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Progress Report

Natural Repository Analogue Program

October 1—December 31, 1980

University of California



LOS ALAMOS SCIENTIFIC LABORATORY

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Natural Repository Analogue Program

October 1—December 31, 1980

Compiled by

David B. Curtis

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NATURAL REPOSITORY ANALOGUE PROGRAM

October 1 - December 31, 1980

Compiled by

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ABSTRACT

One fission product, molybdenum, has been found in rocks which were taken at distances between 1 and 40 meters from reactor zones. We conclude that this molybdenum was mobilized in the nearby zones of criticality, transported over distances up to a few tens of meters and redeposited in these rocks. In contrast, the same samples contain undetectable quantities of both fissionogenic ruthenium or of the ^{235}U depleted reactor fuel. The redistribution processes enriched molybdenum by several orders of magnitude relative to ruthenium and uranium. Analyses of the source region will determine whether fractionation of these elements is due to selective mobilization at the source or preferential deposition at the repository.

Ores peripheral to reactor zones are, on the average, deficient in one half of the radiogenic lead (~7000 ppm). Rocks from the conglomerate underlying the mineralized stratum contain, on the average, 6000 ppm of excess lead. One sample contains a remarkable 34,000 ppm of unsupported radiogenic lead. This basal conglomerate must have been a major transport path and repository for lead lost from the ores. Additional samples from this stratum have been taken over distances up to 300 meters from the ore zones and are being analyzed to determine the extent of lead transport over these distances.

The development of methods to prepare and characterize low oxygen fugacity waters has been delayed by problems in the installation of controlled atmosphere boxes.

Two reports are in various stages of preparation. A preliminary draft of a topical report on the immobilization of uranium in nature is in progress. A final draft of a report on Eh-pH diagrams pertinent to the redistribution of elements at Oklo is being prepared for publication as a LAMS document.

I. PERSONNEL

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

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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 which have lead to the extraordinary stability of certain natural minerals and attempts to duplicate these conditions to characterize the stability of man-made 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 which 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 than 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. Since 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 which 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, the metamorphic basement and the overlying sandstone. Analyses of samples from Key Lake is continuing.

In March, 1978, the Office of Nuclear Waste Isolation funded a program to study the retention of fission products in spent nuclear fuel under various conditions of aqueous leaching. This work suggested that phase solubility is an important factor controlling the concentration of actinides and lanthanides in aqueous solutions in contact with spent fuel. A major result of these studies was a realization of the difficulty in preparing and characterizing highly reduced aqueous solutions. Techniques to prepare solutions with very low oxygen fugacities and to characterize their reducing capacities were investigated.

Elemental and isotopic analyses, primarily using mass spectrometric methods, are the principal analytical methods used in these studies. The development of appropriate analytical techniques have comprised an important part of the efforts. The results of this development work has been reported in previous programmatic reports.

IV. PROGRESS DURING THE QUARTER OCTOBER 1 - DECEMBER 31, 1980

In October, 1980 the Oklo program studies and the work on the release of fission products from spent fuel were combined to form the Natural Repository Analogue program funded by the Office of Nuclear Waste Isolation. This is the first quarterly report for this combined effort.

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

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 cm 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 is probably near the bottom of the down-dip extent of this reactor. Samples taken from the south of the present exposure were probably only a few meters down-dip from reactor zone 8.

Fourteen samples from the host rocks and eight samples from the reactor zone were selected, ground and sieved for analyses. The location of these samples are presented in Table I. In this table all samples are located relative to an arbitrary point located roughly at the N-S midpoint of the exposed reactor zone.

Positive signs refer to distances north of this point on the N-S axis and east of it on an E-W axis. All samples are roughly on the same horizontal plane except ORZ-9-007 and 008. These two samples were taken 4.3 meters up-dip from the floor of the mine. The coordinates for these two samples in Table I are projections onto the horizontal plane of the exposed reactor zone.

Composites of some samples were prepared by mixing constituents in roughly equal proportions. The identification of the samples which comprise these composites are given in Table I. These and several uncomposited samples representing a spatial distribution in three directions around ORZ-9 have been analyzed for concentrations of fissionogenic and/or natural molybdenum, ruthenium, uranium, thorium and isotopes of lead. The results of these analyses are given in Tables II and III.

