

U.S. GEOLOGICAL SURVEY CIRCULAR 1069



Short Papers of the  
U.S. Geological Survey  
Uranium Workshop, 1990

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# Short Papers of the U.S. Geological Survey Uranium Workshop, 1990

Edited by KENDELL A. DICKINSON

Papers presented March 20, 1990, at the Denver Federal Center  
and at the Sheraton Hotel, Lakewood, Colorado

U.S. GEOLOGICAL SURVEY CIRCULAR 1069

U.S. DEPARTMENT OF THE INTERIOR  
MANUEL LUJAN, JR., Secretary



U.S. GEOLOGICAL SURVEY  
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UNITED STATES GOVERNMENT PRINTING OFFICE: 1992

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U.S. Geological Survey  
Federal Center, Box 25425  
Denver, CO 80225

**Library of Congress Cataloging-in-Publication Data**

U.S. Geological Survey Uranium Workshop (1990 : Denver Federal Center and Lakewood, Colo.)  
Short Papers of the U.S. Geological Survey Uranium Workshop, 1990 / edited by Kendell A. Dickinson.  
p. cm. -- (U.S. Geological Survey Circular ; 1069)  
"Papers presented March 20, 1990, at the Denver Federal Center and at the Sheraton Hotel, Lakewood, Colorado."  
Includes bibliographical references.  
1. Uranium ores—United States—Congresses. 2. Uranium ores—Geology—United States—Congresses. I. Dickinson, Kendell A., 1931- . II. Geological Survey (U.S.) III. Title. IV. Title: Short papers of the US Geological Survey Uranium Workshop, 1990.  
V. Series.  
TN490.U7U54 1990  
553.4'932'0973—dc20

# PREFACE

By Kendell A. Dickinson<sup>1</sup>

This Circular contains abstracts and short articles from oral presentations and posters presented at the 1990 Uranium Workshop sponsored by the Branch of Sedimentary Processes, U.S. Geological Survey. The workshop was held on March 20, 1990, at the U.S. Geological Survey on the Denver Federal Center and at the Sheraton Hotel, Lakewood, Colorado. The last workshop of this type was held in 1977 and was titled the Uranium and Thorium Resource and Research Conference.

Readers interested in additional information about papers presented at the meeting should contact the authors directly. Mailing addresses for each author may be found in the footnotes on the first page of each paper contained in this Circular.

Interest in uranium was unexpectedly high at the workshop considering the present (March 1990) low spot price for  $U_3O_8$  and the recent unpopularity of nuclear power. Most people realize, however, that nuclear power will continue to play an important energy role both in the United States and abroad. The workshop played an important role in providing a platform for the exchange of ideas, especially in areas such as surficial uranium deposits and breccia pipe deposits. The growth of knowledge in these fields has been substantial since interest in uranium waned as the National Uranium Resource Evaluation (NURE) program ended in the early 1980's.

It is important that knowledgeable and experienced uranium geologists in both industry and government be available to make many of the important uranium-related decisions that lie ahead—this would be especially important in the event of a future national energy crisis.

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Manuscript approved for publication June 18, 1991.

<sup>1</sup>U.S. Geological Survey, Box 25046, Mail Stop 939, Denver Federal Center, Denver, Colorado 80225.



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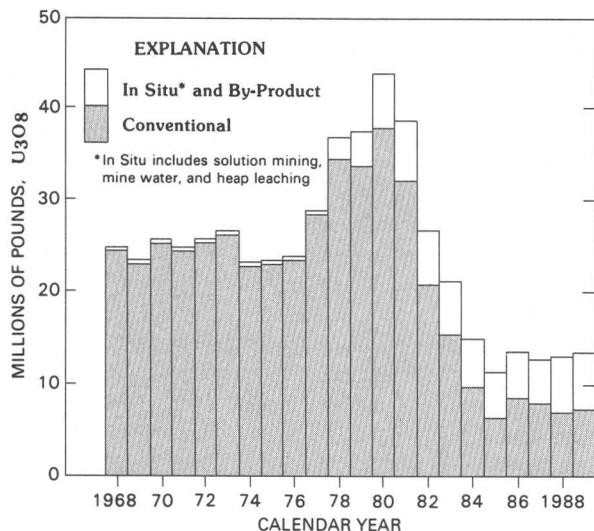
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# The State of the U.S. Uranium Industry in 1989

By William L. Chenoweth<sup>1</sup>

The domestic uranium industry continues to operate at a reduced level due to low prices and increased foreign competition. The Secretary of Energy declared the industry to be nonviable for the period from 1984 to 1988, and a similar declaration is expected for 1989. Exploration and development drilling continues at the rate of 2 to 3 million ft per year in areas of producing mines and recent discoveries: northwest Arizona, northwest Nebraska, south Texas, Wyoming, southwest Colorado, and southeast Utah. Production of uranium concentrate during 1989 is estimated at 13.8 million pounds of uranium oxide ( $U_3O_8$ ) (fig. 1). For 1989, conventional mining methods account for approximately 55 percent of the production in New Mexico, Arizona, Utah, Colorado, and Wyoming (fig. 1), while the remaining 45 percent comes from solution (in situ) mining, from mine-water recovery, and from by-products of copper production and the manufacture of phosphoric acid.



**Figure 1.** United States uranium concentrate production, 1968–1989. Data from Energy Information Administration (1989). Production for 1989 is estimated.

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During 1989, underground mining took place in the Grand Canyon region of Arizona; Ambrosia Lake area, New Mexico; Crooks Gap, Wyoming; and in the Uravan mineral belt of Colorado and Utah. Due to the high vanadium content of the ores in the Uravan area (as much as 10 times the uranium content), vanadium is the principal metal recovered, and uranium is considered a by-product. Two open-pit mines were operating in 1989: one in Shirley basin, Wyoming, and another in McMullen County, Texas. Solution mining was done in the Powder River Basin, Wyoming, and in south Texas. The Crow Butte project in Dawes County, Nebraska, should receive final permits for commercial operation in 1990. Uranium is recovered from water circulating through inactive underground mines at Ambrosia Lake, New Mexico. Uranium is also recovered from the manufacture of phosphoric acid at plants in central Florida and southern Louisiana. The plants in Louisiana process phosphate rock that is barged in from Florida. Uranium that was recovered from phosphate operations amounted to approximately 3 million pounds of  $U_3O_8$  in 1989 (22 percent of the total U.S. production). A plant that recovered uranium from copper leach solutions at Bingham Canyon, Utah, was placed on standby in early 1989. Unmined deposits, such as those in the Church Rock, New Mexico, area, are being investigated for the possible application of solution-mining technology.

In 1989, ore from conventional mines was processed at four mills: Shirley basin, Wyoming; Blanding, Utah; Ambrosia Lake, New Mexico; and Hobson, Texas. In January 1990, both the Shirley basin and Ambrosia Lake plants were placed on standby. The Shirley basin mill will reopen in mid-1990, when stripping is completed and mining commences at a new open pit in the Shirley basin. Late in 1989, the Section 23 mine at Ambrosia Lake, New Mexico, closed, and the Sunshine Bridge uranium recovery plant in Louisiana was placed on standby. In early 1990, the last underground mine (Mt. Taylor) at Ambrosia Lake closed, and several solution mining operations in Wyoming and Texas were placed on standby. Uranium concentrate production in 1990 could drop to approximately 8 million pounds of  $U_3O_8$ .

The discovered uranium resources in the United States are quite large, and the potential to discover additional resources is excellent. However, higher prices and a strong market will be necessary for their exploitation.

## REFERENCE CITED

Energy Information Administration, 1989, Uranium Industry Annual 1988: U.S. Department of Energy Report DOE/EIA-0478(88), 121 p.

# U.S. Uranium Reserve Assessment

By Taesin Chung<sup>1</sup>

The uranium raw materials program of the U.S. Department of Energy (DOE) was formerly conducted through its Grand Junction Office (GJO). In 1983, the resources of GJO were drastically reduced, and the activity for uranium information gathering and reporting, including reserve assessment, was transferred to the Energy Information Administration (EIA). EIA is an independent unit of DOE concerned with information gathering and analysis. Undiscovered uranium resource evaluations are performed by the U.S. Geological Survey through an interagency agreement with DOE established in 1983.

Information on uranium reserves and related industry activities is released by EIA in publications, primarily the Uranium Industry Annual, which summarizes the findings of the annual survey questionnaire. Additional information is released in a report entitled Domestic Uranium Mining and Milling Industry as part of the annual industry viability assessment. Information is also provided in collaboration with the joint activities of the International Atomic Energy Agency, especially in the periodic publication *Uranium Resources, Production, and Demand*, which covers worldwide uranium activities. EIA presents its findings at various technical meetings such as the U.S. Council for Energy Awareness annual uranium seminars.

Uranium reserve assessments developed by EIA since 1984 are largely dependent on data provided from replies to the annual questionnaires sent to industry. Companies report "economic" reserves as well as production data and exploration and marketing activities.

Reserves or reasonably assured resources at various cost levels are determined by analysis of the property-level estimates of reserves completed by GJO as of December 31, 1983. EIA adjustments to the GJO estimates include dele-

tion of properties that are reported as mined out, subtraction of production, and "erosion" adjustments that recognize losses from reserves of higher cost reserves as production proceeds. Currently, EIA does not estimate reserves of individual property from basic drill hole data.

Increasing concern and some criticism has been expressed concerning the methodology in use by EIA and that the types of information being developed are not as reliable as before. Estimation techniques employed by companies providing reserve estimates are not uniform. Credibility is affected by reliance on company estimates made with a variety of techniques and assumptions and the adjustment of EIA reserve files without consideration of the fundamental developments at each property. Reliance on questionnaires has reduced the high level of trust formerly maintained between industry and GJO. As the needs for data and the resources available to make uranium reserve estimates have changed, alternate approaches recommended by independent reviewers are being considered. The overall recommendation includes modifying the survey questionnaire, auditing company-supplied information on a property-by-property basis, and reestablishing ore deposit parameters to more closely define reserves in light of current conditions. The EIA continues to work towards implementation of an improved system of uranium reserve estimation. A redesigned survey questionnaire is currently under final review. Proposed changes include a shorter and more concise scope and a more realistic survey for in-situ leach operations. Priorities for company reviews on a property-by-property basis have been established; these priorities are based on those companies that have the largest reserves or active properties and on reserves appropriate for exploitation by new mining methods. Meetings with individual companies to verify reserves and to discuss estimation techniques have been scheduled. EIA staff will be utilized for all future reserve assessments. Cataloging and evaluation of basic data in EIA files has begun.

EIA has developed in-house microcomputer software programs to provide a reserve estimation capability independent of the estimates provided by companies. The programs were written to estimate reserves from basic drill hole data. EIA is continuing to make improvements on the reserve estimation system using an on-site contractor and support from Oak Ridge National Laboratory.

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# Uranium Resources in New Mexico

By Virginia T. McLemore<sup>1</sup> and William L. Chenoweth<sup>2</sup>

For nearly three decades (1950's–1970's), the Grants uranium district produced more uranium than any other district in the world, while other areas in New Mexico yielded minor quantities of uranium ore. The total uranium production in New Mexico from 1948 through 1989 was more than 327 million pounds of  $U_3O_8$  concentrate. New Mexico contains most of the Nation's uranium resources even though declining market conditions have forced closure of all uranium mines in the State (January, 1990). New Mexico contains about 89 million pounds of  $U_3O_8$  in economic reserves as of December 31, 1988, or 24 percent of the total economic reserves in the United States (fig. 1). Economic reserves are estimated by individual companies and are submitted to the Energy Information Administration (EIA), U.S. Department of Energy. Figures reported by the EIA do not include all 120 million pounds of uranium in reserves at the Mt. Taylor mine that is owned by Chevron Resources Co. (Alief and Kern, 1989). New Mexico also contains about 177 million pounds of  $U_3O_8$  in the \$30 per pound forward-cost category and 447 million pounds of  $U_3O_8$  in the \$50 per pound forward-cost category of 61 percent and 45 percent of the total domestic reasonably assured resources as estimated by the EIA (fig. 1) (Energy Information Administration, 1989). Reasonably assured resources are estimates of grade and tonnage in known deposits that can be recovered within given production-cost ranges.

Most of New Mexico's uranium resources occur in sandstones of the Morrison Formation (Upper Jurassic), which produced more than 338 million pounds of  $U_3O_8$  from 1948 to 1989. Three types of uranium deposits occur in the Morrison Formation: primary, redistributed, and remnant uranium deposits. Primary uranium deposits are less than 8 ft thick, average more than 20 percent  $U_3O_8$ , are low in vanadium, have sharp ore-to-waste boundaries, and are inti-

mately associated with humate (McLemore and Chenoweth, 1989). The ore at the Mt. Taylor mine (fig. 2) is of the primary type. Redistributed uranium deposits are younger than primary uranium deposits, are typically more than 8 ft thick, have diffuse ore-to-waste boundaries, are brownish to light-gray because they contain less humate material than primary deposits, and are formed from primary deposits by a regional oxidation front. The Mary No. 1 deposit (fig. 2) is a redistributed uranium deposit. Remnant uranium deposits are the preserved remains of primary deposits that are left behind in oxidized sandstones after the oxidation front that formed redistributed deposits moves downdip. Blackjack No. 1 is an example of a remnant deposit. Smaller uranium deposits found in New Mexico include other sandstone deposits, limestone uranium deposits, other sedimentary rocks hosting uranium deposits, vein-type uranium deposits, and igneous and metamorphic rocks containing disseminated uranium (McLemore and Chenoweth, 1989). Sandstone uranium deposits in the Morrison Formation, and possibly those in the Dakota Sandstone (Upper Cretaceous), have potential for future development.

Exploration for uranium has essentially ceased in the State (January, 1990). However, a few companies are examining the Grants district deposits for solution-mining potential (in situ leach). Since 1963, Homestake and Kerr McGee (now Rio Algom Mining Corporation) have extracted uranium from water circulated through uranium mines: about 5.9 million pounds of  $U_3O_8$  or 1.8 percent of the total uranium production from New Mexico has been produced from mine water. Solution mining has been tested at a few deposits in New Mexico. This type of mining has lower costs and fewer environmental problems than conventional mining methods.

New Mexico has significant uranium reserves and resources, especially in the Grants uranium district (fig. 1). However, these deposits are much lower in grade and somewhat deeper than Proterozoic unconformity-type deposits in Canada and Australia. Future development of uranium resources in New Mexico will depend upon (1) an increase in the price for uranium, (2) the lowering of production costs for uranium, perhaps by the use of solution mining (Holen and Hatchell, 1986, 1988), (3) discovery of higher grade deposits or a rise in the mining-grade cutoff, and (4) help for mining companies with the complex tasks of applying for permits and licenses and implementing required environmental regulations.

<sup>1</sup>New Mexico Bureau of Mines and Mineral Resources, Socorro, New Mexico 87801.

