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Natural Repository Analogue Program

January 1—March 31, 1981

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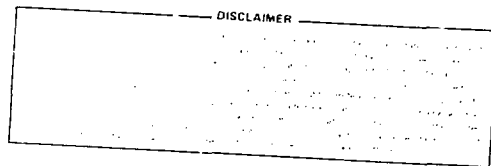
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Natural Repository Analogue Program

January 1—March 31, 1981

Compiled by
David B. Curtis



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NATURAL REPOSITORY ANALOGUE PROGRAM

JANUARY 1 - MARCH 31, 1981

Compiled by
David B. Curtis

ABSTRACT

Samples from Oklo Reactor zone-9 (ORZ-9) have been analyzed for the isotopic abundances of Nd, Ce, Ru, and Mo. Interpretation of the Nd data has begun as part of the effort to reconstruct the operating parameters of the reactor. The study of ORZ-9 and the peripheral rocks is being enhanced by additional analytical capabilities. A procedure was developed to measure uranium isotopic ratios with high precision. This new method was used for the analysis of rocks peripheral to ORZ-9. Two rocks containing relatively small quantities of uranium were depleted in ^{235}U . The result demonstrates that small quantities of uranium were removed from the reactor zone and redistributed over distances of several tens of meters.

Procedures are being designed to make high precision measurements of the relative abundances of barium isotopes. They will be used as part of a study of the transport of alkali and alkaline earth elements at Oklo.

Samples from distances up to 300 meters from the known mineralized area at Oklo have been selected and prepared in an effort to identify element transport paths over longer distances. Lead isotope analyses have been started on these samples.

A sample from the Athabasca sandstone, overlying the uranium ores at Key Lake, and another from the transition zone at the unconformity between the sandstone and the basement were subjected to sequential leaches designed to preferentially dissolve specific minerals. Lead isotopic analyses on the leaches yielded two sets of data, which indicate the loss of uranium or the addition of lead from a radiogenic source early in the geologic history of the rocks.

Preliminary drafts of two topical reports were completed and copies circulated for review. The subject of the report by Clarence Duffy and Allen Ogard is "Uraninite Immobilization" and the other by Douglas Brookins discusses element mobility at the Oklo deposit.

An inert-atmosphere glove box has been installed and tested. Experiments to produce and measure low-oxygen-fugacity water systems are being installed.

I. PERSONNEL

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

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T. M. Benjamin
E. A. Bryant
J. H. Capps
D. B. Curtis
C. J. Duffy
W. D. Eford
A. J. Gancarz
A. E. Norris
A. E. Ogard
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II. PROGRAM OBJECTIVE

Geologic burial is the favored method being considered for the disposal of commercially generated radioactive wastes. Efforts to evaluate the effectiveness of geologic media in isolating such wastes from the biosphere are limited by the necessity to consider periods of time much greater than that recorded by human experiences. The Natural Repository Analogue program is a research effort to study the processes and conditions relevant to the retention and migration of elements in the Earth's crust. The program examines the geologic record, which does contain information regarding the retention of elements over appropriate periods of time. Laboratory work identifies conditions that have led to the extraordinary stability of certain natural minerals and attempts

to duplicate these conditions to characterize the stability of manmade materials over comparable periods of time in geologic storage.

III. PROGRESS REPORTED PREVIOUSLY

Funding for the United States' participation in the international investigation of the Oklo natural fission reactor phenomenon commenced in fiscal year 1975. The first formal report of progress in this program was the annual report of fiscal year 1976 issued in November 1976. The Oklo phenomenon refers to the occurrence of self-sustaining fission chain reactions in a series of very rich uranium ore pockets located in an extensive Precambrian pitchblende deposit in Gabon, Africa. The uranium formed critical masses about 2×10^9 years ago. The duration of criticality was several hundred thousand years. During criticality, approximately 10 tons of uranium were fissioned. Studies of the Oklo phenomenon have shown that many fission products were retained at the sites where they were generated. Other products from uranium decay or fission have been shown to be missing in whole or in part from the fossil reactor cores. Our studies have examined the spatial, temporal, and chemical features of the processes that fractionated and redistributed the fission and radioactive decay products. Previous reports have discussed the fractionation and redistribution of ^{99}Tc relative to ruthenium, ruthenium relative to uranium, and lead relative to uranium. These studies determined the time when the Oklo ores were formed, and identified continuous volume diffusion of radiogenic lead from uraninite grains as the process by which lead is fractionated from uranium. Transport paths have been identified in the ores and in the rocks that confine the ores. Limits have been placed on the times when the element redistributions occurred.

