklo with implications for other similar geologic environments.

I. LOW-TEMPERATURE AND LOW-PRESSURE AQUEOUS ENVIRONMENT

It is convenient to discuss low temperature and pressure environments in terms of pH and Eh (the oxidation potential under non-ideal conditions) in the presence, or possible presence, of water.

First, however, let us briefly summarize the assumptions and necessary equations for the Eh equation. As given by Garrels and Christ (1965) every oxidation-reduction can be written:

$$\text{reduced state} = \text{oxidized state} + ne^- , \qquad \text{(C-1)}$$

where n = the number of electrons (e^-). The corresponding half cell potential is given by:

$$Eh = E^o + \frac{RT}{nF} \ln \frac{\text{(oxidized state)}}{\text{(reduced state)}} , \qquad \text{(C-2)}$$

where Eh is the half-cell potential relative to the standard hydrogen electrode and E^o is the standard half-cell potential, i.e., the voltage of the half-cell when the activities are unity for all species entering in the half-cell reaction. In the above equation, R = gas constant (0.001987 kcal/deg), T = temperature (298.15°K), F = Faraday constant (23.06 kcal/volt-gram-equivalent). The free energy of any reaction involving oxidation or reduction is expressed by the equation:

$$\Delta G^o_R = n E^o F , \tag{C-3}$$

and thus E^o is related to the equilibrium constant by:

$$E^o = -\frac{RT}{nF} \ln K . \tag{C-4}$$

For reactions not at standard state conditions, we know that:

$$\Delta G^o_R = \Delta G^o_R + RT \ln K , \tag{C-5}$$

and similarly for the oxidation potential of a half cell reaction under non-standard state conditions:

$$E = E^o + \frac{RT}{nF} \ln K , \tag{C-6}$$

where E is written as Eh and referred to as the oxidation potential. At one atmosphere pressure and 298.15 K we thus write the equation for Eh as:

$$Eh = E^o + \frac{0.059}{n} \log K . \tag{C-7}$$

As an example of an Eh equation consider the two hypothetical reactions given below:

$$2\ MO + H_2O = M_2O_3 + 2H^+ + 2e^- , \tag{C-8}$$

and

$$M^{2+} + 2\ H_2O = MO_2 + 4H^+ + 2e^- . \tag{C-9}$$

The Eh equation for Eq.(C-8) is:

$$Eh = E^o + \frac{0.059}{2} \ln (H^+)^2 , \qquad \text{(C-10)}$$

or

$$Eh = E^o - 0.059 \text{ pH} , \qquad \text{(C-11)}$$

because the activities of solid species and the electron are taken as unity. For Eq.(C-9) we write:

$$Eh = E^o + \frac{0.059}{2} \log \frac{(H^+)^4}{(M^{2+})} , \qquad \text{(C-12)}$$

and

$$Eh = E^o + \frac{0.059}{2} \log \frac{1}{(M^{2+})} - 0.0118 \text{ pH} , \qquad \text{(C-13)}$$

and the E^o term will be modified by the $\frac{(.059)}{2}$ log $\frac{1}{(M^+)}$ term. Thus when aqueous species other than (H^+) are involved then the E^o calculated from the ΔG^o_R of the reaction is modified accordingly.

The limits for the aqueous environment are set by the reaction:

$$2\ H_2O \text{ (liq.)} = 2\ H_2 \text{ (g)} + O_2 \text{ (g)}, \qquad \text{(C-14)}$$

which can be written in terms of the two half cell reactions:

$$2\ H_2O \text{ (liq.)} = O_2 \text{ (g)} + 4H^+\ 4e^- , \qquad \text{(C-15)}$$

and

$$H_2 \text{ (g)} = 2\ H^+ + 2e^- , \qquad \text{(C-16)}$$

where the presence of water is implied for Eq. (C-15) because of the presence of H^+ ion. The limiting boundaries for the natural aqueous environment is thus when P_{O_2} = 1 atm and when P_{H_2} = 1 atm for Eqs.(C-15) and (C-16), respectively.