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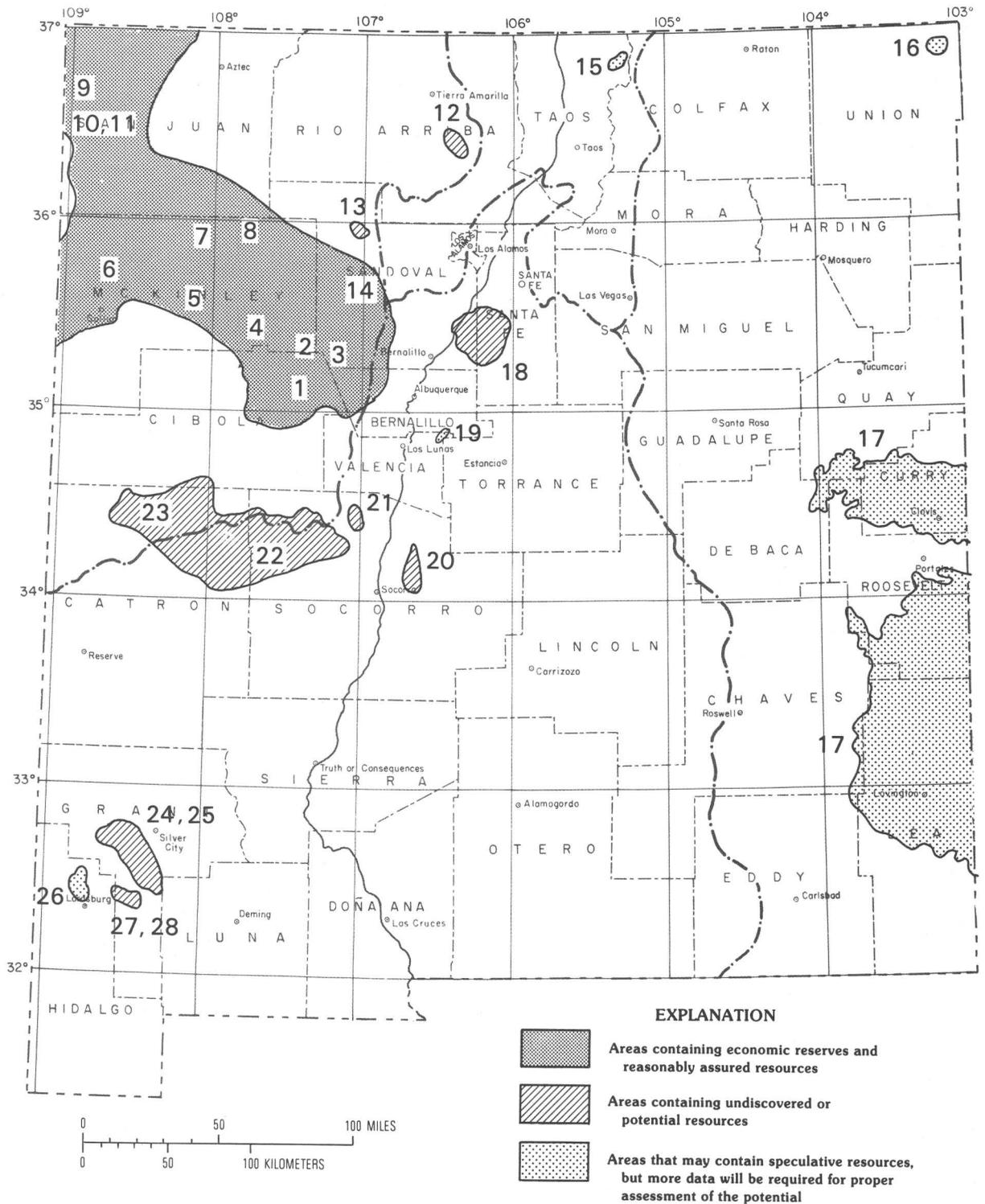
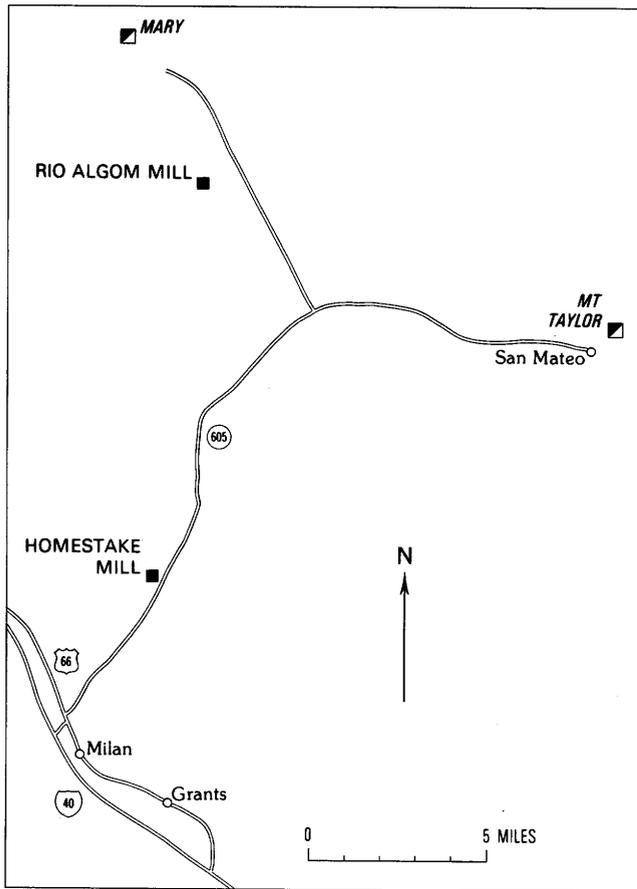


Figure 1. Uranium potential in New Mexico in 1989 (from McLemore and Chenoweth, 1989; portions modified from U.S. Department of Energy, 1980). Location numbers refer to table 1. The international terminology for the classification of uranium resources, recently adopted by the DOE, is used in this figure (Energy Information Administration, 1989).

**Table 1.** Uranium districts in New Mexico shown on figure 1

[Adapted from McLemore and Chenoweth, 1989]

District or Area	Type of Deposit
1. Laguna, Grants uranium district	Sandstone deposit in Morrison Formation, Limestone deposit
2. Marquez, Grants uranium district	Sandstone deposit in Morrison Formation, Limestone deposit
3. Bernabe Montano, Grants uranium district	Sandstone deposit in Morrison Formation, Limestone deposit
4. Ambrosia Lake, Grants uranium district	Sandstone deposit in Morrison Formation, Limestone deposit, Sandstone deposit in Dakota Sandstone
5. Smith Lake, Grants uranium district	Sandstone deposit in Morrison Formation, Limestone deposit
6. Church Rock, Grants uranium district	Sandstone deposit in Morrison Formation, Sandstone deposit in Dakota Sandstone
7. Nose Rock, Grants uranium district	Sandstone deposit in Morrison Formation
8. Chaco Canyon area, Grants uranium district	Sandstone deposit in Morrison Formation
9. Carrizo Mountains, Shiprock district	Sandstone deposit in Morrison Formation
10. Chuska Mountains, Shiprock district	Sandstone deposit in Morrison Formation, Limestone deposit
11. Tociito Dome area	Sandstone deposit in Morrison Formation
12. Abiquiu	Sandstone deposit in Dakota Sandstone
13. Mesa Portales area	Sandstone deposit in Tertiary rocks
14. Collins-Warm Springs district	Sandstone deposit in Morrison Formation
15. Vermejo Park area	Possible epithermal vein, granitic rocks or pegmatites
16. Black Mesa area	Fracture-controlled uranium deposits
17. Ogallala Formation in eastern New Mexico	Possible surficial uranium deposit
18. Hagan Basin area	Sandstone in Tertiary rocks
19. Manzano Mountains-Manzanitas Mountains area	Possible vein-type or disseminated magmatic deposit
20. Socorro area (Aqua Torres, Marie No. 1, Lucky Don, Little Davie mines)	Fracture-controlled uranium deposits
21. Ladron Mountains	Fracture-controlled uranium deposits
22. Hook Ranch-Riley area	Sandstone in Cretaceous-Tertiary rocks
23. Red Basin-Pietown area	Sandstone in Cretaceous-Tertiary rocks
24. Telegraph district	Epithermal vein
25. Malone district	Epithermal vein
26. Lordsburg Mesa area	Surficial uranium deposit
27. Gold Hill district	Pegmatite
28. Bound Ranch area	Epithermal vein



**Figure 2.** Location map of uranium mines mentioned in the text, Grants uranium district, New Mexico.

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# New Assessments of Uranium Endowment for Two Regions in the United States

By Warren I. Finch,<sup>1</sup> Charles T. Pierson,<sup>1</sup> Richard B. McCammon,<sup>2</sup> James K. Otton,<sup>1</sup> Hoyt B. Sutphin,<sup>3</sup> and Karen J. Wenrich<sup>1</sup>

The U.S. Geological Survey began a program to assess the undiscovered uranium endowment in selected areas of the United States as a result of a 1984 Memorandum of Understanding between the U.S. Department of Energy and the U.S. Department of the Interior. Uranium endowment is defined as the uranium estimated to be present in rock with a grade of at least 0.01 percent  $U_3O_8$ . The economic portion of endowment is calculated using a higher grade cutoff, commonly 0.10 percent  $U_3O_8$ . A proposed new assessment program is outlined in the report by Finch and McCammon (1987); the new assessments are intended to supplement and update those made by the U.S. Department of Energy (1980) during their National Uranium Resource Assessment (NURE) Program. Since 1984, the U.S. Geological Survey has developed a new assessment method called the deposit-size-frequency (DSF) method (Finch and McCammon, 1987); this technique is a modification of the NURE method. Two regions have been assessed using the DSF method: the Colville-Okanogan area, Washington and Idaho, and the Grand Canyon region, Arizona and Utah.

The DSF method consists of a modification of the NURE uranium endowment (U) estimation equation ( $U=A \times F \times T \times G$ ), where factors F and T are replaced by a single factor (see McCammon, this volume). In this equation, F is the fraction of area (A) that is favorable for endowment, and T equals the number of short tons of endowed rock per unit area. The combined F and T factor is the summation of the estimates of the number of deposits of different size within the area being assessed, or, in other words, the spatial density of deposits; hence, the name "deposit-size-frequency." The distribution of the average grade (G) of endowment is the same in both methods. The DSF method requires (1) that a deposit-size-frequency (a matrix of the lower limit, most likely value, and upper limit for the number of deposits in each size class) be established in a control area, which is a well-known to fairly well known area, and (2) that the geo-

logic factors that produced this frequency be determined. Using these requirements for a control area, the assessor estimates the size frequency of undiscovered deposits for the favorable area based on similarity to the control area. The probabilistic estimates in 5 percent intervals between 5 and 95 percent of undiscovered uranium endowment are calculated using the computer program TENDOWG (McCammon and others, 1988). These estimates for two regions are shown in figures 2, 3, and 4.

The undiscovered uranium endowment was estimated in 1986 for "young organic-rich uranium deposits" in the Colville-Okanogan favorable area in the Sandpoint and Spokane  $1^\circ \times 2^\circ$  quadrangles, Washington and Idaho (fig. 1). These uranium deposits occur in surficial organic-rich fluvial, alluvial, and lacustrine sediments laid down during the last 15,000 years (Johnson and others, 1985). The deposits average from 0.03 to about 0.10 percent  $U_3O_8$  and contain from a few hundred pounds to as much as a million pounds of  $U_3O_8$ . The uranium endowment in the Colville-Okanogan favorable area is estimated to lie between about 6,700 and 122,000 short tons of contained  $U_3O_8$ , and the mean undiscovered uranium endowment is 35,300 short tons  $U_3O_8$  (Finch, Otton, and others, 1990), as shown by the probability distribution of estimated short tons in figure 2. The uranium endowment is divided about evenly between the Sandpoint and Spokane quadrangles.

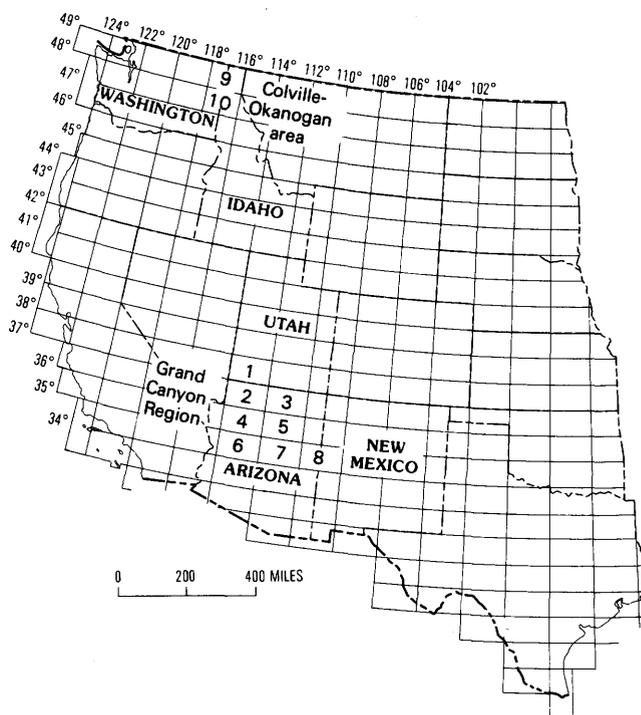
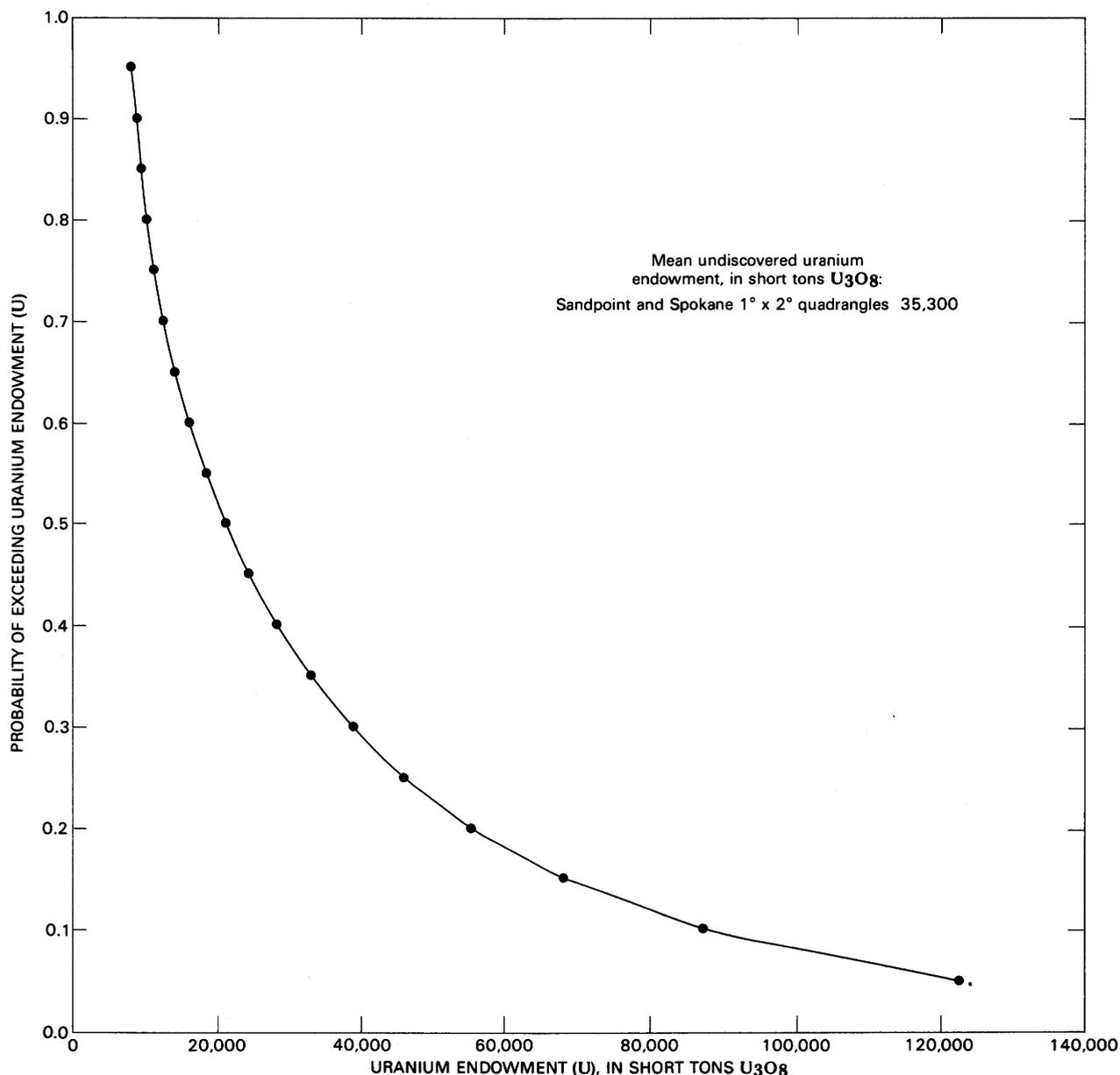


Figure 1. Index map showing the location of the NTMS  $1^\circ \times 2^\circ$  quadrangles mentioned in this report. (Cedar City, 1; Grand Canyon, 2; Marble Canyon, 3; Williams, 4; Flagstaff, 5; Prescott, 6; Holbrook, 7; St. Johns, 8; Sandpoint, 9; Spokane, 10)

<sup>1</sup>U.S. Geological Survey, Box 25046, Mail Stop 939, Denver Federal Center, Denver, Colorado 80225.