To extend the work to physical, chemical, and geologic environments different from those found at the Oklo mines, samples from the uranium ore body at Key Lake, in the northwest corner of the Canadian Province of Saskatchewan, have been studied. Because there is no evidence that the rich uranium ores at Key Lake attained nuclear criticality, these studies have been confined to the fractionation and redistribution of lead produced by radioactive decay of uranium and thorium: A massive redistribution of uranium, thorium, and lead occurred in metamorphic rocks that house the ores and underlie the Athabasca sandstone. This element redistribution was contemporaneous with the deposition of the overlying sandstone 1.3×10^9 years ago. Relative excesses and

deficiencies of radiogenic lead identify extensive mobilization and redistribution of elements in the ores, and metamorphic basement and the overlying sandstone. Analyses of samples from Key Lake are continuing.

IV. PROGRESS DURING THE QUARTER, JANUARY 1 - MARCH 31, 1981

A. Fractionation and Redistribution of Fission Products at Oklo Reactor Zone 9 (ORZ-9) (Tim Benjamin, David Curtis, Alex Gancarz, Bill Maeck, and Don Rokop).

1. Introduction. An experiment has been designed to study the fractionation of fission products and the uranium parent in a well-defined zone of nuclear criticality at the Oklo mines, and the redistribution of the fractionated elements within the reactor zone, and external to it, in the host rocks. Reactor zone 9 is located roughly 200 meters to the south of zones 1-6, the areas that were first found to have been natural fission reactors. There are three identified regions of criticality near reactor zone 9. Zone 7 lies roughly 10 meters to the north of zone 9 and zone 8 is located about 10 meters to the south.

Crudely, reactor zone 9 was a plate shaped structure extending along the stratigraphic dip. The axis extending up-dip was several meters long and the N-S axis in the stratigraphic plane was of similar length. The E-W axis, up and down in a stratigraphic sense, was only a few centimeters wide. A cross section of this reactor and the rocks surrounding it were exposed at the bottom of the Oklo mine during the sampling trip by A. J. Gancarz in September 1979. This exposure provided a unique opportunity to obtain samples at well defined locations in and around an area that had sustained nuclear criticality. At the horizontal plane where the samples were taken, the N-S extent of the reactor zone had narrowed to about 3 meters from a maximum of about 10 meters. The plane where the samples were taken was probably near the bottom of the down-dip extent of this reactor. Samples taken from the south of the present exposure were a few meters down-dip from reactor zone 8. Fourteen samples from the host rocks and eight samples from the reactor zone were ground, sieved, and prepared for analyses. The locations from which these samples were taken are identified in the first quarterly report for fiscal year 1981.

2. Characterization of Oklo Reactor Zone 9. Eight samples from the reactor zone are being analyzed for the isotopic abundances of molybdenum, ruthenium, cerium, neodymium, uranium, and lead. These data will be used to reconstruct the operating parameters of the reactor and thus characterize the relative abundances of the different chemical species produced by the fission processes. Comparison of the relative fission-produced abundances with the measured abundances of the same species provides a measure of the chemical stability of the reactor zone during and after the time these regions sustained nuclear criticality.

The analyses have been completed. However, only the data for neodymium have been studied and are reported here. Table I presents the relative neodymium isotopic abundances in six samples from reactor zone 9. Two additional samples are being reanalyzed to verify the original data. The results in Table I have been used to reconstruct the operating parameters of the reactor, which are given in Table II. Data analysis was done by a constrained least squares method, considering contributions to the neodymium isotopic abundances from four sources: 1) neutron capture by ^{141}Pr , 2) thermal neutron fission of ^{235}U , 3) thermal neutron fission of ^{239}Pu , and 4) natural neodymium. Neutron capture by ^{141}Pr was an insignificant factor in all the samples. In three of the samples, ^{239}Pu fission contributed an insignificant proportion to the neodymium. In the other three samples, ^{239}Pu fission appears to be a small, but significant, contributor to the neodymium content of the sample. The proportion of ^{239}Pu fission is not precisely defined, because there is a strong correlation between neodymium produced by ^{235}U fission and that produced by ^{239}Pu . This is not the situation for fissionogenic isotopes of ruthenium. Analysis of the ruthenium data should provide a more precise estimate of the contribution of ^{239}Pu to the fissionogenic components in these samples.