2. Migration of Fissionogenic Elements from Reactor Zone 9.

Data in Table II shows that rocks from within a few meters of the zones of criticality contain abundant fissionogenic molybdenum. Subsequent analyses will determine if the nearby reactor zones are correspondingly deficient in this fission product. If the data do establish these zones as a potential source of the mobilized molybdenum it will provide evidence of transport of this element over distances of up to 40 meters sometime since the reactors were critical 2×10^9 years ago. These processes enriched molybdenum relative to both ruthenium and uranium. The extent of this enrichment is shown in Table IV. The Mo/Ru fractionation factor is a comparison of the ratio of measured fissionogenic molybdenum to the limit of fissionogenic ruthenium relative

TABLE I
LOCATIONS OF SAMPLES RELATIVE TO N-S MIDPOINT OF REACTOR ZONE 9
AT THE EXPOSED HORIZONTAL PLANE

<u>Sample Number</u>	<u>Distance from Reference Point</u>		<u>Comments</u>
	<u>N-S Axis (m)</u>	<u>E-W Axis (m)</u>	
	<u>Reactor Zone</u>		
ORZ-9-005	+1.6	0	
ORZ-9-004	0	0	
ORZ-9-035	0	-0.05	
ORZ-9-030	-1.3	+0.15	
ORZ-9-036	-0.75	0	
ORZ-9-028	-1.4	-0.05	
ORZ-9-015	-1	0	
ORZ-9-016	-1	0	0.1M downdip from 015
	<u>Host Rock</u>		
Host Rock			
ORZ-9-021	-2.5	-0.8	
ORZ-9-020	-2.5	-0.5	Composite C-2
ORZ-9-022	-4.2	-0.9	
ORZ-9-023	-4.2	-1.1	Composite C-3
ORZ-9-024	-4.2	-1.5	
ORZ-9-025	-6.4	-0.9	
ORZ-9-026	-6.4	-1.4	Composite C-4
ORZ-9-027	-6.4	-2.1	
ORZ-9-001	0	+6.5	
ORZ-9-002	0	+4.5	Composite C-1
ORZ-9-003	0	+1.5	
ORZ-9-007	+1.1	-2.5	
ORZ-9-008	+1.1	-2.5	4.3 M updip
ORZ-9-029	+40	+20	F _B Stratigraphic Section

TABLE II
ELEMENTAL AND ISOTOPIC ABUNDANCES IN HOST ROCKS EXTERNAL TO OKLO REACTOR ZONE 9*

Sample Number	Fission Product Abundance		Natural Element Abundance				
	^{99}Ru (10^{-9}g/g)	Mo (10^{-9}g/g)	Ru (10^{-9}g/g)	Mo (10^{-9}g/g)	U (10^{-6}g/g)	Th (10^{-6}g/g)	Pb 10^{-6}moles/g
ORZ-9-007	$<2 \times 10^{-2}$	8.27×10^1	$<2 \times 10^{-1}$	2.29×10^2	5.4 5.8**	2.96×10^2	3.99×10^3
ORZ-9-008	$<2 \times 10^{-2}$	7.95×10^1	$<2 \times 10^{-1}$	2.36×10^2	≤ 1.4 3.8**	3.5×10^1	3.12×10^2
ORZ-9-029	$<2 \times 10^{-2}$	8.27×10^1	$<2 \times 10^{-1}$	1.66×10^3	$\leq 9 \times 10^{-1}$ 8 $\times 10^{-1}**$	1.1×10^1	8.62
ORZ-9-C1	$<3 \times 10^{-2}$	5.70×10^3	$<2 \times 10^{-1}$	1.29×10^5	8.14×10^3 7.95 $\times 10^3**$	6.4×10^1	2.35×10^3
ORZ-9-C2	≤ 8.8	$\leq 2.1 \times 10^1$	3×10^1	$\leq 2.8 \times 10^2$	8.3×10^1 8.5 $\times 10^1**$	1.1×10^1	1.76×10^3
ORZ-9-C3	≤ 6.3	$\leq 2.7 \times 10^1$	2.8	$\leq 9 \times 10^1$	1.9×10^1 1.9 $\times 10^1**$	2	1.35×10^2
ORZ-9-C4	$<2 \times 10^{-1}$	1.36×10^2	<2	2.76×10^2	3.95×10^2 3.82 $\times 10^2**$	9	6.57×10^2
Blank	≤ 1	$<2.0 \times 10^1$	6.3	2.90×10^2	$\leq 8 \times 10^{-2}$	<4	

*All analyses by isotope dilution mass spectrometry unless specified.