<sup>2</sup>U.S. Geological Survey, Mail Stop 920, National Center, Reston, Virginia 22092.

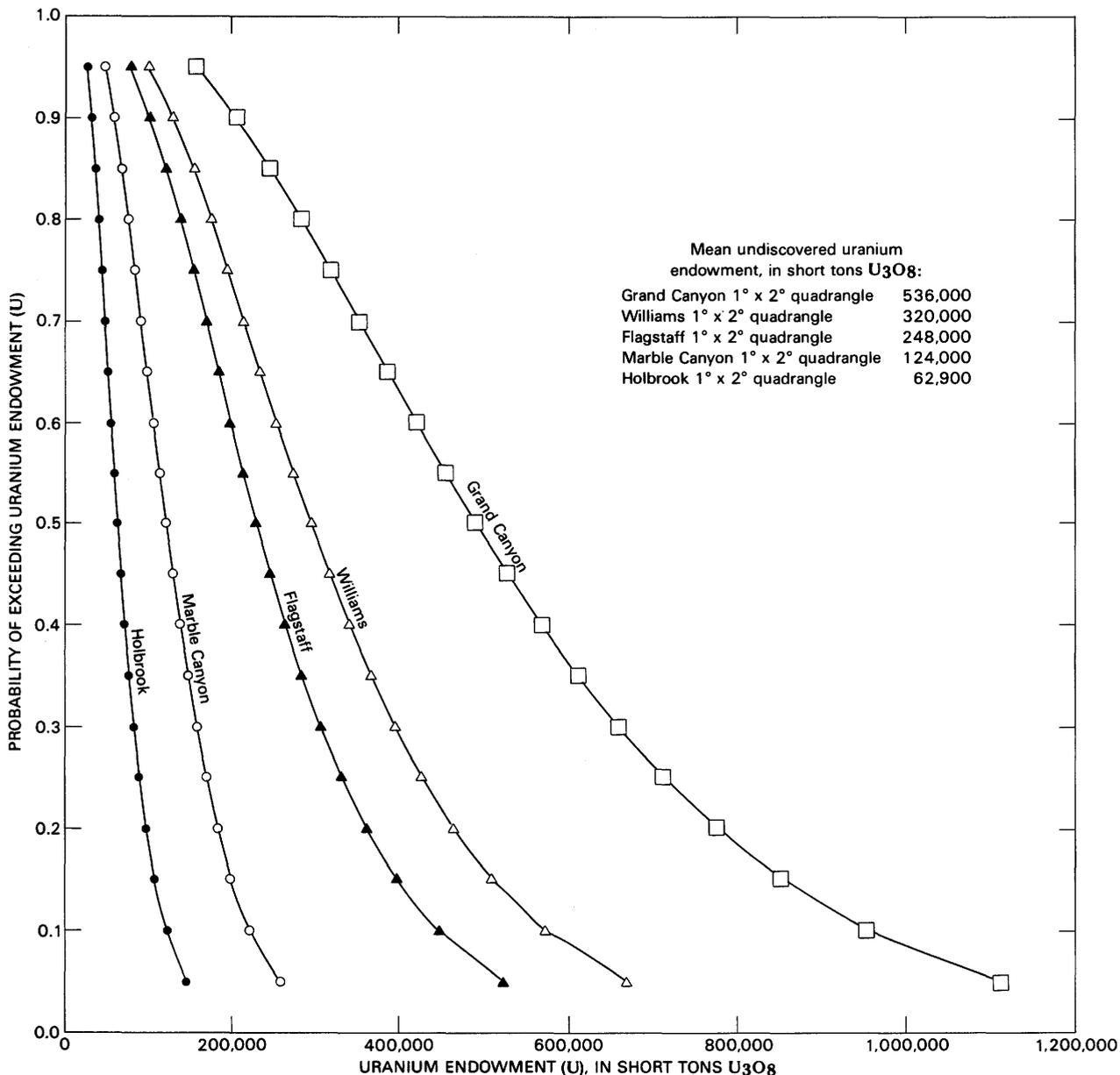
<sup>3</sup>USPCI, 5665 Flatiron Parkway, Boulder, Colorado 80301.



**Figure 2.** Plot of the probability distribution of estimates of undiscovered uranium endowment for the Colville-Okanogan area, Sandpoint and Spokane 1°x2° quadrangles, Washington and Idaho. The odds are 9 to 1 that the true unconditional endowment (in short tons U<sub>3</sub>O<sub>8</sub>) is between the values plotted for the 5 and 95 percent probabilities.

The undiscovered uranium endowment was estimated in 1987 for the solution-collapse breccia pipes in the Grand Canyon region in the Grand Canyon, Marble Canyon, Williams, Flagstaff, Prescott, Holbrook, and St. Johns 1°x2° quadrangles in Arizona and the Cedar City 1°x2° quadrangle in Utah (fig. 1). The uranium deposits occur in nonvolcanic breccia pipes that formed as a result of solution collapse into

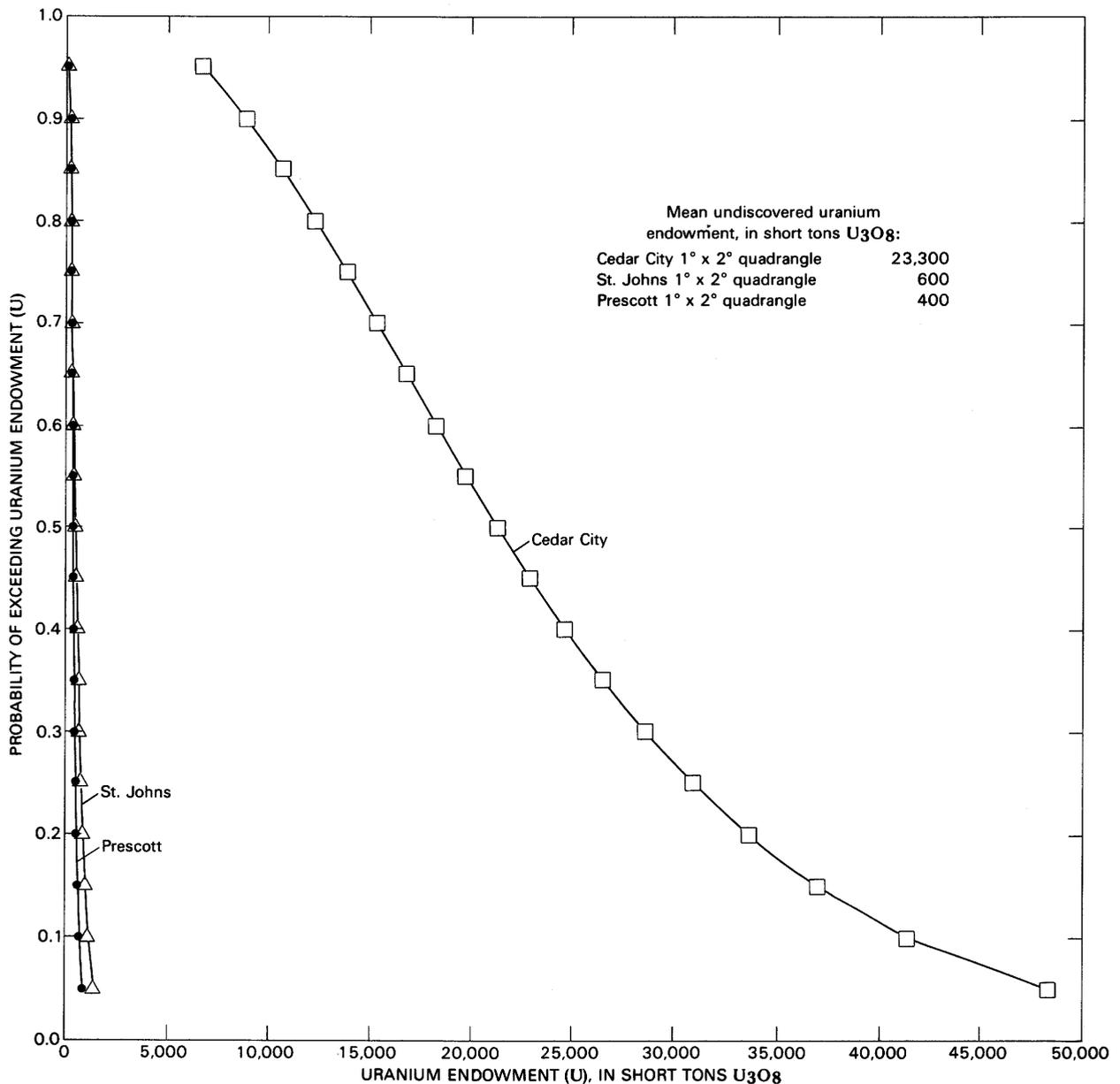
the Mississippian Redwall Limestone and by stoping of the overlying Pennsylvanian, Permian, and Triassic rocks (Wenrich, 1985). Most of the uranium deposits are high grade by U.S. standards, averaging between 0.43 and 0.65 percent U<sub>3</sub>O<sub>8</sub>. Typical deposits contain 125,000 to 500,000 short tons of ore, yielding 1 million to 6 million pounds of U<sub>3</sub>O<sub>8</sub>. The uranium endowment was estimated for 26 favorable



**Figure 3.** Plots of the probability distribution of estimates of undiscovered uranium endowment for the Grand Canyon, Williams, Flagstaff, Marble Canyon, and Holbrook 1°x2° quadrangles, Grand Canyon region, Arizona. For each quadrangle, the odds are 9 to 1 that the true unconditional endowment (in short tons U<sub>3</sub>O<sub>8</sub>) is between the values plotted for the 5 and 95 percent probabilities.

areas that total 16,728 mi<sup>2</sup> within the eight quadrangles. Figures 3 and 4 show the probability distributions of estimated short tons of uranium endowment within the eight quadrangles. About 41 percent of the mean uranium endowment is in the Grand Canyon 1°x2° quadrangle, where most of the mining activity has occurred. About 93 percent of the en-

dowment is within the Grand Canyon, Marble Canyon, Williams, and Flagstaff 1°x2° quadrangles. The undiscovered mean endowment in the Prescott and St. Johns 1°x2° quadrangles is insignificant because of their small favorable areas. The mean uranium endowment for the entire region totals about 1,300,000 short tons U<sub>3</sub>O<sub>8</sub> (Finch, Sutphin, and



**Figure 4.** Plots of the probability distribution of estimates of undiscovered uranium endowment in the Cedar City 1°x2° quadrangle, Utah, and the St. Johns and Prescott 1°x2° quadrangles, Arizona. For each quadrangle, the odds are 9 to 1 that the true unconditional endowment (in short tons U<sub>3</sub>O<sub>8</sub>) is between the values plotted for the 5 and 95 percent probabilities.

others, 1990). This value is about eight times the total endowment of 158,000 short tons U<sub>3</sub>O<sub>8</sub> estimated for these breccia pipes by the U.S. Department of Energy 1980 NURE Program (U.S. Department of Energy, 1980). The larger USGS uranium endowment value is due to three factors: (1)

The DSF method allows for greater partitioning of input data and results in less biased (generally larger) estimates, (2) significantly greater knowledge of the grade and tonnage of deposits discovered since 1980, and (3) greatly improved understanding of the geology of the region.

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# Uranium Endowment Estimate Calculations

By Richard B. McCammon<sup>1</sup>

On September 20, 1984, the Memorandum of Understanding (MOU) between the Energy Information Administration (EIA) of the U.S. Department of Energy (DOE) and the U.S. Geological Survey (USGS) of the U.S. Department of Interior (DOI) was signed. This MOU was a continuant to the MOU between DOE and DOI dated November 12, 1983, that provided for continuing the assessment of the Nation's uranium resources following the national assessment by DOE during the period 1974–1983 under the National Uranium Resource Evaluation (NURE) program. The 1984 EIA/USGS MOU returned to the USGS the full responsibility for uranium resource assessment.

The equation that was used to estimate the uranium endowment in each of the 704 favorable areas identified in the NURE program was defined as follows:

$$U = A \times F \times T \times G \times P$$

where

U is the unconditional uranium endowment in short tons of  $U_3O_8$  above a cutoff grade of 0.01 percent  $U_3O_8$ ,

A is the projected surface area of favorable ground in square miles,

F is the fraction of A that is underlain by endowment,

T is the short tons of endowed rock per square mile within  $A \times F$ ,

G is the average grade of endowment, in decimal form, and

P is the probability of occurrence, a factor that expresses the likelihood that one or more deposits actually exist within the favorable area.

The equation was applied using values of A, F, T, G, and P obtained from the principal scientist by a team of elicitors. Factor A was treated as a constant and assigned a single value. Factors F, T, and G were treated as random variables whose values were estimated by the principal scientist in each of three categories: lower (5 percent probability), most likely (mode), and upper (95 percent probability). Factor P, the probability of occurrence, was a single number estimated by the principal scientist. The computer program that was used to calculate the unconditional uranium endowment (U) has been described by Ford and McLaren (1980).

Principal scientists, who were usually geologists, had great difficulty in estimating values for factors F and T. Factor T is essentially a measure of the size of the deposits and

depends upon the area, density, and thickness associated with the deposits. It was difficult for the geologist to conceptualize the size of undiscovered deposits in terms of short tons per square mile. Factor F was even more difficult to judge because, to estimate F, it was necessary for the geologist to estimate the projected surface area of undiscovered deposits. More often than not, estimates for F were obtained by asking the principal scientist how many more deposits of a particular type of deposit were likely to exist in the favorable area. Using data for known deposits, estimates for both F and T were then derived.

It is more natural for a geologist to think in terms of the number and size of undiscovered deposits when being asked to make subjective judgments about the undiscovered resources within an area. The difference between this approach and the approach adopted in the NURE program is perhaps best seen in figure 1. The drawing in figure 1 illustrates that factor F is an abstraction and does not lend itself to identifiable and measurable geologic features, such as the character of sedimentary or structural forms in the area. The post-NURE characterization of undiscovered deposits in figure 1 has been adopted by the USGS and has resulted in a modified NURE method called the deposit-size-frequency (DSF) method. The method has been described by Finch and McCammon (1987). The equation that is now used to estimate the uranium endowment in a favorable area is defined as follows:

$$U = A \left\{ \sum_{i=1}^k \left( \frac{n_{ic}}{A_c} \right) T_i \right\} GLP$$

where

k is the number of deposit-size classes,

$n_{ic}/A_c$  is the spatial density (number of deposits per unit area) of deposits of size  $T_i$  (short tons of endowed rock) in the  $i$ th deposit-size class within a control area  $A_c$ ,

$A_c$  is the control area from which estimates of  $n_{ic}/A_c$  are taken,

L is the optional scaling factor that expresses the relation between the endowment in the favorable area and that in either the control area or in some designated subarea for which estimates of the number of deposits in different size classes have been made, and

U, A, G, and P are defined as before.

The equation is applied using values for A,  $k$ ,  $\frac{n_{ic}}{A_c}$ ,  $T_i$ , G,

L, and P obtained from the principal scientist by a team of elicitors. Factors A, G, and P are obtained as before. Factor k and each  $T_i$  are treated as a constant and assigned a single

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# Uraniferous Wetlands— Young Uranium Deposits

By Douglass E. Owen<sup>1</sup>

Wetlands are common in montane and subalpine settings in the western United States, and accumulations of peat and organic-rich sediments in these environments range from less than 30 cm to more than 10 m thick. Wetlands form along spring lines in valley floors and adjacent to springs and seeps, or where drainage has been restricted by glacial moraines, debris slides, or beaver dams. Some of these wetlands contain significant concentrations of uranium because uranium is readily sorbed from the water by the abundant organics present in wetland sediments. Sorption is highly efficient because the uranyl ion ( $\text{UO}_2^{2+}$ ) forms strong complexes with the abundant humic and fulvic acids present in wetland sediments. Geochemical enrichment factors (GEF) of 10,000 to 1 or greater are well documented to exist between the peat/organic-rich sediments and the uranium-bearing waters that carry uranium into the wetlands.