3. Fissionogenic Elements in Rocks Peripheral to Reactor Zone 9. The identification of ^{235}U -depleted uranium in rocks external to the reactor zones is important in evaluating the geochemical stability of this element in the Oklo environment. Such identification requires the ability to do high-precision measurements on small quantities of uranium. There are two criteria that must be met to fulfill this need: 1) The quantity of uranium introduced during chemical separation (the blank) must be insignificant relative to the amount of uranium being measured. 2) The mass spectrometer measurements must

TABLE I
NEODYMIUM ISOTOPIC ABUNDANCES IN SAMPLES FROM OKLO REACTOR ZONE 9

Sample Number	Fissiogenic (10^{-3} g/g)	Natural (10^{-3} g/g)	Relative Isotopic Abundance (%)						
			^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{148}Nd	^{150}Nd
ORZ-9-004	0.38	1.53	21.58	14.77	25.11	10.38	16.73	6.25	5.17
ORZ-9-005	0.30	1.79	23.13	14.30	24.49	9.82	16.85	6.12	5.29
ORZ-9-028	0.85	1.04	14.83	18.06	26.50	12.88	16.21	6.88	4.63
ORZ-9-030	0.75	1.00	15.42	17.89	26.27	12.68	16.25	6.81	4.67
ORZ-9-035	0.41	1.95	22.40	14.43	24.90	10.09	16.80	6.16	5.21
ORZ-9-036	0.35	0.40	14.30	18.51	26.49	13.13	16.12	6.90	4.55
Natural	--	--	27.03	12.14	23.82	8.30	17.23	5.79	5.69
$^{235}\text{U}_{\text{th}}$	--	--	--	28.81	26.57	18.99	14.43	8.04	3.15
$^{239}\text{Pu}_{\text{th}}$	--	--	--	27.26	23.06	18.44	15.17	10.11	5.96

TABLE II
OKLO REACTOR ZONE 9 OPERATING PARAMETERS CALCULATED FROM NEODYMIUM ISOTOPIC ABUNDANCES^a

Sample#	¹⁴¹ Pr+n	Neodymium Source Components (%)			Fissions/g	$\frac{^{239}\text{Pu}_{\text{th}}}{^{235}\text{U}_{\text{th}}}$
		Natural	²³⁵ U _{th}	²³⁹ Pu _{th}		
ORZ-9-004	∅	79.92 ± .15	20.08 ± .14	∅	7.67 ± .05 × 10 ¹⁸	∅
ORZ-9-005	∅	35.57 ± .08	14.43 ± .07	∅	6.05 ± .03 × 10 ¹⁸	∅
ORZ-9-028	∅	55.07 ± .46	40.90 ± 3.05 ^b	4.04 ± 3.17	1.74 ± .04 × 10 ¹⁹	0.13 ± .11
ORZ-9-030	∅	57.23 ± .42	39.43 ± 2.74	3.33 ± 2.86	1.52 ± .04 × 10 ¹⁹	0.11 ± .10
ORZ-9-035	∅	82.88 ± .13	17.12 ± .12	∅	8.08 ± .06 × 10 ¹⁸	∅
ORZ-9-036	∅	53.07 ± .39	44.11 ± 2.61	2.82 ± 2.71	7.14 ± .15 × 10 ¹⁸	0.08 ± .08

^aUncertainties reflect the uncertainty in the least squares analysis but do not include the analytical uncertainties associated with the data.