**Delayed Neutron Counting Activation Analyses.

TABLE III
NUCLIDIC AND ISOTOPIC ABUNDANCES IN HOST ROCKS EXTERNAL TO OKLO REACTOR ZONE 9

Sample Number	^{206}Pb (10^{-9} moles/g)	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{238}\text{U}/^{204}\text{Pb}$	$^{232}\text{Th}/^{204}\text{Pb}$
ORZ-9-007	1.66×10^5	0.0221	0.1405	0.00039	3.74×10^{-1}	2.0×10^1
ORZ-9-008	1.33×10^3	0.0220	0.1143	0.00028	4.26×10^1	4.1×10^2
ORZ-9-029	1.90×10^1	0.7843	0.3805	0.01630	1.08×10^1	1.5×10^2
ORZ-9-C1	1.01×10^4	0.0133	0.1091	0.00027	1.22×10^4	1.0×10^2
ORZ-9-C2	7.58×10^3	0.0096	0.1131	0.00018	2.59×10^2	3.5×10^1
ORZ-9-C3	5.83×10^2	0.0134	0.1080	0.00024	5.66×10^2	6.2×10^1
ORZ-9-C4	2.85×10^3	0.0082	0.1069	0.00015	3.75×10^3	9.1×10^1

TABLE IV
ELEMENT FRACTIONATION FACTORS* IN HOST ROCKS EXTERNAL TO OKLO REACTOR ZONE 9

Sample Number	Mo/Ru	$^{206}\text{Pb}/^{238}\text{U}$	$^{208}\text{Pb}/^{232}\text{Th}$
ORZ-9-007	$>10^3$	1.82×10^4	9.8
ORZ-9-008	$>10^3$	2.24×10^2	1.0
ORZ-9-029	$>10^3$	1.5×10^1	7.8×10^{-1}
ORZ-9-C1	$>5 \times 10^4$	8.1×10^{-1}	1.3
ORZ-9-C2	-	5.7×10^1	4.7
ORZ-9-C3	-	2.00×10^2	3.0
ORZ-9-C4	$>1.7 \times 10^2$	4.7	2.0

*See text for explanation of fractionation factors.

to the ratio of the fission yields of these same two elements. This enrichment in rocks to the east of the reactor zone is more than four orders of magnitude. Similarly fissionogenic molybdenum in these rocks is highly enriched relative to the uranium fuel from which it was produced. The presence of fissioned uranium would produce measured values of $^{235}\text{U}/^{238}\text{U}$ less than normal (0.00726). Preliminary measurements of this ratio show no deviations from the normal ratio. Further analysis of the reactor material will determine whether these elemental fractionations resulted from selective mobilization of molybdenum at the source or preferential deposition of the element in these rocks.

B. Redistribution of Uranium, Thorium and Lead at the Oklo Site (David Curtis, Alex Gancarz, John Cappis)

The lead isotope and uranium abundances that have been determined in Oklo materials indicate that these rocks have been paths for a mobile phase which either selectively removed or deposited one or the other of this parent-daughter pair. The data obtained shows areas of relative lead enrichment and others of lead depletion. For instance, uranium ores around reactor zones 1-6 used to determine the age of the Oklo deposit are lead deficient (Gancarz, 1978). By contrast, samples from the quartz pebble conglomerate which underlies the ores are highly enriched in lead (Gancarz, *et. al.*, 1980). Ratios of isotopic and nuclidic abundances of lead, uranium and thorium in the rocks around reactor zone 9 are presented in Table III. The $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ fractionation factors in Table IV are the measured lead daughter (corrected for an initial component) relative to the measured actinide parent compared to the relative abundances of these two nuclides in 2.0×10^9 year old materials [i.e., $^{206}\text{Pb}/^{238}\text{U} = (e^{\lambda_{238} \times 2.0 \times 10^9} - 1)$]. Fractionation factors greater than unity indicate enrichment of lead relative to the actinide element. Values less than unity indicate a relative lead deficiency. With the exception of the sample from F_B (029) the rocks all show small excesses of radiogenic lead relative to thorium. The composite C-1, a very uranium rich sample, is the only one of the ORZ-9 samples that is deficient in lead relative to uranium. Sample ORZ-9-007 is a quartz conglomerate from the basal section that we previously identified as a lead transport path (Gancarz, *et. al.*, 1980). This sample contains four orders of magnitude more ^{206}Pb than could have been produced in 2.0×10^9 years by the decay of the measured abundance of ^{238}U . Sample ORZ-9-008, a black shale, is also enriched in radiogenic lead, but to a far lesser degree than the quartz conglomerate, ORZ-9-007, taken from the same