Of 145 wetlands sampled by the U.S. Geological Survey (USGS) in the Rocky Mountains of Colorado, 30 percent of the wetlands contained moderate uranium concentrations (20 to 99 ppm, maximum observed values), 15 percent contained high concentrations (100 to 999 ppm), and 1 percent contained very high concentrations (1,000 to greater than 3,000 ppm). All values are reported on a dry-weight basis and are from auger samples taken over one-foot intervals. Elsewhere, USGS scientists assessed the uranium content of two small wetlands near Lake Tahoe in the Carson Range of Nevada. Average grades of 1,500 ppm and 800 ppm uranium were determined and total uranium contents were calculated at 15,000 and 24,000 kg, respectively. The only wetland uranium deposit in the United States that has been mined is the Flodelle Creek deposit in northeastern Washington State. The USGS estimates that this deposit contains 450,000 kg of uranium; however, only about 500 kg of uranium was produced before ore processing problems and the low price of uranium forced closure of the mine.

Because the sorptive processes responsible for concentrating uranium and other metals in organic-rich wetland sediments are reversible, both anthropogenic and natural disturbances may have serious environmental consequences. If a wetland is partly or completely drained, the subsequent oxidation of organic-rich sediments may rapidly liberate metals that have been accumulating from very dilute solutions for thousands of years; this could impact the quality of

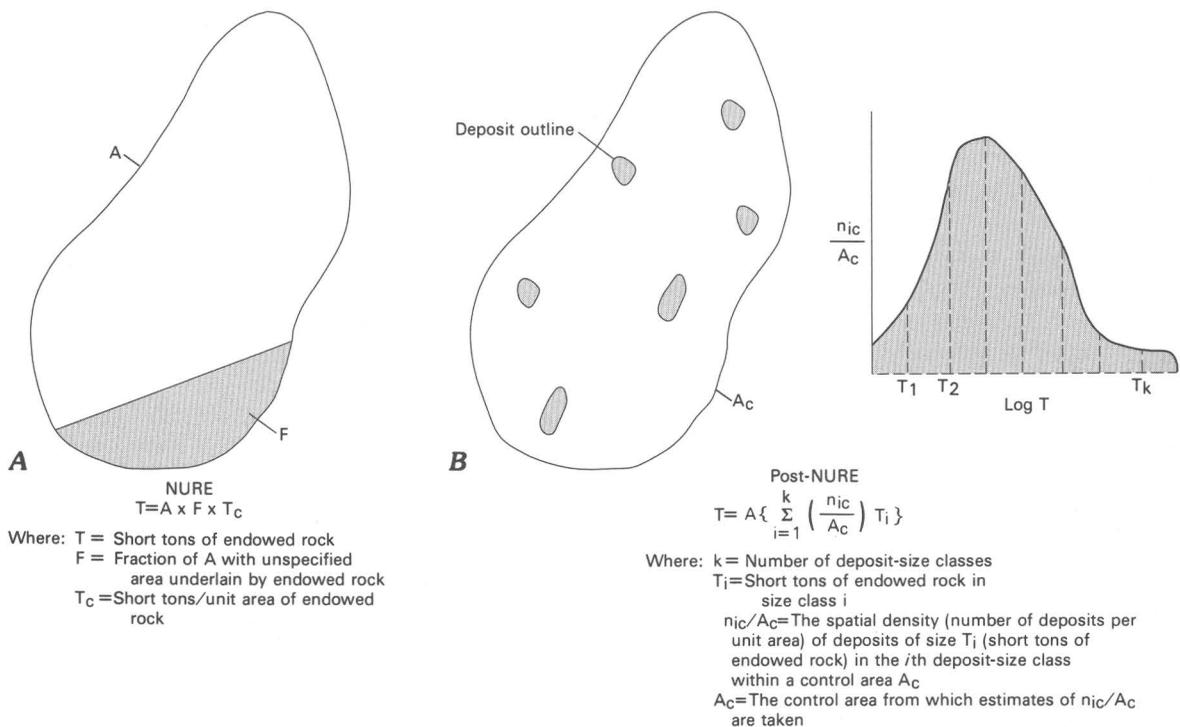
local ground and surface waters. Acid leaching caused by mine drainage into wetlands (there are more than 10,000 abandoned mines in Colorado alone) and the over-liming or addition of certain types of phosphate fertilizers to hydric soils may also release uranium from wetlands into water systems. Because uranium wetlands are of environmental and health concern, extraction of uranium for the purposes of protecting the environment and safeguarding public health may be justified. In addition, profit may be realized from the sale of the extracted uranium.

The wetlands studied are of late Pleistocene to Holocene age; therefore, their uranium is in gross disequilibrium (excess) compared with its more radioactive daughter products. Because of their low radioactivity, these deposits generally are not detected with airborne or hand-held gamma-ray spectrometers or scintillometers. As a consequence, exploration must be based on specialized radiometric methods (delayed neutron activation) or on direct chemical measurements of uranium content. Two beneficial consequences of the low radioactivity associated with uranium wetlands are: (1) Radioactivity of tailings will be 1 to 10 percent of that in conventional mines of similar grade, and (2) radiation hazard to the miners will be minimal.

Reconnaissance for uranium wetlands is performed most effectively by measuring the uranium content of spring waters that feed wetlands and by examining existing data for uranium in ground water, such as that from the National Uranium Resource Evaluation program (NURE). Even with a GEF that is greater than 10,000 to 1, waters entering wetlands should contain at least 20 ppb uranium to concentrate significant amounts of uranium. For example, if incoming waters have a uranium concentration of 25 ppb and the operative GEF is 20,000 to 1, then the potential uranium concentration in peaty sediments is approximately 500 ppm. Ground water uranium concentrations greater than 20 ppb also indicate that the country rocks in the area are fertile; i.e., they contain significant quantities of labile uranium. Limited experience suggests that highly fractured granitic rocks with moderate to high concentrations of uranium and a history of deep weathering and recent glaciation are likely to be sources of labile uranium. Once a uranium wetland is identified, exploration is continued by sampling wetland sediments by hand auger. The auger samples are dried and analyzed for uranium content. Individual wetland uranium deposits tend to be small (less than 500,000 kg) and of modest average grade (0.05 to 0.12 percent); therefore, exploration must focus on finding clusters of deposits rather than on finding one large or exceptionally high grade deposit.

The economic feasibility of development at a particular deposit will depend upon local hydrology, vegetation cover, land use, nature of uranium fixation, access, and the prevailing price of uranium. The only uranium wetland in the United States to be mined for its uranium, Flodelle Creek, used heap leaching to extract uranium from organic-rich sed-

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**Figure 1.** Comparison of F in A, NURE with B, post-NURE representation of endowment. The reader is referred to Finch and McCammon (1987) for a complete explanation of terms. Modified after Finch and McCammon (1987).

value. Factors  $\frac{n_{ic}}{A_c}$  and L are treated as random variables whose values are estimated by the principal scientist as lower (5 percent probability), most likely (mode), and upper (95 percent probability) values. The computer program to calculate U using this equation is described by McCammon and others (1988).

In effect, factors F and T have been replaced with factors that relate explicitly to the number and size of undiscovered deposits within a favorable area. By asking the principal scientist to estimate these factors, the DSF method not only further segregates the estimate of endowment as compared to the NURE method, but it also emphasizes more of the everyday experience of exploration geologists. The DSF method is particularly well suited to frontier areas where information concerning undiscovered uranium deposits is scant. Finally, the DSF method preserves continuity with the NURE method: by allowing k to equal 0, a principal scientist can estimate F and T as before, making the calcula-

tion of U using the DSF method indistinguishable from the calculation of U using the NURE method. The compatibility of the two methods serves to preserve the estimates of endowment made in the NURE program and ensures continuity in making new assessments using the DSF method.

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iments. In situ leaching of uranium from uraniumiferous wetlands is a possible alternative method of mining. Lixivants composed of ammonium bicarbonate and ammonium carbonate (both of which are strong fertilizers) are environmentally benign and are relatively efficient in removing uranium from wetland sediments. An advantage of in situ leaching is that it leaves the wetland intact, thus preserving the extractive capacity of the wetland. However, in situ leaching is impractical in wetlands with heavy shrub cover or where wetland hydrology short circuits the leach cycle by rapid loss or addition of fluids. Both in situ and heap leaching could utilize a mobile processing plant with ion

exchange columns carried on flat bed semitrailers. This type of processing is compatible with the exploitation of numerous small deposits that may be present in a particular favorable area.

In addition to adding to the U.S. uranium resource base, the identification of these young uranium deposits provides opportunities to better understand processes leading to the formation of syngenetic uranium deposits. The study of uraniumiferous wetlands also provides data for models of contaminant transport in organic-rich surficial environments and has implications for both radionuclide and toxic waste disposal.

# Response of Douglas Fir to Uraniferous Ground Water: A Case Study with Implications for Environmental Monitoring

By Robert A. Zielinski<sup>1</sup> and R. Randall Schumann<sup>2</sup>

The positive biogeochemical response of plants to concealed uranium deposits is well documented in the geologic literature. The apparent uptake of uranium by plants is undoubtedly aided by its high solubility in oxidizing waters as uranyl-carbonate or uranyl-phosphate complexes or as complexes with humic or fulvic acids. The relative solubility of uranium compared to other heavy metals of economic interest may confound efforts to precisely locate buried deposits because plant or soil media can record rather wide dispersion of uranium from a particular source. However, the explorationist's problem of uranium dispersion by ground water may be turned to the advantage of environmental scientists. For example, biogeochemical indications of uranium dispersal from buried natural or man-made sources might supplement more direct, but more limited, measurements of ground water quality and flow patterns.

This field study was designed to further test the hypothesis that biogeochemical sampling may be used to map the transport of uranium by shallow, uraniferous ground water. We sampled Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] and associated soils in a small drainage containing anomalously uraniferous surface and ground water (Zielinski and others, 1987). The objective of this study was to test whether the distribution of biogeochemical anomalies exhibited any regularity that could be related to observed or inferred pathways of ground water movement in the drainage. The results, which were elaborated by Zielinski and Schumann (1987), strongly suggest that, in areas containing uraniferous water, the magnitude of biogeochemical anomalies is highly influenced by the degree of root zone exposure to such waters.

The study was confined to slopes surrounding the upper reaches of the north fork of Flodelle Creek, Stevens County, Washington. This very limited drainage basin (4.1 km<sup>2</sup>) contains abundant labile uranium, as evidenced by anoma-

lously uraniferous surface and ground waters (20–320 ppb U) and by the occurrence of uranium enrichments (0.01–0.9 weight percent U) in organic-rich valley-fill sediments (Johnson and others, 1987). The valley slopes are underlain by a two-mica monzogranite of Cretaceous age that is covered by 1–2 m of relatively permeable glacial till. Topographic relief in the drainage is about 183 m, and slopes are generally 30–65 percent. The well-drained slopes are vegetated primarily by Douglas fir: this dictated the choice of this species for sampling.

Douglas fir was sampled at 200-ft (61 m) intervals along a series of slope traverses designed to provide continuous coverage of both sides of the upper 2 km of the valley. Additional shorter traverses allowed for the sampling of some slopes at different elevations. A subset of six samples was collected in the vicinity of a slope spring. All 129 localities were visited during a dry five-day period in August 1985. At each site we noted the elevation and collected at least 400 g of 30–50 cm lengths of the most recent growth (twigs and needles). At every fifth site we collected a soil sample of silt-loam from a depth of 15–25 cm—this is well within the root zone of the trees sampled.

All plant matter was first air-dried at 40 °C and then shaken and sieved to separate twigs and needles. Separates were ashed to yield approximately 1 g of ash for analysis. Soil samples were also air dried and sieved to remove plant litter or occasional particles larger than fine sand. All uranium analyses of plant ash and soils were done by a delayed neutron method that had a detection limit of 0.2 ppm and an estimated precision of ±10–30 percent (relative standard deviation).

The uranium content of needle ash ranged from 0.2 to 5.8 ppm. Analysis of the positively skewed frequency distribution by two statistical methods provided an estimated threshold value of 1.0 ppm; this value was exceeded by 27 of the 129 determinations. Most of the anomalously uraniferous samples were located on the west side of the valley, on lower parts of the slope, and in two distinct sections of slope traverses.

The entire data set was evaluated by statistical methods to determine the degree of correlation between the uranium in needle ash and other measured variables (table 1). A strong positive correlation with the uranium in twig ash suggests that twigs are an equally acceptable sample medium. A strong negative correlation with elevation data supports the indication that uraniferous samples tend to be located on lower slopes. A lack of correlation with the uranium content in soils suggests that soil-bound uranium is not readily available for uptake by the root system. Finally, a negative correlation with ash content of needles suggests that needles are not significantly contaminated by windblown dust.

The locations of anomalous samples are readily explained using a model that accounts for the observed or inferred movement of shallow ground water in the drainage.

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Table 1. Correlation coefficient matrix<sup>1</sup> based on analysis of Douglas fir and associated soils, north fork, Flodelle Creek, Washington

	Ash Content of Needles (129)	Ash Content of Twigs (29)	Log [U] Needle Ash (129)	Log [U] Twig Ash (29)	Log[U] Soil (29)	Elevation (122)	Delta Elevation (122)
Ash Content of Needles	--	--	--	--	--	--	--
Ash Content of Twigs	<b>0.60</b>	--	--	--	--	--	--
Log [U] Needle ash	<b>-0.30</b>	-0.20	--	--	--	--	--
Log [U] Twig ash	0.07	-0.17	<b>0.88</b>	--	--	--	--
Log [U] Soil	-0.41	-0.34	0.16	-0.08	--	--	--
Elevation	<b>0.23</b>	-0.06	<b>-0.60</b>	<b>-0.67</b>	-0.18	--	--
Delta Elevation	0.11	0.19	<b>-0.67</b>	<b>-0.65</b>	-0.16	<b>0.85</b>	--

<sup>1</sup> Values in bold print are significant at the 99% level of confidence, based on the possible number of paired values for each correlation. The number of determinations of each variable are given in parentheses. Elevation values do not include seven samples collected near the slope spring that were considered to be strongly influenced by the spring. Delta elevation values are the estimated heights above the valley floor.

Anomalous samples were situated as follows: (1) in the immediate vicinity of a slope spring on the west side of the valley, (2) along a linear trend that includes the spring and parallels the strike of the valley (this suggests a structurally controlled zone of upwelling water), (3) at the toe of an alluvial fan deposited by an intermittent tributary stream (some ground water seeps were observed in a trench cutting the toe) and, (4) at lower slope sites that were more likely to experience prolonged water saturation and greater fluctuations in the water table related to subsurface runoff. The lack of anomalous samples near the drainage divide (an area of the valley bottom where the water table is relatively deep) is consistent with the model.

The results of this study confirm that biogeochemical sampling may be used to monitor the transport of anomalous amounts of uranium by shallow ground water. This method of environmental monitoring deserves further investigation,

particularly if it can be expanded to include other plant species or other elements.

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# Uranium Series Disequilibrium in a Young Surficial Uranium Deposit, Northeastern Washington

By Robert A. Zielinski,<sup>1</sup> Charles A. Bush,<sup>2</sup> and  
John N. Rosholt<sup>3</sup>

Concentration of uranium in surficial, organic-rich sediments is a recently recognized phenomenon that has both economic and environmental implications. Wetlands in which locally uraniferous ground water intercepts accumulations of highly sorbent organic matter, such as peat, are particularly favorable settings for surficial uranium accumulations. Despite uranium concentrations as high as several thousand parts per million (ppm) in dried peats, their low radioactivity thwarts exploration efforts based on conventional radiometric methods. Emplacement of uranium in late Pleistocene or Holocene time is simply too recent to permit significant buildup of radioactive daughter products such as <sup>226</sup>Ra or <sup>214</sup>Pb. Complete buildup of equilibrium abundances of uranium daughter products takes approximately 400,000 years.

Although daughter product abundances are low, they are amenable to measurement by specialized radiometric techniques such as high-resolution gamma-ray spectrometry and thin-source alpha spectrometry. In this study, we performed such measurements on core samples from a uraniferous peat in northeastern Washington State. The results indicate the relative mobility of uranium and some of its chemically diverse daughter products in this surficial environment and permit calculation of apparent U-series ages of uranium emplacement. The U-series ages can be compared to independently determined depositional ages of host peats to develop a history for uranium mineralization at the site.