^bThe fissiogenic neodymium spectra from ²³⁵U_{th} and ²³⁹Pu_{th} are strongly correlated, producing large errors in the component proportions while maintaining small errors in the total fissions/g.

be precise enough to distinguish small variations in the isotopic ratios. A procedure has been developed which appears to meet these criteria. The procedure involves preliminary separation of uranium from the mass of the sample by anion exchange chromatography. Final cleanup is done by electrodeposition of uranium on a platinum cathode. This electrode is delivered to the spectroscopist, who reverses the polarity; the uranium dissolves from what is now the anode and redeposits on a rhenium cathode that serves as the source in the mass spectrometer. Initial evaluations have shown that 9×10^{-11} grams of uranium were introduced by the procedure. Mass spectrometry of the separated uranium appears to be capable of measuring $^{235}\text{U}/^{238}\text{U}$ with a precision of 0.1%. A thorough evaluation of the capabilities of the procedure is continuing.

This procedure has been used to measure uranium isotopic ratios in the rocks peripheral to reactor zone 9. The results of these analyses are given in Table III. Included in this table are the average and standard deviation of 12 analyses of isotopically normal uranium. This average includes a number of samples measured during the analytical development under less-than-optimum conditions. The standard deviation for this value is probably three times greater than that which should properly be associated with the analysis of the samples. Despite this conservative estimate of the precision of the analysis, samples ORZ-9-008 and ORZ-9-029 contain uranium that is significantly depleted in ^{235}U .

In theory, this result might be attributed to in situ depletion by fission from leakage neutrons from the zone of reaction. However, there are two lines of evidence which suggest that this is not the case. 1) Sample ORZ-9-007 is from virtually the same location as ORZ-9-008. A flux of leakage neutrons should have affected the uranium isotopic abundances similarly, yet 007 is isotopically normal and 008 is 2.6% depleted in ^{235}U . 2) Sample ORZ-9-029 is ~45 meters from ORZ-9, the closest known source of neutrons. This is certainly beyond the range of neutrons produced in this reactor zone. Samples 008 and 029 contain uranium that has been removed from the reactor zone, transported over distances of meters and tens of meters, respectively, and redeposited in the rocks where it was found. The failure to identify isotopic shifts in samples C1, C2, and C4 does not signify the absence of depleted uranium in these samples. Large uranium concentrations increase the detection limits for depleted uranium. For instance, 5 ppm of 2.6% depleted ^{235}U , such as is seen in 008, would produce isotopic shifts in C-1, C-2, and C-4 that are less than 1/3

TABLE III
ISOTOPIC ABUNDANCES OF URANIUM IN HOST ROCKS EXTERNAL TO REACTOR ZONE 9
MEASURED BY HIGH PRECISION ISOTOPE DILUTION MASS SPECTROMETRY

<u>Sample Number</u>	<u>(10⁻⁶ g/g)</u>	<u>Relative Isotopic Abundance (%)</u>	
		<u>²³⁸U</u>	<u>²³⁵U</u>
ORZ-9-007 ^a	6.84	99.28 ± 0.3	0.719 ± 0.002
ORZ-9-008	4.94	99.30	0.701 ₅
ORZ-9-029	9.41 x 10 ⁻¹	99.29	0.710 ₂
ORZ-9-C1	8.27 x 10 ³	99.28	0.721 ₃
ORZ-9-C2	9.37 x 10 ¹	99.28	0.719 ₇
ORZ-9-C4	4.05 x 10 ²	99.28	0.720 ₆
Natural ^b		99.28 ± 0.4	0.720 ± 0.003

^a Average of three analyses.

^b Average of twelve analyses.

of the uncertainty stated for natural uranium in the table, and even below the lower limit of uncertainty that we believe more accurately represents the precision of the uranium isotopic analyses of the samples.

B. Redistribution of Uranium, Thorium, and Lead at the Oklo Site (John Capps, David Curtis, Wes Efurd, Alex Gancarz, and Don Rokop)

Small quantities of fission products were produced in the Oklo reactors relative to the amount of analogous natural elements in the surrounding rock. This small relative abundance presents a difficulty in tracing fissiogenic components over large distances: as the distance from the reactor increases, the isotopic signatures may be diluted beyond the limits of analytical detection.