Finally, before proceeding to aspects of plutonium chemistry in terms of Eh and pH consider Figs. C-1 and C-2 (from Garrels and Christ, 1965). The former shows the "normal" measured range of Eh and pH in natural waters and the latter is a convenient reference for an overall view of the aqueous environment.

II. GEOCHEMICAL DATA FOR SOME PLUTONIUM SPECIES AND REACTIONS

Many of the data for plutonium species and reactions are summarized by Cleveland (1971), other data are from Latimer (1961), and still others have been calculated. As plutonium chemistry has been studied more extensively under

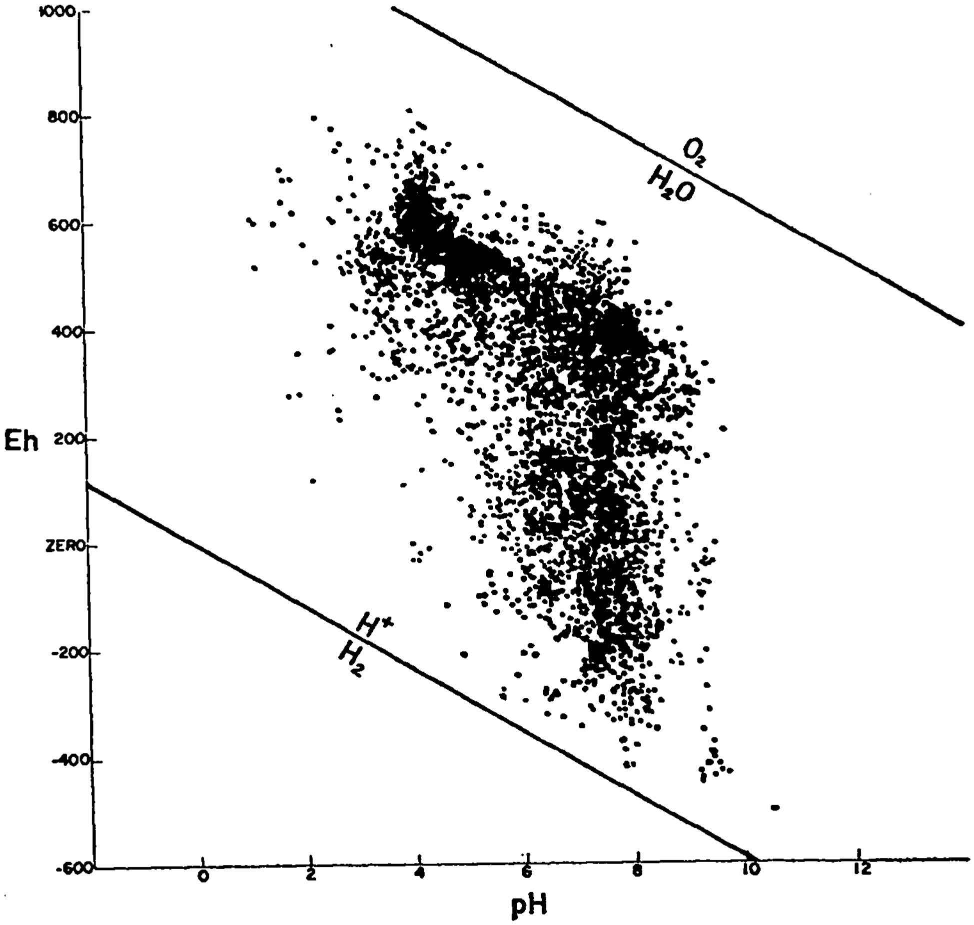

Fig. C-1.
Distribution of Eh-pH measurements of natural aqueous environments (from Garrels and Christ, 1965).