The core site is located along the uppermost reach of the north fork of Flodelle Creek, Stevens County, Washington (Johnson and others, 1987). Organic-rich valley-fill sediments from this drainage contain as much as 9,000 ppm U (dry basis) and were the target of an aborted mining effort in the early 1980's. Sediments at the core site were undisturbed by mining, which was restricted to wider parts of the valley farther downstream. The peat and organic-rich silt and sand at the core site were deposited in a shallow pond that formed

when unconsolidated glacial till slumped off the valley slopes and restricted drainage. A continuous piston core 5.0 cm in diameter and 292 cm in length was collected and split into 16 lithologically distinct intervals. Composite samples representing each interval were dried, crushed and homogenized prior to analysis (Zielinski and others, 1986). The depositional age of the sediments was estimated by identification of the 6,700–7,000-year-old Mazama ash at a depth of 50–55 cm (Zielinski and Otton, 1986) and by recognition of glaciofluvial sediments of approximately 12,000–15,000 years B.P. at the bottom of the core. Additional age control was indirectly available from <sup>14</sup>C dating that was used at other sites in the drainage to confirm the identification of the Mazama ash.

Uranium concentrations determined by a delayed neutron method range from 140 to 2,790 ppm on a dry weight basis and are positively correlated with organic matter content (fig. 1). In contrast, thorium concentrations show a much narrower range of less than 10 to 40 ppm and are not correlated with organic matter content. These observations and previous results from size-fraction analyses and fission-track radiography (Otton and Zielinski, 1986) indicate preferential enrichment of uranium in finer grained organic matter. The degree of uranium enrichment is substantial, considering that the estimated uranium content of locally derived silicate detritus is less than 20 ppm.

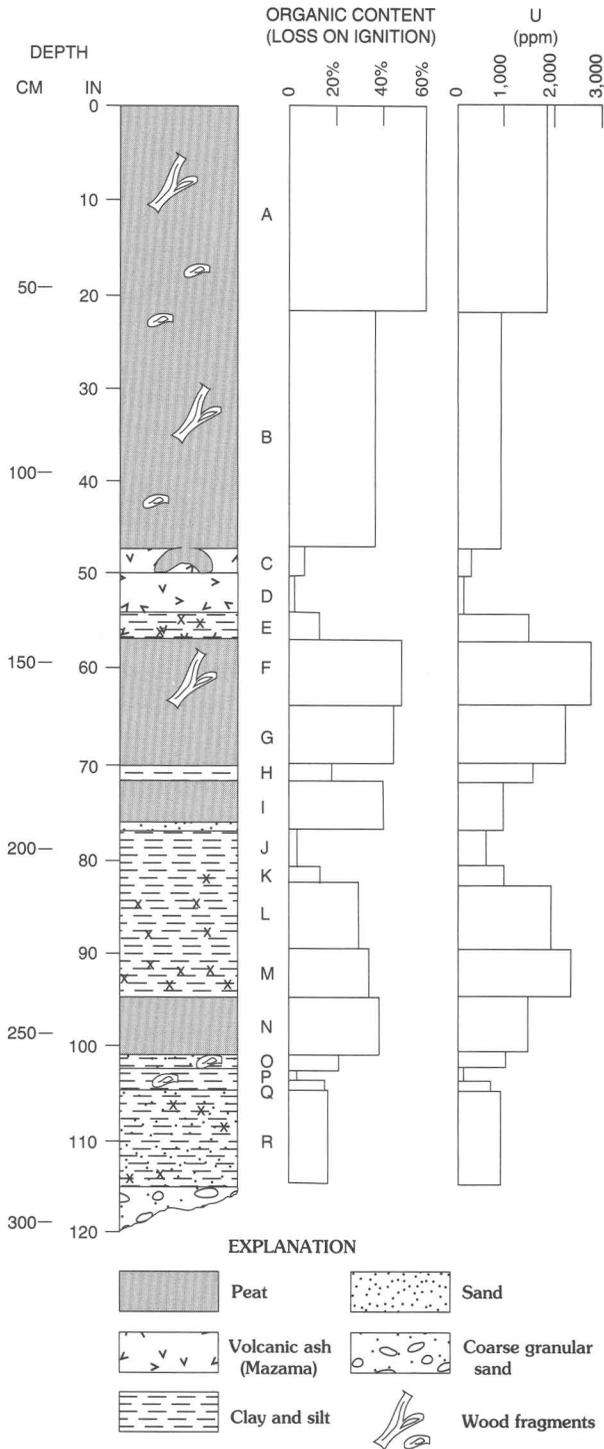
The uranium isotopic composition of the core samples, as determined by radioisotope dilution-alpha spectrometry, indicated a rather narrow range of <sup>234</sup>U/<sup>238</sup>U activity ratios of 1.30–1.38. These alpha activity ratios are similar to the values of 1.27–1.38 reported for modern springs in the drainage (Zielinski and others, 1987). These results suggest that local waters had a uniform isotopic composition throughout the history of the deposit. An alternative explanation requires equilibration of the entire sediment column with modern waters; however, such uniform open-system access of uranium to the sediment column is unlikely considering the lithologic diversity of the samples and the evidence for approximate closed-system behavior of <sup>234</sup>U and its immediate daughter <sup>230</sup>Th presented below.

Apparent uranium emplacement ages for ten intervals of core were calculated using the measured decay-generated buildup of <sup>230</sup>Th daughter relative to <sup>234</sup>U parent. After correction for the generally minor contributions of detrital <sup>230</sup>Th, the apparent ages show a general increase as a function of depth and are in fair agreement with the estimated ages of host sediments (fig. 2). For example, apparent ages of intervals C and E bracket that of interval D, which contains the Mazama ash. With the exception of the deepest interval which may be receiving modern input of uranium from upwelling water, the trend of age with depth approaches the limiting age of basal, post-glacial sediments of 12,000–15,000 years B.P. These observations indicate that most of the measured intervals approximate closed sys-

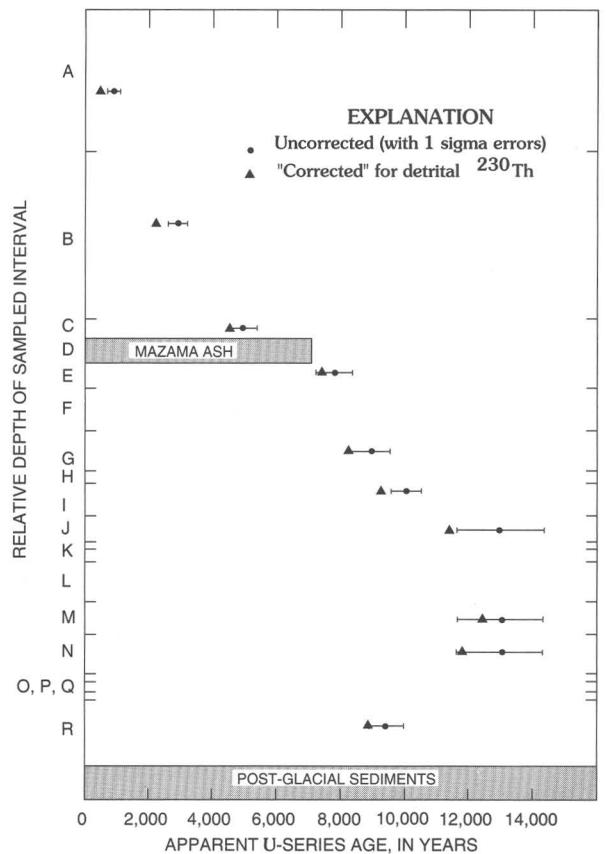
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<sup>3</sup>Deceased 1991.



**Figure 1.** Generalized lithologic log of the studied core. Histograms indicate the concentrations of organic matter and uranium in the sampled intervals. Intervals O, P, and Q were combined for subsequent analyses.



**Figure 2.** Apparent  $^{230}\text{Th}/^{234}\text{U}$  ages of ten measured intervals, corrected for detrital  $^{230}\text{Th}$  and plotted as a function of depth. Ruled intervals provide independent estimates of depositional age and are included for comparison. Letters refer to intervals shown on figure 1.

tems with respect to  $^{234}\text{U}$  and  $^{230}\text{Th}$  and record a period of uranium uptake early in their depositional history. This history of uranium uptake spans the entire post-glacial period and is probably occurring today in the shallower intervals and, perhaps, in the deepest intervals. Present access of uraniumiferous water to the site is as surface flow and as plumes of upwelling ground water that emerge as open spring pools. The core site is within a few m of one such pool that has concentrations of dissolved uranium in excess of 300 ppb (Zielinski and others, 1987).

The abundances of other uranium daughters, in addition to  $^{230}\text{Th}$ , are similarly 10–100 times below that required for radioactive equilibrium. These other decay-generated species are not, however, as immobile as thorium and are subject to additional redistribution in the sediment column. For example, deficiencies of  $^{226}\text{Ra}$  daughter ( $t_{1/2}=1602$  y)

relative to  $^{230}\text{Th}$  parent occur in most of the deepest intervals and are too large, based on the elapsed time since sediment deposition and uranium emplacement. This implies some redistribution of decay-generated radium, resulting in a net loss of radium from the studied core. The residence of this mobilized radium is unknown, but radium may accumulate in clay-rich intervals in or below the cored section.

Deficiencies of  $^{226}\text{Ra}$  relative to  $^{210}\text{Pb}$  are observed throughout the core. These deficiencies probably result from recent radium loss as described above and (or) preferential, core-wide gain of deeper sourced  $^{222}\text{Rn}$  gas that streams upward and leaves a trail of relatively immobile and longer lived  $^{210}\text{Pb}$  daughter ( $t_{1/2}=22.3$  y). Upwelling ground water carries radon gas to the site of the open spring pool (Otton and Reimer, 1991). In addition, sorption of minor amounts of radium on clays in the underlying post-glacial sediments may provide local, deep sources of radon daughter.

Our results suggest that  $^{230}\text{Th}/^{234}\text{U}$  dating of uraniumiferous peats may provide minimum ages for underlying glacial tills. Although radiocarbon dating is commonly employed for peats formed within the last 40,000 years, measurements of  $^{230}\text{Th}/^{234}\text{U}$  can extend the datable range to approximately the last 350,000 years.

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# Geology of the Holocene Surficial Uranium Deposit of the North Fork of Flodelle Creek, Northeastern Washington

By Samuel Y. Johnson,<sup>1</sup> James K. Otton,<sup>1</sup> and David L. Macke<sup>2</sup>

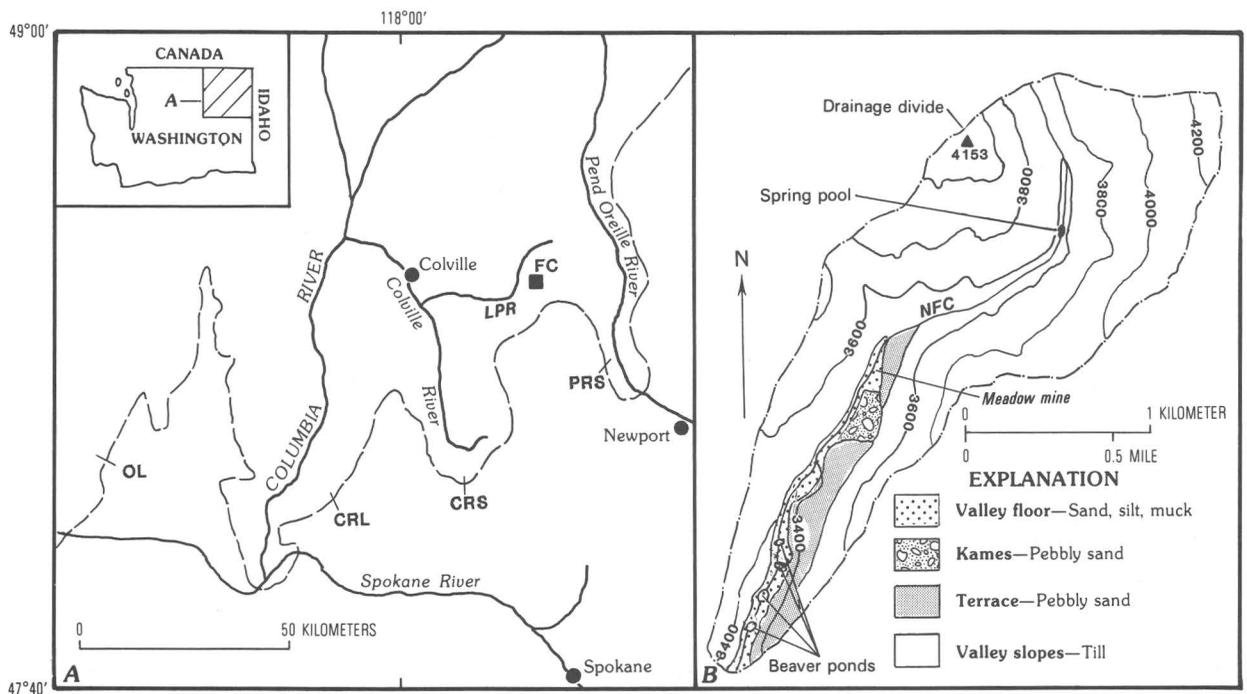
The north fork of Flodelle Creek drainage basin in Stevens County, northeastern Washington (fig. 1), contains the first surficial uranium deposit to be mined in the United States. The uranium was leached from granitic bedrock and

precipitated or adsorbed in organic-rich pond sediments. The distribution of the pond sediments and the uranium they contain was strongly influenced by relict glacial topography, slope processes, and beaver activity.

The Cordilleran ice sheet covered the north fork of Flodelle Creek drainage basin during the Fraser (late Wisconsin) glaciation (fig. 1). Till and outwash were deposited on the valley slopes and floor as ice receded. Outwash incision and melting of stagnant ice led to formation of a terrace and kames. Shortly after deglaciation, a small (about 50 by 20 m) pond (the spring pool of fig. 1B) formed in the upper part of the valley when unconsolidated glacial sediment slumped off the valley slopes and restricted drainage. Fluvial processes dominated in the central and downstream parts of the valley for several thousand years after deglaciation even though drainage was partly restricted by kames. Beavers occupied and built dams on the wide outwash plains beginning about 5,000 years B.P. Beaver ponds in the central part of the basin subsequently filled with sediment and were abandoned, whereas downstream ponds remained relatively free of clastic input and are presently occupied by beavers. The Meadow mine (figs. 1B, 2) occupies the site of a former beaver-pond complex.