The decay of uranium produces lead in much greater quantities than the fission products. Consequently, lead is more likely to be a detectable tracer of element movement over long distances than the fission-produced elements. The quartz pebble conglomerate immediately underlying the mineralized strata at Oklo has previously been identified as a major transport path for radiogenic lead from the ores. Samples of this basal conglomerate have been taken from cores extending for several hundred meters to the east of the currently identified ores. These samples have been ground and sieved, and preliminary uranium assays have been completed. Lead isotopic analyses have been started.

A strongly recrystallized quartz sandstone was the primary rock type that was seen in selecting the samples. However, fractures containing secondary minerals and bands of altered rock often occurred in the cores. These regions were preferentially sampled, along with portions of the quartz matrix that was thought to be representative of the major mass of the rock. Sample locations and brief descriptions of the samples are given in Table IV. Locations are in meters on a grid established by the Compagnie des Mines d'Uranium Franceville (COMUF), the mining company at Oklo.

C. Retention and Transport of Alkali and Alkaline Earth Elements at Oklo (John Capps, David Curtis, Wes Efurd, and Ted Norris)

Radioactive isotopes of strontium and cesium are of particular concern with respect to short-term environmental hazards. These, other isotopes of the same elements, and rubidium and barium were produced in substantial quantities in the zones of nuclear criticality at Oklo. We have initiated experiments to begin to study the geochemical stability of these elements in the Oklo rocks.

TABLE IV
 DESCRIPTIONS AND LOCATIONS OF SAMPLES CHOSEN FOR THE OKLO LONG TRAVERSE (OLT) EXPERIMENT

<u>Sample Number</u>	<u>Location^a</u>			<u>Comments</u>
	<u>X</u>	<u>Y</u>	<u>Z</u>	
OLT-133-1	357	-240	176	Typical sandstone
OLT-133-2	357	-240	176	Slightly altered conglomerate (3mm pebbles)
OLT-25-1	277	-240	202	Rust red coloration
OLT-25-2	277	-240	200	2-3mm pebble conglomerate
OLT-25-3	277	-240	194	Typical sandstone
OLT-22	196	-240	186	Typical sandstone
OLT-11	117	-240	288	Typical sandstone
OLT-9-1	78	-240	313	Iron oxide filled fracture
OLT-9-2	78	-240	340	Yellow friable band
OLT-9-3	78	-240	327	Open fracture, galena on surface
OLT-9-4	78	-240	327	Sandstone matrix 2cm from fracture
OLT-83	58	-240	350	Altered with fine fractures
OLT-7	39	-240	361	Typical sandstone

^aZ=0 is roughly 400 meters beneath the surface. Therefore, the larger the value of Z, the closer to the surface. Known ores are roughly located at between Y = +160, -350, X = ±50 and Z greater than 250. Oklo reactor zone 9, is located Y = -230, X = 97, and Z = 320 in this matrix.

Barium isotope abundances are being measured in samples from reactor zone 9 of the Oklo mine and in rocks peripheral to this zone. The purpose of this work is to obtain data about the migration and retention of fissionogenic cesium and barium in the Oklo natural repository. Four of the seven stable isotopes of barium can be formed from uranium fission. The fission yield of ^{136}Ba , one of the four fissionogenic barium isotopes, is sufficiently shielded by stable ^{136}Xe that alteration of its natural abundance by fission will not be detectable in this work. We expect to measure the fissionogenic components of ^{135}Ba , ^{137}Ba , and ^{138}Ba . The cesium precursors of these three barium isotopes have vastly different half-lives: 3×10^6 years, 30 years, and 32 minutes, respectively. We hope to infer the times of fractionation of cesium and barium relative to the time of formation of the fission products through knowledge of the precursor half-lives and measurement of the barium isotopic abundances.