conditions very different from a low-temperature and-pressure natural environment, many uncertainties exist in the data. This will be evident when the various reactions and the resultant Eh-pH diagram are discussed. The extremely complex behavior of plutonium under high T and P conditions in the presence of both strong electrolytes and/or non-electrolytes, often in water-deficient systems, has allowed various investigators (summarized by Cleveland, ibid.) to comment on plutonium systematics in a rigorous fashion. By analysis of the data, those reactions and data which are most probable for the natural environment can be tabulated. Consider the following half-cell reactions (all in 1 M HCl):

couple	E^o	Valence of Pu Product
$Pu^{3+} - Pu^{4+}$	+ 0.914 V	IV
$Pu^{3+} - PuO_2{}^{2+}$	+ 1.0238 V	VI
$Pu^{4+} - PuO_2{}^{+}$	+ 1.1895 V	V
$Pu^{4+} - PuO_2{}^{2+}$	+ 1.054 V	VI
$PuO_2{}^{+} - PuO_2{}^{2+}$	+ 0.9122 V	VI

Some of the complexities for the above set of data are immediately apparent. For example, Pu(V) can exist under certain conditions at E^o values lower than those at which Pu (IV) is stable. The disproportionation of Pu^{4+} is well established, and an important net reaction (Cleveland, 1971) is:

$$3Pu(IV) + 2H_2O = 2Pu(III) + 4H^+ + Pu(V) . \qquad (C-17)$$

Pu(VI) is noted in some experiments, but Pu(IV) is apparently always the dominant species below an oxidation potential of approximately 0.9 V, and its abundance is enhanced as a function of increased radioactivity. This last fact is important with reference to Oklo because of the formation of ^{239}Pu from ^{238}U.

Thus a "first approximation" Eh-pH diagram considers only Pu(IV) as reduced and Pu(VI) as oxidized species. The relevant data are:

Species	ΔG^o_f (kcal/m)	References
PuO_2	- 240.4	Cleveland (1971)
$Pu(OH)_4$	- 340	Latimer (1961)
Pu^{4+}	- 118.3	Latimer (1961); also calc'd.
$PuO_2{}^{2+}$	- 183.5	Latimer (1961); also calc'd.
$PuO_2(CO_3)_2^{2-}$	- 455.6	calc'd. (Brookins, unpub.)

Free energy data for non-Pu bearing species may be obtained from Robie and Waldbaum (1968). The reason for selecting the five species listed above is primarily to construct an Eh-pH diagram equivalent to that for the U-C-H-O system (Fig. A-1). This appears feasible for the oxides, hydroxides, Pu(VI), and Pu(IV) species; but $PuO_2(CO_3)_2^{2-}$ is the only carbonate complex of Pu considered similar to uranium dicarbonate or tricarbonate species since the basic Pu-carbonate complexes $(PuO_2CO_3OH)^-$ and $(PuO_2CO_3(OH)_2)^{2-}$ are not stable in the Eh-pH stability field for water.

The first two Eh-independent reactions to be considered are:

$$PuO_2 + 4H^+ = Pu^{4+} + 2H_2O \; ; \quad K_{so_1} = 10^{-6.2} \; , \tag{C-18}$$

and

$$Pu(OH)_4 = Pu^{4+} + 4(OH)^- \; ; \quad K_{so_2} = 10^{-52} \; . \tag{C-19}$$

For Eq. (C-18), if an activity of 10^{-8} molal(m) is assumed for Pu^{4+} then pH is determined to be 0.45. If the Pu^{4+} activity is increased then the pH drops to even more acidic conditions.

For Eq. (C-19), there is some uncertainty for K_{so_2}; values from 10^{-52} to 7×10^{-56} being given by Cleveland (1971). For the former, pOH = 11 and hence pH = 3. Thus 3 may be used with a reasonable degree of confidence as an upper pH limit for the possible dissolution of Pu-oxide or Pu-hydroxide with $(Pu^{4+}) = 10^{-8}$. From the data given in the previous table, PuO_2 is stable relative to $Pu(OH)_4$;