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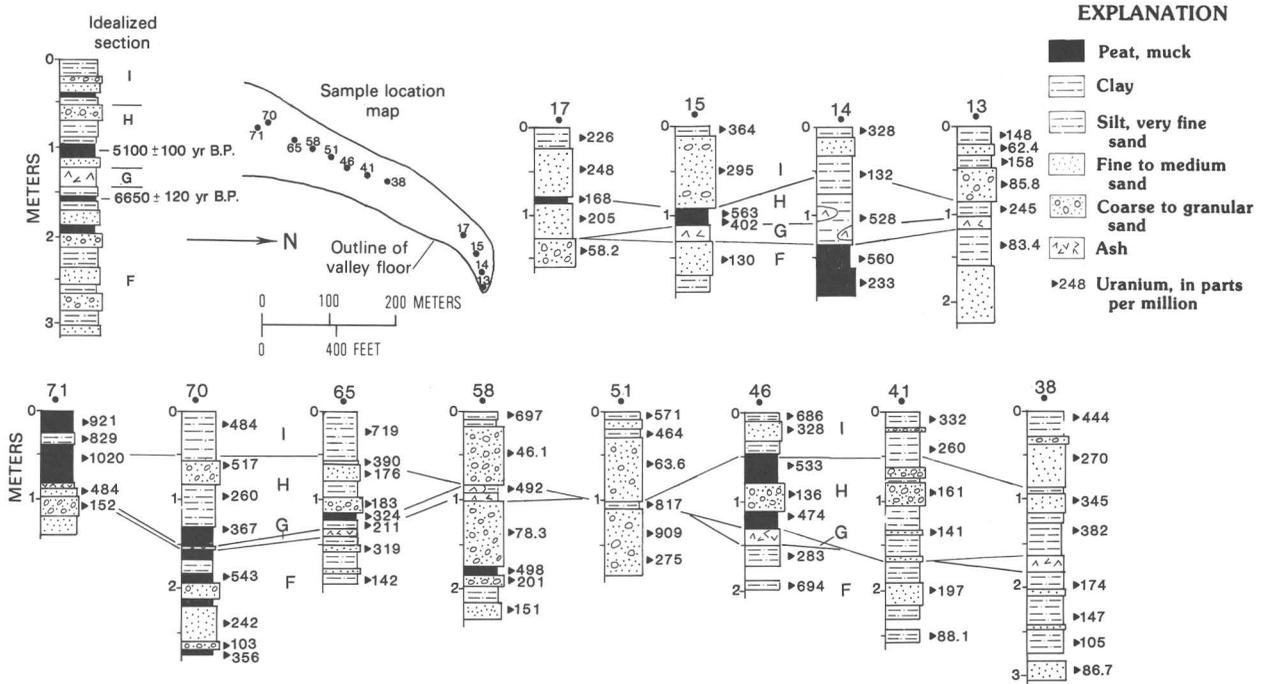
**Figure 1.** A, Map showing the location of the north fork of Flodelle Creek drainage basin (FC). Dashed line shows approximate limit of lobes of the Cordilleran ice sheet during the Fraser glaciation. Other abbreviations are: CRL, Columbia River lobe; CRS, Colville River sublobe; LPR, Little Pend Oreille River; OL, Okanogon lobe; and PRS, Pend Oreille sublobe. B, Map of surficial deposits of the north fork of Flodelle Creek (NFC) drainage basin. Contours in feet.

Ponds in the drainage basin trapped fine-grained, organic-rich sediments. These organic-rich sediments provide a suitable geochemical environment for precipitation and adsorption of uranium leached from granitic bedrock into ground, spring, and surface waters. Uranium concentrations in organic-rich sediments in the spring pool and Meadow mine (fig. 2) are as high as 8,960 and 1,020 ppm, respectively. Processes of pond formation have thus been important in the development of surficial uranium deposits

in the north fork of Flodelle Creek drainage basin and may have similar significance in other areas.

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**Figure 2.** Stratigraphy and uranium (U) concentration (determined by delayed neutron activation) of samples taken along the axis of the Meadow mine in the north fork of Flodelle Creek drainage basin. Stratigraphic units F, G, H, and I are described in detail in Johnson and others (1987). Unit G is the Mazama ash. Ages shown for the upper part of unit F and the lower part of unit H are  $^{14}\text{C}$  dates on organic matter. Modified from Johnson and others (1987).

# Arid-Land Surficial Uranium Deposits—A Review of Examples and Their Modes of Occurrence

By Sigrid Asher-Bolinder<sup>1</sup> and James K. Otton<sup>1</sup>

Surficial uranium deposits are formed in near-surface sedimentary environments and are predominantly syngenetic. They are generally Tertiary to Holocene in age, and deposits less than 500,000 to 250,000 years old may be deficient in gamma- and beta-active uranium (U) daughter products. Present-day arid and semiarid regions containing surficial uranium deposits are characterized by climatic conditions in which potential evaporation exceeds actual precipitation by factors of 5 to 20.

Figure 1 indicates the localities of several arid-land surficial uranium deposits (ALSUDS). Classification of ALSUDS has been based on depositional environments (Toens and Hambleton-Jones, 1984; Otton, 1984), on dominant associated mineralogies or organic-rich materials specific to climate and physical setting (Carlisle, 1984), or on processes leading to deposition of the uranium deposits (Boyle, 1984). As with other mineral deposits, ALSUDS result from: (1) physical and chemical processes that liberate U from its source terrain, (2) transport mechanisms that carry U in solution to suitable environments, and (3) physical and (or) chemical concentration and trapping mechanisms that can deposit U.

The source terrains for ALSUDS are generally igneous rocks of felsic to intermediate composition (such as granite, granodiorite, welded or airfall tuff) or felsic metasedimentary rocks. Source rocks may contain 2–50 ppm U, some of which is dissolved and transported by surface waters or shallow ground waters during or following physical and chemical weathering. Physical processes that make U available for chemical weathering include grusification, regolith development, jointing, faulting, and glacial scouring. Uranium dissolves in slightly acidic to alkaline oxidizing waters and forms complexes of uranyl carbonates or phosphates.

Although surface stream flow is an obvious transport mechanism for U-bearing waters, flow from springs and seeps and subsurface flow through soil, regolith, or sediment also provide a significant flux of U to areas of concentration and precipitation.

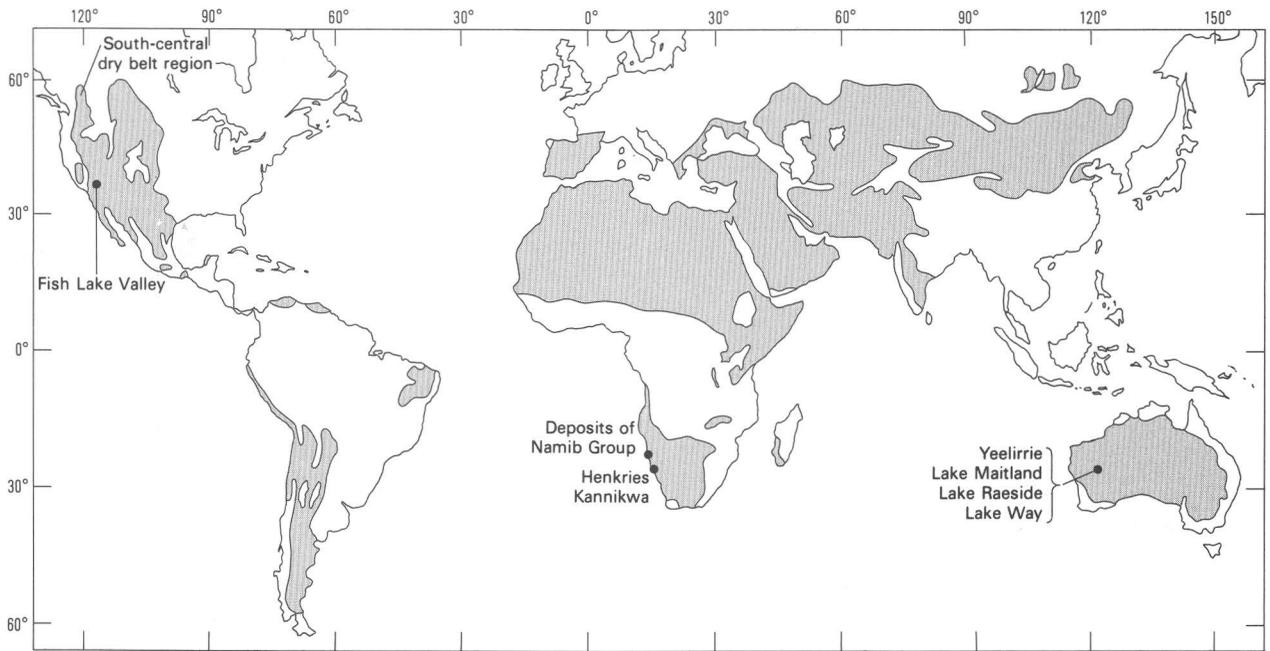
The high ratio of evaporation to precipitation in arid and semiarid regions is primarily responsible for the concen-

tration of U and other cations in surface waters and in shallow subsurface waters. Upwelling of subsurface waters into the vadose zone may be caused by topographic, lithologic, or structural barriers to subsurface hydrologic flow. Subsurface waters may rise to the surface in lake and playa basins or stream valleys, especially along buried topographic highs. Basinward fining of sediments may result in loss of permeability and upwelling of subsurface waters at the lacustrine or deltaic margin. Springs and seeps may form in areas of differential permeability such as along faults and flexures.

The concentration of U relative to other ions, the speciation of other ions, and the pH and Eh of the solution determines whether U can be removed from that solution and in what form it will accumulate. Uranium minerals in ALSUDS commonly include carnotite and, less commonly, autunite, tyuyamunite, and schroëckerite. Carnotite ( $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$ ) can form only when there is adequate potassium, vanadium, and U in solution; it is stable over a fairly broad pH range, from approximately 3 to 8.7. Adsorption of uranyl and uranous ions by organic matter, diatomite, clays, or iron or manganese oxyhydroxides is controlled to some degree by the water's pH (optimally 4–7 for organic matter and 5–7 for clays), the degree of humification of organic matter, and Eh. In strongly alkaline waters, U may remain complexed with carbonates, inhibiting adsorption of U unless the Eh of the environment is strongly reducing (Boyle, 1984). As U-bearing waters well up into the zone of evaporation  $P_{CO_2}$  drops, and decreased confining pressures cause destabilization of uranyl carbonate complexes, making U more available for precipitation or adsorption.

The physical and chemical mechanisms responsible for U concentration operate in several environments common to arid and semiarid climates. In western Australia and Namibia, in recent and (or) ancient fluvial systems, carnotite-bearing nonpedogenic calcrete has accumulated in the centers of low-gradient valleys where U-rich groundwaters intersect the evaporative zone (Carlisle and others, 1978). The Yeelirrie calcrete U deposit (Cameron, 1984) and those in the Namib Group of Namibia (Hambleton-Jones, 1984a) are among the best known examples. The long-term tectonic stability and surface exposure in those areas have produced deeply weathered, permeable regoliths that are the source of U. Below the zone of evaporation, these regoliths also allow lateral and downstream migration of slightly acidic, U-bearing ground waters. As these waters migrate toward the zone of evaporation in the valley center, they become progressively more alkaline and saline. At the basin center, valley-fill calcrete and associated carnotite precipitate as cements and grain coatings in fluvial sediments. Because carnotite is more soluble than calcrete, it is redissolved and redistributed in the valley center by infrequent summer rains. Rains, confined largely to the summer months, are rapidly evaporated if they do not quickly percolate below the zone of evaporation. In contrast, in cooler and (or) wetter climates, or in less

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**Figure 1.** Arid and semiarid regions of the world (pattered) showing arid-land surficial uranium deposits mentioned in the text. Modified from Meigs (1953).

porous soils, soil moisture remains in the zone of evaporation and promotes formation of pedogenic calcrete within the soil column (Carlisle and others, 1978). Pedogenic calcrete is a less favorable host for carnotite accumulation than valley fill calcrete because lateral and downstream movement of ground water is reduced, and U is not transported to a site of high evaporation where concentration can occur.

Another environment suited to the concentration and deposition of ALSUDS is the closed or partially closed basin that may contain playas, alkaline lakes, deltas, or marshes associated with springs having year-round flow. Within these sedimentary environments, U may be deposited as carnotite, or it may be adsorbed onto organic- or oxyhydroxide-rich, clayey, or diatomaceous material (Carlisle, 1980). Examples of ALSUDS in closed or restricted basins include carnotite-bearing deltaic, fluvial, and playa sediments of Lakes Maitland (Cavaney, 1984), Raeside (Gamble, 1984), and Way (French and Allen, 1984) in western Australia. The lacustrine and playa basins of the south-central dry belt of British Columbia (Culbert and others, 1984) trap U in organic matter and clays under both oxidizing and reducing conditions. The Kannikwa and Henkries deposits of South Africa host U in reduced, organic-rich diatomaceous earth (Hambleton-Jones, 1984b). In Fish Lake Valley, Nevada, U is concentrated by organic-rich marsh sediments (Macke and others, 1990).

In ALSUDS, as in other surficial uranium deposits, disequilibrium may be noted between the chemical values of U

in a deposit and the equivalent values of U suggested by radiometric assay methods. This disequilibrium may be explained in two ways: Either the U is so recently deposited as to have had insufficient time for the ingrowth of gamma- and beta-active daughters, or the U has been leached from its original site of deposition, leaving unsupported radioactive daughters behind. These factors complicate the assessment of potential ALSUDS deposits and emphasize the relatively ephemeral nature of such deposits. Any short-term influx of groundwater may produce gradients in pH, Eh, and salinity that can lead to differential solution and precipitation of U. Longer-term changes in climate or base level can affect local and regional groundwater levels, either further concentrating U or carrying it away. Given these factors, ALSUDS may be seen as possible sources of contamination of water supplies in semiarid to arid regions, or they may be seen, in a longer view, as transient preconcentrators that may have supplied dissolved U to more conventional sedimentary U deposits developed in the past.

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# Hydrogeology of San Juan Basin Uranium Deposits—The Brine-Interface Model Revisited

By Richard F. Sanford<sup>1</sup>

For many years geologists thought that tabular-type uranium deposits in Triassic and Jurassic sedimentary rocks of the Colorado Plateau formed at the interface between two solutions of different salinity, although the evidence was largely circumstantial. A more recent hypothesis, the lacustrine-humate model, proposed that just one fluid was involved in uranium precipitation, and this fluid moved downward from the mudflat facies of a paleolake into underlying fluvial sands. New hydrogeologic modeling and comparison with modern hydrogeologic systems suggest that at least three compositionally distinct fluids existed during uranium deposition in the Upper Jurassic Morrison Formation and that two of these fluids caused uranium deposition by mixing at a brine interface in zones of ascending regional flow. This new model integrates, for the first time, observed associations of uranium deposits with fluvial sandstones, underlying evaporites, overlying lacustrine mudstones, and syndepositional topographic depressions.

Reconstruction of the Late Jurassic paleogeography and paleohydrology of the southwestern United States indicates that the San Juan Basin area was the discharge zone for a 400,000-km<sup>2</sup> drainage basin that extended to the Mogollon highlands. Recharge to the Morrison Formation had three main sources: (1) deep gravity- and compaction-driven flow of meteoric and formation water, (2) shallow, gravity-driven flow of meteoric water, and (3) shallow density-driven flow of playa-lake water.

Deep ground water originated as infiltration of meteoric water in the distant Mogollon highlands, flowed north and east toward the basin, and discharged at the playa margin. Compaction of sediments yielded minor additional deep ground water. The deep ground water that was thus discharged was saline due to reaction with detrital grains and dissolution of evaporite minerals, especially anhydrite from the Middle Jurassic Todilto Limestone. Infiltration by direct recharge at the outcrop yielded shallow ground water that

became slightly alkaline and saturated with calcium carbonate during down-dip flow toward the basin. This relatively fresh ground water rose, discharged at the lake shoreline, and formed a buoyant lens above the denser, saline ground water. Under some conditions, density-driven playa-lake water descended through the lake sediments, moved outward through the Westwater Canyon Member of the Morrison Formation, and then rose and discharged at the playa lake margin. Reaction of this fluid with volcanic ash produced characteristic alkaline-lake mineral assemblages in lacustrine muds and underlying fluvial sands. The regional topographic low and the hydrologic barrier created by the playa lake caused a regional upward flow and discharge at the carbonate mudflat zone bordering the playa lake.

The Grants uranium region closely coincides with the zone of discharge and mixing of the three ground-water types. The association of uranium deposits with lacustrine mudstones can best be explained by the tendency of ground water to discharge at topographic depressions in which standing water often accumulates. Deposits such as the Jackpile Sandstone Member of the Morrison and Paguate Tongue of the Dakota Sandstone, which are not overlain by lacustrine mudstones, were also created in zones of discharge and mixing; only the topographic depression is revealed by thickened sediments characteristic of syndepositional subsidence. The flow system around topographic depressions also explains the association of uranium deposits with underlying evaporites and supports the brine-interface model.

In contrast, no hydrogeologic simulations or modern analogs have suggested any systematic downward flow in the mudflat facies as required by the lacustrine-humate model. Further, diagenetic evidence is either consistent with different flow directions or contradicts the model of downward flow. For example, the pattern of iron-titanium oxide destruction in the Westwater Canyon Member is equally consistent with downward flow from the Brushy Basin Member of the Morrison or with lateral, down-dip flow from the outcrop. Abundant pedogenic calcite in the mudflat is strong evidence of upward-flowing, discharging ground water.