The barium isotopic abundance measurements will require high-precision mass spectrometric techniques. Necessary supplies for this work were received this quarter, including 9 mg of >55% ^{130}Ba for use as a spike, 2 mCi ^{133}Ba for use in tracing the barium chemical separation through a cation exchange column, and 200 g ultrahigh purity $\text{Ba}(\text{NO}_3)_2$ for use as a primary barium standard. Five samples of Oklo material were assayed for barium to estimate the sensitivity that will be required in the mass spectrometric analyses. Solutions of the samples were analyzed for barium concentrations by inductively coupled plasma emission spectroscopy. The results are shown in Table V. This table also contains the fission product molybdenum abundances measured in the same samples. These are the same results that were published in the last quarterly report. The molybdenum data were used to calculate the mass of ^{135}Ba , ^{137}Ba , and ^{138}Ba that would result from the same number of fissions as those that yielded the observed fission product molybdenum. The natural barium was calculated from measured abundances assuming normal isotopic composition. The ratio of fission product barium to natural barium is shown in the last three columns of Table V for the three barium isotopes of interest. These data indicate that extremely good precision will be required to insure detection of fissionogenic barium for these Oklo samples.

Mass spectrometric experiments were performed to determine optimum procedures for barium. The starting point was the barium analysis procedure

TABLE V
ESTIMATED MASS SPECTROMETRIC SENSITIVITIES FOR FISSIONGENIC BARIUM DETECTION

Sample	Measured Ba (g/g rock)	Measured Fission Product Mo (ng/g rock)	$\frac{^{135}\text{Ba}_{th}^a}{^{135}\text{Ba}_N^b}$	$\frac{^{137}\text{Ba}_{th}^h}{^{137}\text{Ba}_N^a}$	$\frac{^{138}\text{Ba}_{th}}{^{138}\text{Ba}_N}$
ORZ-9-C-1	1.59×10^{-3}	5700	2.0×10^{-2}	1.1×10^{-2}	2.0×10^{-3}
ORZ-9-C-2	8.98×10^{-4}	<21	$<1.3 \times 10^{-4}$	$<7.4 \times 10^{-5}$	$<1.3 \times 10^{-5}$
ORZ-9-C-3	7.17×10^{-4}	<27	$<2.1 \times 10^{-4}$	$<1.2 \times 10^{-4}$	$<2.1 \times 10^{-5}$
ORZ-9-C-4	6.82×10^{-4}	136	1.1×10^{-3}	6.3×10^{-4}	1.1×10^{-4}
ORZ-9-029	1.89×10^{-4}	83	2.4×10^{-3}	1.4×10^{-3}	2.4×10^{-4}

^aSubscript th refers to fission produced isotope calculated from measured fissionogenic Mo abundances.

^bSubscript N refers to natural isotopic composition calculated from measured Ba abundances assuming normal isotopic composition.

published by O. Eugster, et al.* All of our work has been done with natural barium samples. We use the barium abundances listed in the paper just cited to measure our instrumental fractionation. Our goal is to maximize the efficiency of barium ionization and to minimize the barium isotopic fraction.

The results of the mass spectrometric development work to date are summarized here. The optimum filament temperature for stable, efficient barium ionization appears to be 1240°C. At this temperature, the background from tantalum filaments is significantly higher than that from rhenium filaments. Our best results have been obtained when equal portions of a 10- μ l-barium solution aliquot are loaded on each of the two side filaments of a rhenium triple filament ion source. These experiments have been performed with solutions containing ~50 μ g Ba/ml, but with various concentrations of additional ions. Barium ionization was best when the solution was 1.5 N HCl, compared to 4 N HCl and 0.4 N HCl. The sample was blown off the filament at the start of a run using 1.5 HNO₃ as the aqueous medium. In an attempt to ionize BaO, rather than BaCl₂, a solution of barium in 1.5 N HCl was flashed to the oxide on a filament in another run. Good intensity was obtained, but the stability was too poor to obtain barium isotopic abundance data. Additional experiments will be done to load barium onto the filaments from H₂SO₄ and from HF solutions, to see if ionization and isotopic fractionation characteristics of the mass spectrometric analyses can be improved.

D. Element Redistribution in Sedimentary Rocks at Key Lake (John Cappis, David Curtis, and Alex Gancarz)

Previous work on lead, uranium, and thorium migration at Key Lake identified a consistent pattern of excess lead or deficient uranium in the Athabasca sandstone that overlies the Key Lake deposit. To better understand the meaning of this observation, we selected two samples that contained large amounts of radiogenic lead (high values of ²⁰⁶Pb/²⁰⁴Pb) for further analyses. These samples were identified as KL-16 and KL-13 in the original report. The latter will be identified as KL-794 in the future; KL-16 is an unconsolidated sandstone from the Athabasca. It was not necessary to grind and sieve it because it disintegrated upon handling. Sample KL-794 was from the unconformity between the basement and the sandstone. It was altered and porous; grains were coated with minerals tentatively identified as sulfides.