$$Pu(OH)_4 = PuO_2 + 2H_2O \; ; \quad K_3 = 10^{+9.8} \; . \tag{C-20}$$

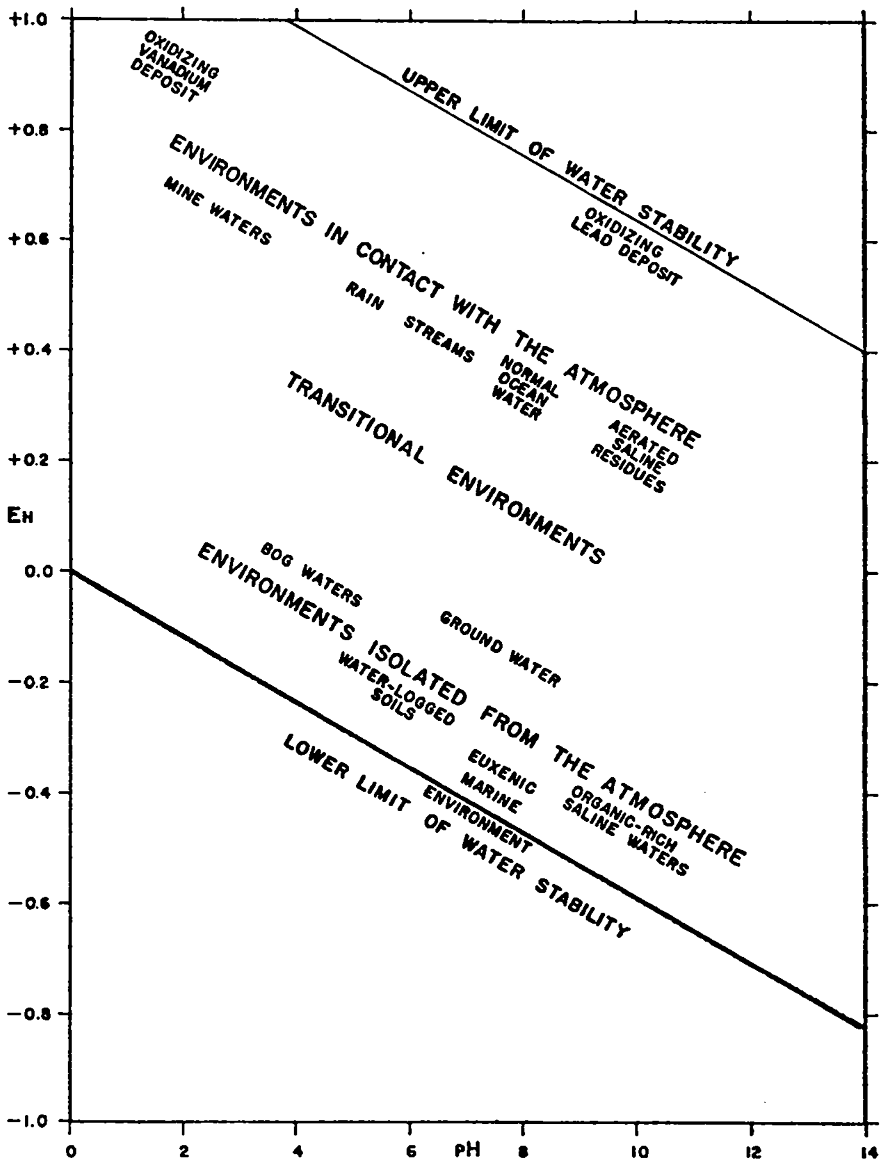

Fig. C-2.
Approximate position of some natural environments as characterized by Eh and pH (from Garrels and Christ, 1965).

Thus any $Pu(OH)_4$ which might form in nature will age to PuO_2; this behavior is exactly analogous to $Fe(OH)_3$ aging to Fe_2O_3.

The only other Eh-independent reaction to be considered is:

$$PuO_2^{2+} + 2(CO_3)^{2-} = PuO_2(CO_3)_2^{2-} \; ; \; K_4 = 10^{+14.9} \; . \qquad \text{(C-21)}$$

From the second dissociation constant for H_2CO_3 a pH value of 5.8 is calculated with $PuO_2{}^{2+}$ on the low pH side.