location. Analyses of the nearby reactor materials will attempt to identify lead deficient regions which may have been the source of the excess lead in these samples. Samples representing a much greater spatial array are also being analyzed to identify sources, repositories and transport paths of lead and/or uranium redistributed over distances of several hundred meters.

References

- A. J. Gancarz (1978) U-Pb Age (2.05×10^9 years) of the Oklo Uranium deposit. Natural Fission Reactors International Atomic Energy Agency, pp. 513-520.
- A. Gancarz, G. Cowan, D. Curtis, and W. Maeck, (1980) ^{99}Tc , Pb and Ru Migration Around the Oklo Natural Fission Reactors Scientific Basis for Nuclear Waste Management ed. Clyde J. M. Northrup, Jr. pp. 601-608.

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

A Vacuum Atmospheres controlled inert-atmosphere glovebox and a Dri-Train purification system have been received from the vendors and are being installed in the alpha wing of the radiochemistry laboratory. A two month delay in the receipt of a Los Alamos-approved hydrogen gas manifold needed for the purification system will delay the start up of the glovebox. This glovebox will be used for experiments pertaining to Eh buffer systems and other methods of producing and measuring low oxygen fugacity water systems.

D. Topical Report on Uranium Immobilization (Clarence Duffy)

Effort has been directed toward an understanding of the immobilization of uranium in the Earth's crust. The most important factor in determining the mobility of uranium seems to be the redox state of the transporting fluid. This is a conclusion borne out both by uranium ore deposit mineralogy and by the known thermochemistry of uranium. The fact that uraninite and pitchblende, both UO_2 , are the most common uranium ore minerals argues for the importance of reducing conditions in immobilizing this element since these phases can crystallize only in a reducing environment.

The presence of reducing conditions in a given geologic environment is a more difficult question. Many minerals, particularly ferrous iron bearing minerals, are capable of reducing solutions in contact with them; but at the low temperatures of interest in nuclear waste isolation, very long times may be needed for equilibration of solid and fluid phases. Measurement of the redox state of geologic fluids is difficult. Oxygen concentrations under geologically reducing conditions are much too low to be measured directly.

Some attempt has been made to make such measurements electrochemically with platinum electrodes. However, it is generally accepted that platinum electrodes give a qualitative measure of the redox state of a solution, but generally can not be used quantitatively.

E. Eh-pH Diagrams (Douglas Brookins)

A final report on the application of Eh-pH diagrams to problems of element retention and transport at Oklo has been finalized for distribution as LAMS and ONWI reports. The diagrams were constructed for temperatures of 200°C and 25°C and one bar of pressure. Elements which possess only one oxidation state in natural systems, and are unaffected by oxidation-reduction of other species cannot be addressed in terms of Eh-pH diagrams. However, it is useful to overlay boundaries for pH dependent reactions on conventional Eh-pH diagrams. Alkali and alkaline earth elements are present as simple M^{1+} or M^{2+} ions in solution. The presence of barite and several generations of carbonate minerals suggest the retention of barium in the gangue if not in the ore zone minerals. However strontium immobilization may depend on fixation in clay minerals rather than the formation of insoluble sulfates or carbonates. Rubidium and cesium must either be fixed on clay minerals or oxide - hydroxide fracture fillings species, or possibly incorporated into newly formed clay minerals.