* O. Eugster, F. Tera, and G. J. Wasserburg in J. Geophys. Res. 14, 3897 (1969).

Each of these samples was leached by HCl, then leached by aqua regia, and the residue dissolved in HF-HClO₄. The treatment was designed to preferentially dissolve galena (PbS), then the other sulfides, such as pyrites, and finally the silicates. The results of lead isotopic analyses on back of these leaches are presented in Table VI.

The large majority of the lead in the sandstone is associated with the silicate phase (HF-HClO₄). By contrast, nearly 60% of the lead in material from the contact was leached by HCl and was probably present as galena.

Within the uncertainty of the data, the four data points from each sample are perfectly colinear on a plot of ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁷Pb/²⁰⁶Pb. In each case, the colinear data suggest the addition of radiogenic lead or the removal of large quantities of uranium from these rocks early in the geologic history of the region. The result may reflect the mobilization of elements associated with the formation of the ores. Analyses of the Key Lake samples are continuing.

TABLE VI
LEAD ISOTOPIC ABUNDANCE IN LEACHES OF ROCKS FROM KEY LAKE

	Percent of Total	²⁰⁸ Pb	²⁰⁷ Pb	²⁰⁴ Pb
	Lead	²⁰⁶ Pb	²⁰⁶ Pb	²⁰⁶ Pb
KL-16 (HCl)	4 ^b	1.539	0.5978	0.0362
KL-16 (Aqua Regia)	5 ^b	1.560	0.5998	0.0363
KL-16 (HF-HClO ₄)	91 ^a	1.460	0.5633	0.0335
KL-16 (Whole Rock)	(9.44 x 10 ⁻⁵ g Pb/g)	1.460	0.5699	0.0340
KL-794 (HCl)	58 ^b	1.572	0.5281	0.03134
KL-794 (Aqua Regia)	3 ^b	1.379	0.5044	0.02941
KL-794 (HF-HClO ₄)	36 ^b	1.283	0.4932	0.02860
KL-794 (Whole Rock)	(2.03 x 10 ⁻⁴ g Pb/g)	1.436	0.5081	0.02974

^aNo measurement, inferred from mass balance.

^bInaccurate results due to underspiked analyses.

E. Preparation and Characterization of Reduced Aqueous Solutions (Allen Ogard)

The Vacuum/Atmospheres, controlled-inert-atmosphere glove box and Dri-Train purification system are completely installed and tested. Several experiments for producing and measuring low-oxygen-fugacity water systems and negative Eh water systems are being installed inside the glove box.

F. Topical Report on Uranium Immobilization (Clarence Duffy and Allen Ogard)

A preliminary draft of "Uraninite Immobilization" by C. Duffy and A. Ogard has been completed and circulated internally for review and comments.

During the preparation of this topical report, several important conclusions have been reached. The importance of redox conditions for the fixation of uranium has been confirmed. Although other factors, such as pH and anion concentration, affect uranium solubility, the redox state of the solution seems to be the most important variable in the natural environment.

It appears that not all ground waters may be in equilibrium with the rocks through which they flow, although there seems to be a general trend toward more reducing conditions as one moves down an aquifer away from the recharge area. Bacterial activity may be important as a reduction mechanism. Although several redox zones are observed in ground water systems, uranium precipitation in natural low-temperature systems is particularly associated with the sulfate reduction zone. This is particularly pleasing because this observation is in good agreement with current thermodynamic data, which predict uranium solubilities of less than 1 ppb at near neutral pH and reducing conditions under which sulfide becomes dominant over sulfate.

G. Oral Presentations During the Quarter

D. Curtis, "Retention and Transport in the Earth's Crust - The Oklo Experience," Los Alamos National Laboratory Chemistry-Nuclear Chemistry Division seminar, March 6, 1981.

H. Meetings

A. Gancarz attended a workshop in Houston, Texas, March 17, 1981, to assist in the preparation of the ONWI site-characterization program plan.