The only pH-independent reaction is:

$$PuO_2 = PuO_2{}^{2+} + 2e^- , \qquad \text{(C-22)}$$

for which $E^o = 1.23$ V but with $(Pu^{4+}) = 10^{-8}$, $Eh = 0.99$.

For Eh-pH dependent equations we consider:

$$Pu^{4+} + 2H_2O = PuO_2{}^{2+} + 4H^+ + 2e^- , \qquad \text{(C-23)}$$

$$PuO_2 + 2H_2CO_3 = PuO_2(CO_3)_2^{2-} + 4H^+ + 2e^- , \qquad \text{(C-24)}$$

$$PuO_2 + 2HCO_3^- = PuO_2(CO_3)_2^{2-} + 2H^+ + 2e^- . \qquad \text{(C-25)}$$

For Eq.(C-23) $Eh = 1.04 - 0.118$ pH, as the activities of the dissolved plutonium species are equal; for Eq.(C-24) the $Eh = 1.60 - 0.118$ pH, and for Eq.(C-25) we calculated $Eh = 1.22 - 0.059$ pH. For both Eqs.(C-24) and (C-25) the activity of $PuO_2(CO_3)_2^{2-}$ is assumed to be 10^{-8} m and total dissolved CO_2 (as H_2CO_3 or $HCO_3{}^-$, respectively) as 10^{-2} m. Varying either assumed molality will not change the slope but will very slightly change its position. In actuality the activity of H_2CO_3 decreases and the activity of $HCO_3{}^-$ increases as the equilibrium pH of 6.4 between the two is approached, but this is omitted for the Eh-pH diagram (Fig.C-3). In any event, the curvature is so slight that its omission does not seriously alter the boundaries shown in Fig. C-3.

III. APPLICATION OF THE Eh-pH DIAGRAMS FOR Pu-C-O-H AND U-C-O-H-Si SYSTEMS TO OKLO

Fig.C-3 shows that PuO_2 is stable over almost the entire stability field of water; only under extreme acid conditions, pH<1 for Pu^{4+}, or possibly under extremely oxidizing basic conditions, for $(PuO_2(CO_3)^{2-})$ near the upper stability limit of water, are aqueous species stable. It is noteworthy that there exists no "PDC" analog for UDC (uranyl dicarbonate ion; $(UO_2(CO_3)_2(H_2O))^{2-}$). This is no doubt due to the fact that $PuO_2(CO_3)^{2-}$ very nearly falls outside the stability field of water and, in view of the uncertainties of the thermochemical data for this species, this may well be the case.