The stability of elements with an affinity for sulfur are usually easy to address with Eh-pH diagrams. Cadmium, for example, is stable as CdS under reducing conditions and soluble as Cd^{2+} or $HCdO_2^-$ under oxidizing conditions at 200°C. Thus the migration of cadmium, predicted under slightly oxidizing conditions, is consistent with reported measurements of Cd redistribution. Migration under slightly oxidizing conditions is also possible for molybdenum, antimony and possibly ruthenium. The stability of elements which occur as sulfides or the native element under reducing conditions are more difficult to interpret. The Eh-pH diagrams predict retention of indium, tellurium, palladium, silver, tin, technetium and ruthenium, yet evidence has been presented for local migration of the latter four elements. The mechanism for migration of these species under reducing-to-slightly oxidizing conditions is unknown. The possibility of transport as a polysulfide complex is being investigated.

Eh-pH diagrams for yttrium, the lanthanides, zirconium and the actinides predict a high degree of retention for those elements. These predictions are in agreement with measurements of the Oklo ores. Although Ce^{4+} and Eu^{2+} occur

in nature, these and the rest of the REE commonly occur as M^{3+} species. Simple $M(OH)_3$, M_2O_3 species are stable at pH values above about 7-8, and limited data suggest that $M_2(CO_3)_3$ compounds are stable at lower pH values. Data are too sparse to construct an Eh-pH diagram for Cm, but, consistent with observations, the data for other actinides suggest retention of this element. Work is continuing to determine if REE-phosphate and REE-carbonate complexes are important for the retention of lanthanides. Conclusions based upon these REE complexes may be relevant to similar compounds of the actinides for which there are very few data.

There are inconsistencies between the observed retention and transport of bismuth and lead at Oklo and the predictions based upon Eh-pH diagrams. Migration of BiO^+ is predicted under oxidizing, slightly acidic conditions, yet retention is observed. Because of its ionic radius (1.06A), Bi^{3+} may be retained in the nearly identical U^{4+} (1.04A) sites in host pitchblende. Alternately, local formation of Bi_2O_3 mixed with Fe_2O_3 may occur. Under more reducing conditions, polysulfide complexes are evidently not stable with respect to Bi_2S_3 . Lead, produced by radioactive decay of U and Th, is predicted to be retained under sulfate- and sulfide- stable conditions. Galena (PbS), anglesite ($PbSO_4$), and cerussite ($PbCO_3$) occupy most of the stability field of water. Yet remobilized radiogenic Pb is ubiquitous at Oklo. Since lead polysulfides are not uncommon, perhaps transport by such species is possible.

F. Publications and Oral Presentations During the Quarter

1. Publications

A. Gancarz , G. Cowan , D. Curtis , and W. Maeck (1980) ^{99}Tc , Pb and Ru Migration Around the Oklo Natural Fission Reactors. Scientific Basis for Nuclear Waste Management ed. Clyde J. M. Northrup Jr. pp. 601-608.

2. Oral Presentations and Abstracts

D. Brookins, "Alkali and Alkaline Earth Studies at Oklo," Symposium on the Scientific Basis for Nuclear Waste Management, Boston, MA, Nov. 16-21, 1980.

D. Curtis, A. Gancarz, A. E. Norris and A. Ogard, "Natural Analogues of Radionuclide Migration," National Waste Storage Terminal Storage Program Information Meeting, Columbus OH, December 9-11, 1980.

A. Ogard, G. Bentley, E. Bryant, C. Duffy, J. Grisham, E. Norris, C. Orth, and K. Thomas, "Are Solubility Limits of Importance to Leaching?" in Scientific Basis for Nuclear Waste Management, Proc. 3rd Int. Symp. Materials Research Society, Boston, MA, Nov. 16-21, 1980.

- A. E. Ogard and C. J. Duffy, "Eh and Fission Product Solubilities; Two Factors in the Leaching of UO_2 ," Proc. ORNL Conference on the Leachability of Radioactive Solids, Gatlinberg, TN, Dec. 9-12, 1980.
- A. E. Ogard and E. A. Bryant, "The Misused and Misleading IAEA Leach Test," *ibid.*

G. Meetings

- D. Brookins, E. A. Bryant, D. B. Curtis, A. J. Gancarz, and A. E. Ogard attended the Symposium on the Scientific Basis for Nuclear Waste Management in Boston, MA November 16-21, 1980.
- D. B. Curtis and A. J. Gancarz attended the National Waste Terminal Storage Program Information Meeting in Columbus, OH, December 9-11, 1980.