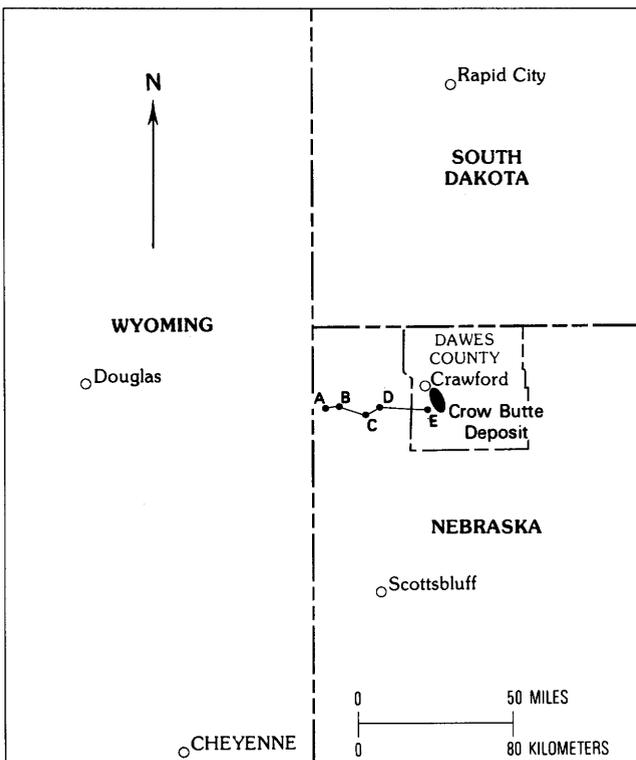
Geologists exploring for sedimentary uranium deposits should look first in uranium provinces where fluvial sandstones overlie evaporites. Within these areas, syndepositional topographic lows, lacustrine mudstones, thicker fluvial sandstone, and low mudstone to sandstone ratios indicate favorable zones for the occurrence of tabular uranium deposits.

# Uranium Mineralization and Favorability in the Oligocene Chadron Formation, Southeastern Wyoming and Northwestern Nebraska

By Paula L. Hansley<sup>1</sup> and  
Kendell A. Dickinson<sup>1</sup>

## INTRODUCTION

Anomalies on oil well gamma-ray logs of the basal sandstone of the Oligocene Chadron Formation led to the discovery of the Crow Butte uranium deposit near Crawford, Nebraska, in 1980 (fig. 1) (Collings and Knode, 1984). The



**Figure 1.** Index map showing locations of the Crow Butte uranium deposit and east-west cross section, A-E.

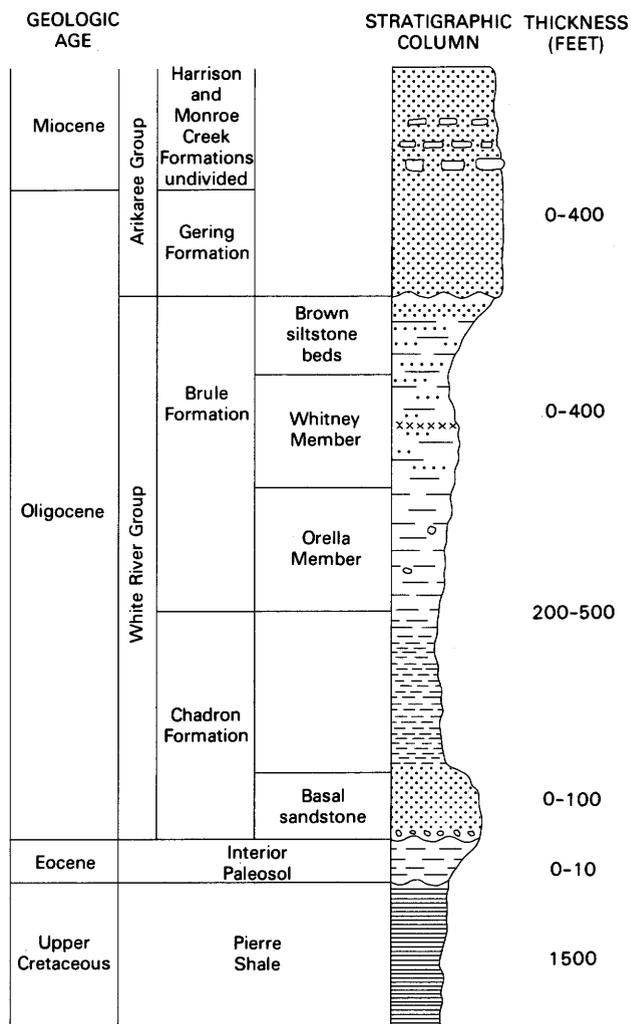
<sup>1</sup>U.S. Geological Survey, Box 25046, Mail Stop 939, Denver Federal Center, Denver, Colorado 80225.

ore-bearing basal sandstone (average grade > 0.25 weight percent uranium) averages 13 m in thickness, and estimated reserves are in excess of 40 million pounds  $U_3O_8$  (Gjelsteen and Collings, 1988; Collings, oral commun., 1990). Ferret Exploration Company of Nebraska, Inc., began mining the ore by an in situ leaching process early in 1991.

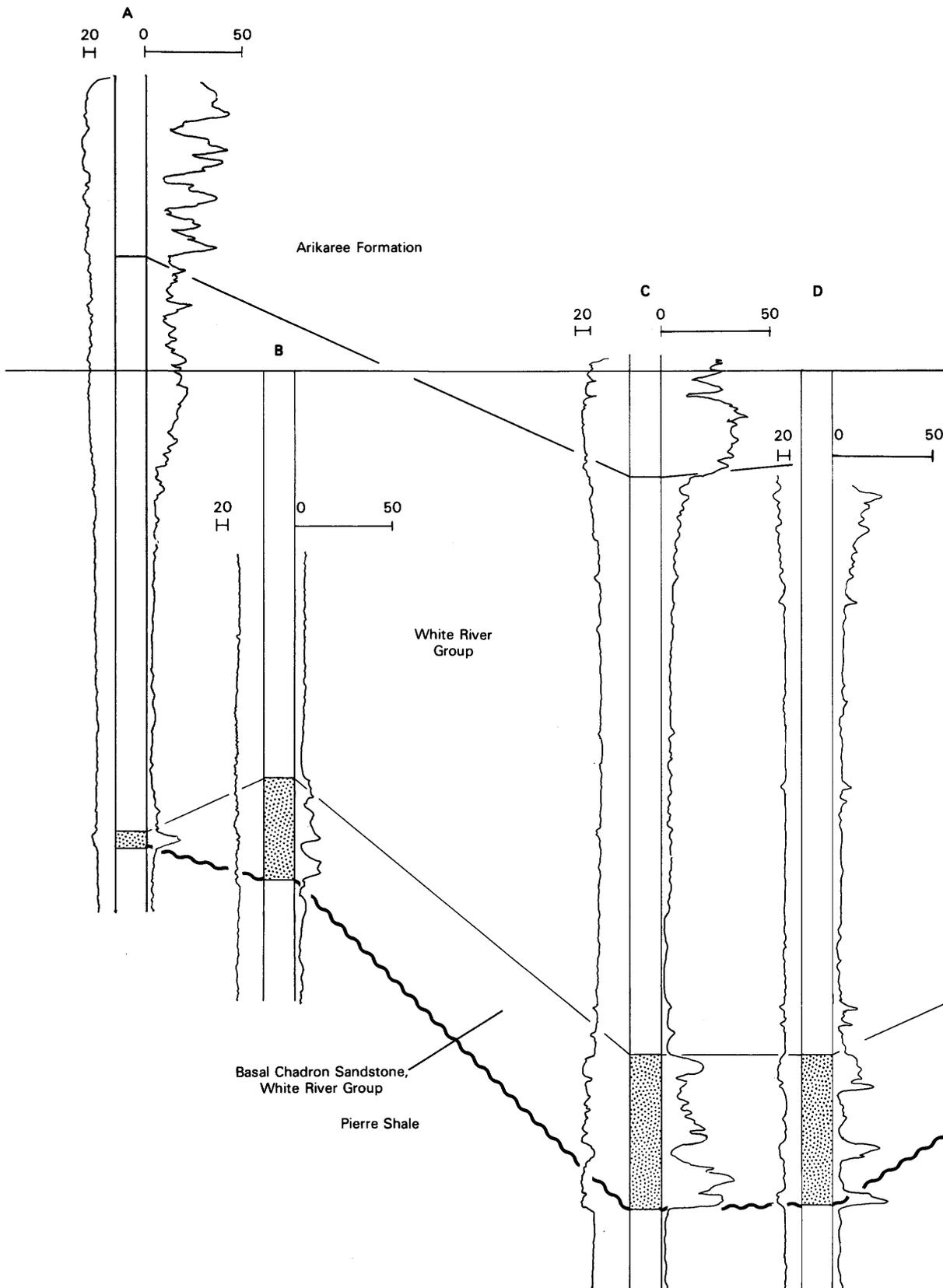
The only part of the White River Group known to be favorable for commercial-size uranium deposits is the basal Chadron sandstone. Compilation of electric log data has revealed other areas that are potentially favorable for uranium where the basal Chadron sandstone is relatively thick.

## STRATIGRAPHY AND GEOLOGIC SETTING

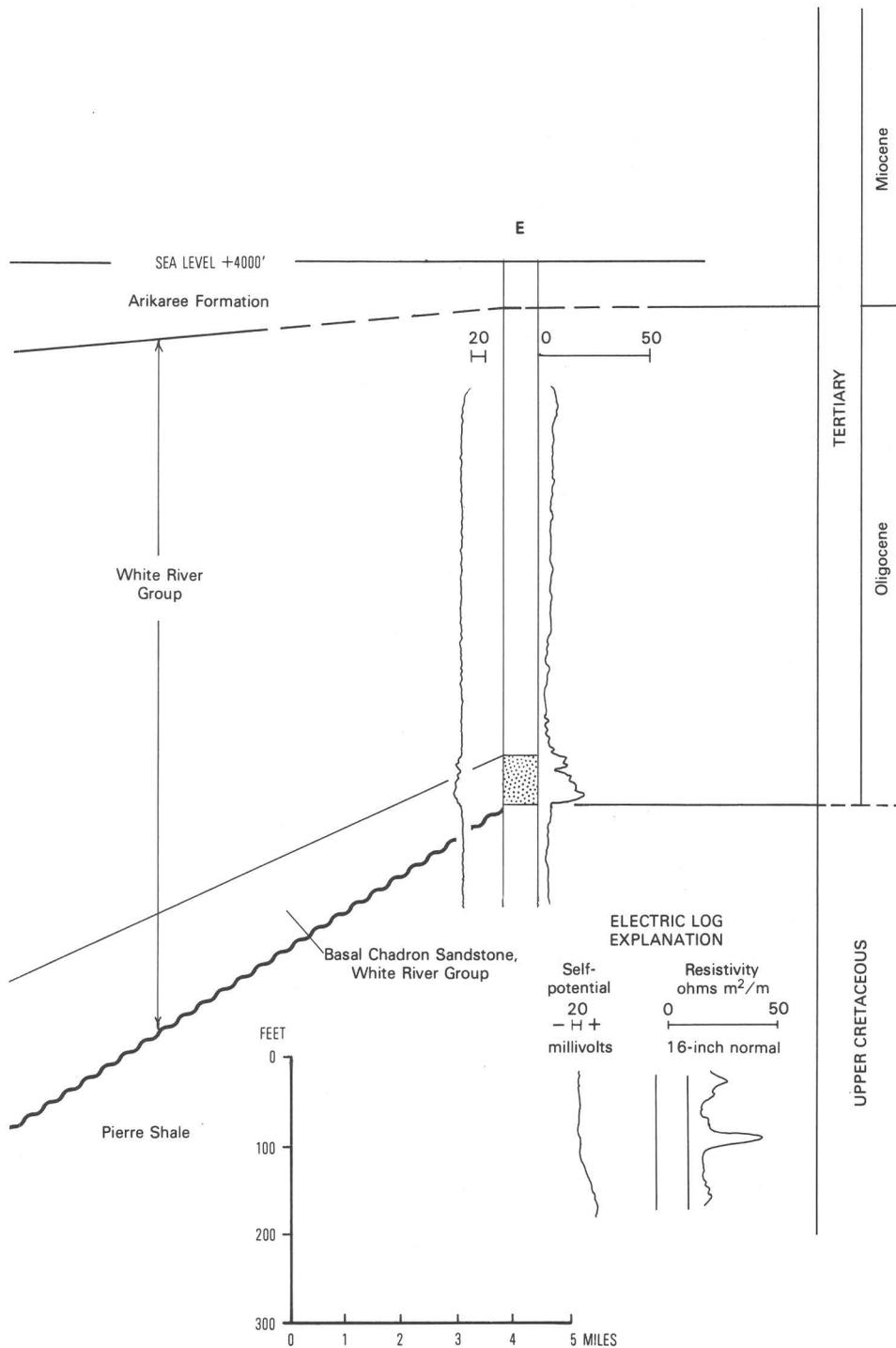
The Oligocene White River Group is divided into the Chadron Formation and the overlying Brule Formation in northwestern Nebraska (fig. 2); however, the White River is



**Figure 2.** Stratigraphy of the White River Group in the vicinity of the Crow Butte uranium deposit, northwestern Nebraska (based on Swinehart and others, 1985).



**Figure 3 (above and facing page).** East-west cross section (see fig. 1) showing development of the basal Chadron sandstone in the vicinity of the Crow Butte deposit. From Dickinson (1990).



undivided in Wyoming. The basal Chadron sandstone, which is found throughout southeastern Wyoming and northwestern Nebraska, was deposited in ancient braided stream channels that eroded into the underlying Upper Cretaceous Pierre Shale. Near Crawford, the uranium-bearing basal Chadron sandstone is overlain by an impervious red clay unit in the upper part of the Chadron Formation. The sandstone channels are scattered throughout southeastern Wyoming, northwestern Nebraska, and possibly parts of southwestern South Dakota and northeastern Colorado. The channel system containing the Crow Butte uranium deposit has been traced from the vicinity of Douglas, Wyoming, eastward and southward to the area south of Crawford, Nebraska, by Dickinson and Wise (1989), Gjelsteen and Collings (1988), and Dickinson (1990).

The basal Chadron sandstone is as much as 350 ft thick in the vicinity of the Crow Butte deposit, but its thickness rarely exceeds 100 ft in other areas. A cross section based on electric log data of the White River Group in the vicinity of the Crow Butte deposit is shown on figure 3.

## SANDSTONE PETROLOGY

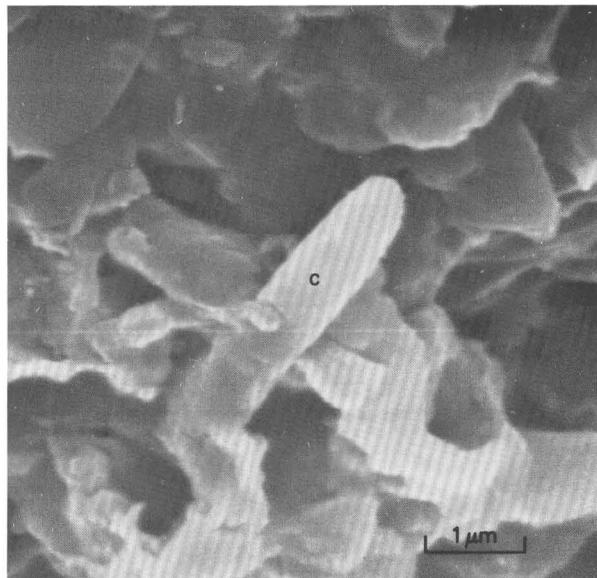
In the Crow Butte deposit, the basal Chadron sandstone is a coarse-grained, tuffaceous, arkosic litharenite composed of poorly sorted angular quartz, plagioclase, and potassium feldspar grains and igneous rock fragments that are loosely packed in a vitric matrix dominated by rhyolitic volcanic ash (Hansley and others, 1989). Major nonopaque heavy minerals are zircon, garnet, and tourmaline with minor amounts of staurolite, epidote, apatite, and biotite; ilmenite and magnetite are the major opaque heavy minerals. Fresh glass shards and feldspar grains and minor authigenic smectite/illite (> 90 percent expandable) indicate that very little diagenetic alteration has taken place.