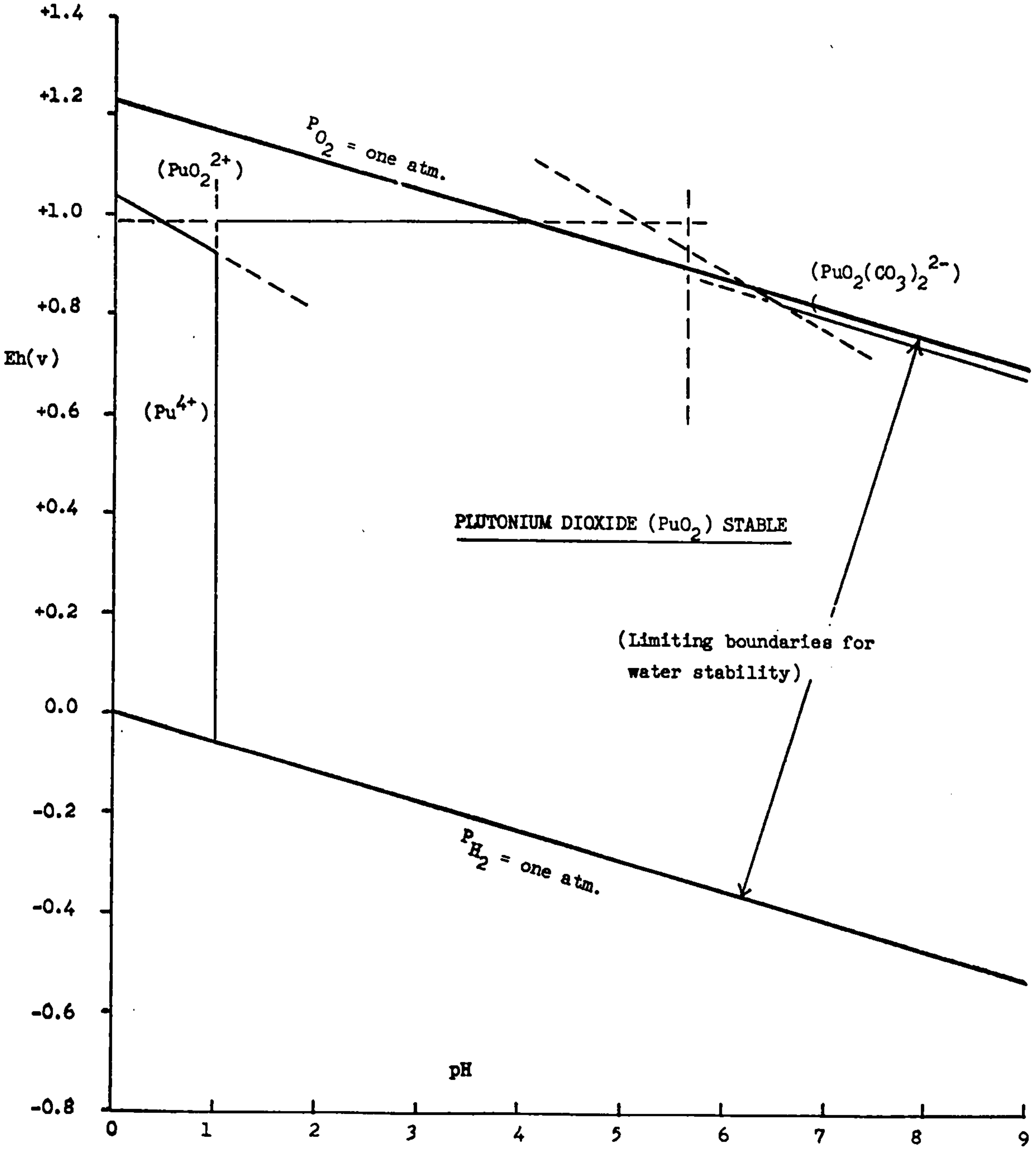

Fig. C-3.
Eh-pH diagram for the Pu-C-H-O system
at standard temperature and pressure.

Comparing Figs.A-1 and C-3 one notes that U (IV) as either UO_2 or $USiO_4$ may oxidize to U (VI) in $(UO_2)^{2+}$, UDC, or UTC depending on the Eh-pH conditions but that Pu in PuO_2 will not. It is significant that not only ^{239}Pu but ^{240}Pu and ^{241}Pu are considered to have remained within the interiors of Oklo urananite grains (Frejacques et al., 1975) even when some uranium remobilization occurred. This should be the case as almost ideal diadochy exists between UO_2 and PuO_2 (Levin et al., 1969). Only by mechanical disintegration and possible colloidal transport could even small amounts of Pu be mobilized. These arguments do not consider mobilization by organo-plutonium complexes, as the organic carbon content of the Oklo reactor zones is exceedingly small.

IV. APPLICATIONS OF Pu Eh-pH DIAGRAM TO OTHER SITES

While Fig. C-3 conveniently explains the retention of plutonium at Oklo it should be emphasized that this diagram is, in theory, applicable to any aqueous system provided that the abundance of organic carbon is low. In fact, the diagram may even apply for organic-rich aqueous systems but this cannot be tested at present due to lack of data.

For possible geologic isolation site selection for plutonium, it is clear that attention should be placed on rock with low total organic carbon and which is buffered (by $CaCO_3$, for example) such that pH is maintained within the rather broad limits of 5 to 9. These criteria should not be difficult to realize.