## URANIUM ORE MINERALOGY

The highest uranium concentrations are in the clay fraction of the sandstone matrix where uranium occurs in submicroscopic coffinite crystals, 2  $\mu\text{m}$  or less in length (fig. 4). Uranium is also present in the amorphous matrix with Si, P, V, Fe, Ca, and Al. Coffinite is closely associated with abundant authigenic pyrite and marcasite. Most of the uranium ore remains in a reduced state; however, local oxidation of primary ore and sulfide minerals has produced tyuyamunite, metatyuyamunite, carnotite, and zippeite.

## GENESIS OF URANIUM ORE

The occurrence of uranium-bearing matrix in sandstone interstices and between mica plates indicates that ore forma-



**Figure 4.** Scanning electron photomicrograph of typical poorly formed, micron-size coffinite crystal (c) in uranium-bearing matrix of Crow Butte ore.

tion took place before compaction, not long after deposition of the basal Chadron sandstone. Uranium was probably derived from alteration of abundant rhyolitic volcanic ash in the White River Formation (Group)—this ash contains an average of 8 ppm uranium in Wyoming (Zielinski, 1983). According to Gjelsteen and Collings (1988), ore formed at oxidation/reduction fronts in a manner similar to that of Wyoming-type roll-front deposits. We propose that oxidizing ground water carrying uranyl dicarbonate complexes moved downdip through permeable basal Chadron channel sandstones and that uranium precipitated on the margins of the channels where a reducing environment was encountered. The reducing environment was caused by concentrations of woody fragments and associated humic organic matter in the Chadron. Bacterially mediated reduction of  $\text{SO}_4$  in the presence of organic matter (e.g., decaying plant matter) produced  $\text{H}_2\text{S}$  and led to chemical reduction and precipitation of uranium and ore-stage iron disulfides. Reduction of uranyl complexes coupled with high silica activity (created by alteration of rhyolitic ash) resulted in formation of coffinite. A schematic diagram showing our proposed roll-front model for ore formation is shown on figure 5.

## SUMMARY AND CONCLUSIONS

The Crow Butte uranium orebody has been interpreted to be a roll-front deposit that formed during early diagenesis. The only part of the White River Group known to be favor-

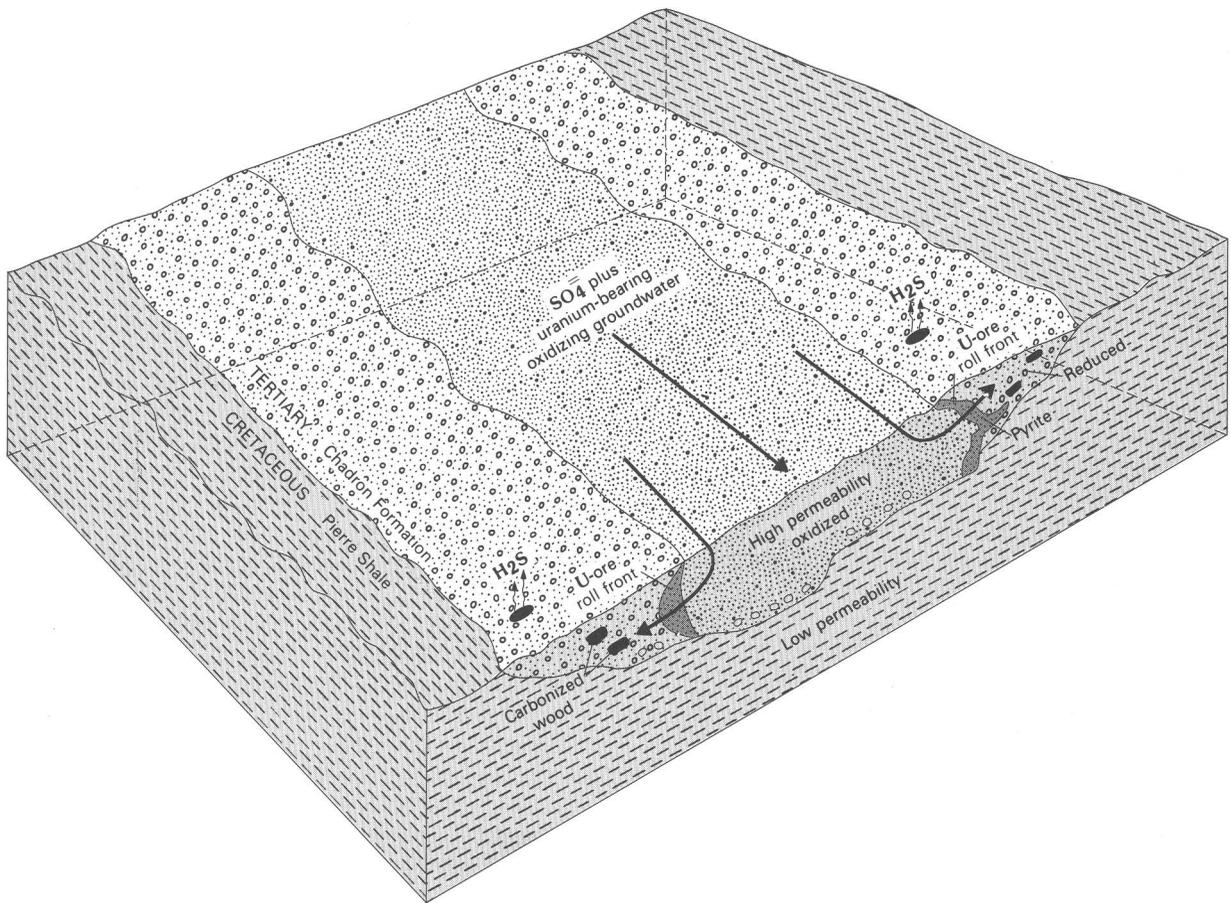


Figure 5. Proposed roll-front model for formation of Crow Butte uranium deposit.

able for commercial-size uranium deposits is the basal sandstone of the Chadron Formation. The occurrence of uranium ore in this basal sandstone may be related to its thickness. Subsurface mapping in southeastern Wyoming and southwestern Nebraska has revealed areas where the sandstone may provide environments favorable for the occurrence of uranium orebodies

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# Uranium in Phosphate Rock—With Special Reference to the Central Florida Deposits

By James B. Cathcart<sup>1</sup>

Uranium is a trace constituent of all apatites in amounts that characteristically range from 30 to 300 parts per million (ppm). Although the discovery that phosphate rock is radioactive was made at about the turn of the century, it was not until uranium was used in atomic weapons that the U.S. Geological Survey began an examination of all sources of the metal, and it was confirmed that the phosphate deposits of the United States contain from 60 to 350 ppm uranium. Subsequent detailed examinations of the Florida and western United States deposits resulted in many published reports that are listed in a phosphate bibliography (Bridges and others, 1983).

Phosphate is found in three distinct types of deposits: guano or derived from guano, apatite of igneous origin, and marine phosphorite deposits. Data on resources, production, and uranium content are shown in table 1; locations are shown on figure 1.

Guano, the excreta of bats and sea birds, contains 10 ppm uranium or less, and total resources are trivial. Guano-derived deposits result when dissolved phosphorus reacts with underlying rocks to form hydroxyapatite or aluminum and iron phosphate minerals. Uranium content ranges from 10 to 80 ppm, but the higher concentrations are found only when the hydroxyapatite is altered to fluorapatite by seawater. Resources and production are limited.

Deposits of igneous apatite occur as intrusive masses, marginal differentiates, veins, and pegmatites. The largest deposits are intrusive masses associated with alkalic rocks. The apatite content of these rocks ranges from a few percent in some veins to as much as 80 percent in intrusive sheets, and resources in individual deposits range from a few thousand to millions of tons. Uranium contents usually range from 10 to 50 ppm, but a sample of apatite from the magnetite deposits at Mineville, New York, contained 7,900 ppm uranium.

Marine phosphorite deposits are known throughout the world and range in age from Precambrian to Holocene. Economic deposits are restricted to late Precambrian–Cambrian,

Ordovician, Permian, Late Cretaceous–Eocene, and Miocene ages. These deposits form large phosphogenic provinces in which resources total hundreds of billions of tons. The deposits form in tectonically stable basins at low latitudes that are open to oceanic upwelling and are away from large sources of clastic diluents. Total potentially minable resources are scores of billions of tons. These deposits contain uranium in amounts that range from 10 to 400 ppm, and individual samples contain as much as 5,300 ppm. The apatite fraction in unaltered deposits ranges from 60 to 90 ppm uranium. Uranium is present in the phosphate minerals apatite and crandallite as U(IV) substituting for calcium in the mineral structure. A small amount of uranium as U(VI) may be adsorbed on the apatite surface.

The distribution uranium in the Florida uranium deposits demonstrates that these deposits are syngenetic. Primary phosphate pellets in the middle Miocene Peace River Formation contain an average of 90 ppm uranium, whereas the uranium content of the pellets in the Bone Valley Formation, reworked from the Peace River in a marine environment, average about 120 ppm. The coarser pebble fraction contains about 150 ppm, and compound pebbles that show several cycles of reworking contain as much as 500 ppm.

In the Florida deposits (fig. 2), uranium content is highest in the coarsest phosphate nodules that are low in  $P_2O_5$  and is lowest in the finest size phosphate pellets that are high in  $P_2O_5$ . Leaching by acid stream water has removed both uranium and  $P_2O_5$  from phosphate grains in deposits in the stream valleys; uranium content there is less than 50 ppm.

The relation of high U to low  $P_2O_5$  in the coarse fraction and low U to high  $P_2O_5$  in the fine fraction is consistent in millions of tons in one mine area and in individual drill hole samples, and the relation holds regardless of the relative amounts of the two fractions. When data from only one size fraction are studied, the relation of U to  $P_2O_5$  is positive. Data analyzed collectively from all size fractions show almost no correlation between U and  $P_2O_5$ . These relations indicate that primary uranium was not introduced into the deposit after deposition of the phosphate: had this been the case, we would expect to see the highest uranium concentrations associated with phosphate that is high in  $P_2O_5$ , is fine grained, and has a large surface area. For example, in an area where acid ground water was draining into a sinkhole filled with phosphate rock, the fine-grained phosphate contained 5,300 ppm U, while the coarser material contained only about 1,000 ppm U.

Apatite is soluble in acid solutions, and under acid ground-water conditions, both phosphate and uranium are dissolved. When the phosphorite is high in carbonate, apatite is not dissolved until almost all of the carbonate is removed: phosphate is then dissolved and  $P_2O_5$  in solution moves downward and may replace underlying carbonate rock. Uranium tends to be enriched in the replacement

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**EXPLANATION**

- **GUANO-DERIVED DEPOSITS**
  - 1. Christmas Island
  - 2. Nauru
- ▲ **IGNEOUS APATITE DEPOSITS**
  - 1. Brazil carbonatite deposits
  - 2. Phalaborwa, South Africa
  - 3. Kola Peninsula, USSR
  - 4. Eppiwala, Sri Lanka
- **MARINE PHOSPHORITE DEPOSITS**
  - 1. Triassic-Permian, Alaska
  - 2. Permian, Northwest United States
  - 3. Ordovician, Tennessee
  - 4. Miocene-Florida, Georgia, and North Carolina
  - 5. Cretaceous, Colombia
  - 6. Precambrian, Brazil
  - 7. Miocene, Baja California, Mexico
  - 8. Ordovician, USSR
  - 9. Cretaceous-Eocene, North Africa
  - 10. Precambrian, Upper Volta
  - 11. Cretaceous-Eocene, Near East
  - 12. Precambrian, Karatau, USSR
  - 13. Cambrian-Precambrian, India, China
  - 14. Cambrian-Precambrian, Mongolia
  - 15. Cambrian, Australia

**Figure 1.** World-wide distribution of major phosphate deposits.

deposits; amounts of as much as 1,000 ppm have been reported in secondary apatite hardpan deposits.

Intensive acid weathering of sandy phosphorites dissolves apatite and produces zones rich in aluminum phosphate minerals. These deposits are characterized by the change of apatite to crandallite and finally to wavellite. Uranium is enriched in these deposits and is preferentially associated with crandallite and apatite at the base of the zone of weathering. Because wavellite is continually formed from crandallite, the uranium in crandallite is mobilized and moves downward, further enriching the underlying apatite that may contain as much as 1,000 ppm U. Isopleth maps of uranium and P<sub>2</sub>O<sub>5</sub> content in coarse phosphate grains in the land pebble district clearly show the effects of acid leaching.

The contour lines are similar to topographic contours: they are deeply indented upstream and form closed contours in the interstream divides. Samples from stream valleys contain only about 50 ppm uranium and 20–25 percent P<sub>2</sub>O<sub>5</sub>, whereas the interstream divides are underlain by phosphate that contains as much as 250 ppm uranium and 35 percent P<sub>2</sub>O<sub>5</sub>.

The phosphate rock in the southern extension of the land pebble district has been leached only in the northern part of the area. Most of the phosphate is in the Peace River Formation, a siliciclastic unit of the middle part of the Hawthorn Group. The uranium content of the phosphate in this formation ranges from 60 to 110 ppm and averages about 90 ppm. Uranium content of the phosphate pellets of the

**Table 1.** Phosphate resources, production, and uranium content

[Leaders (--), no data available; Avg., average uranium concentration (in percent)]

Location	Resources (metric tons)	Production (metric tons)	Uranium concentration (percent)
<b>Guano and guano-derived phosphate</b>			
Worldwide	150 x 10 <sup>6</sup>	1.5 x 10 <sup>6</sup>	0.001–0.008
<b>Igneous phosphate</b>			
Worldwide	3 x 10 <sup>9</sup>	28 x 10 <sup>6</sup>	0.001–0.005
<b>Marine phosphorites</b>			
Florida, land pebble district	1 x 10 <sup>9</sup>	--	0.003–0.030 Avg. (+1 mm) 0.015 Avg. (-1+0.1 mm) 0.010
Florida, southern extension	3 x 10 <sup>9</sup>	--	0.003–0.010 Avg. 0.005
North Florida–South Florida	2 x 10 <sup>9</sup>	46.5 x 10 <sup>6</sup>	0.004–0.011 Avg. 0.006
North Carolina	2 x 10 <sup>9</sup>	--	0.004–0.011 Avg. 0.006
Western U.S.	10 x 10 <sup>9</sup>	--	0.004–0.023 Avg. 0.009
Africa	45 x 10 <sup>9</sup>	52 x 10 <sup>6</sup>	0.004–0.023 Avg. 0.009
Asia	10 x 10 <sup>9</sup>	16 x 10 <sup>6</sup>	0.003–0.020 Avg. 0.008
Europe	10 x 10 <sup>9</sup>	18 x 10 <sup>6</sup>	0.005–0.021 Avg. 0.006
Latin America	6 x 10 <sup>9</sup>	1 x 10 <sup>6</sup>	0.002–0.012 Avg. 0.008
<b>TOTALS</b>	<b>89 x 10<sup>9</sup></b>	<b>135 x 10<sup>6</sup></b>	<b>0.002–0.015</b> Avg. 0.008

carbonate rock in the underlying Arcadia Formation is only about 60 ppm. Deposits of phosphate rock in northern and eastern Florida are similar to the deposits in the land pebble district and its southern extension.

Hardrock phosphates are secondary deposits of apatite that remained after the rocks of the Hawthorn Group were eroded from the crest of the Ocala uplift. The deposits were formed when acid waters dissolved phosphate, and P<sub>2</sub>O<sub>5</sub> in solution was precipitated on and replaced the underlying limestone. The apatite crusts and replacement bodies have been reworked in Pleistocene and Holocene time and form small, erratically distributed phosphate deposits. Uranium contents range from 60 to about 100 ppm, but the P<sub>2</sub>O<sub>5</sub> content of rock produced from these deposits is about 35 percent.

River pebble deposits occur as bars and in floodplains of modern streams that drain phosphate deposits. These deposits are small and low in both P<sub>2</sub>O<sub>5</sub> and U because of leaching by acid stream water.

Uranium is being recovered today from two phosphoric acid plants. One is at the border of Polk and Hillsborough Counties in Florida, and one, using Florida rock, is at Uncle Sam, Louisiana. Each plant produced about 1 million pounds of uranium in 1988.

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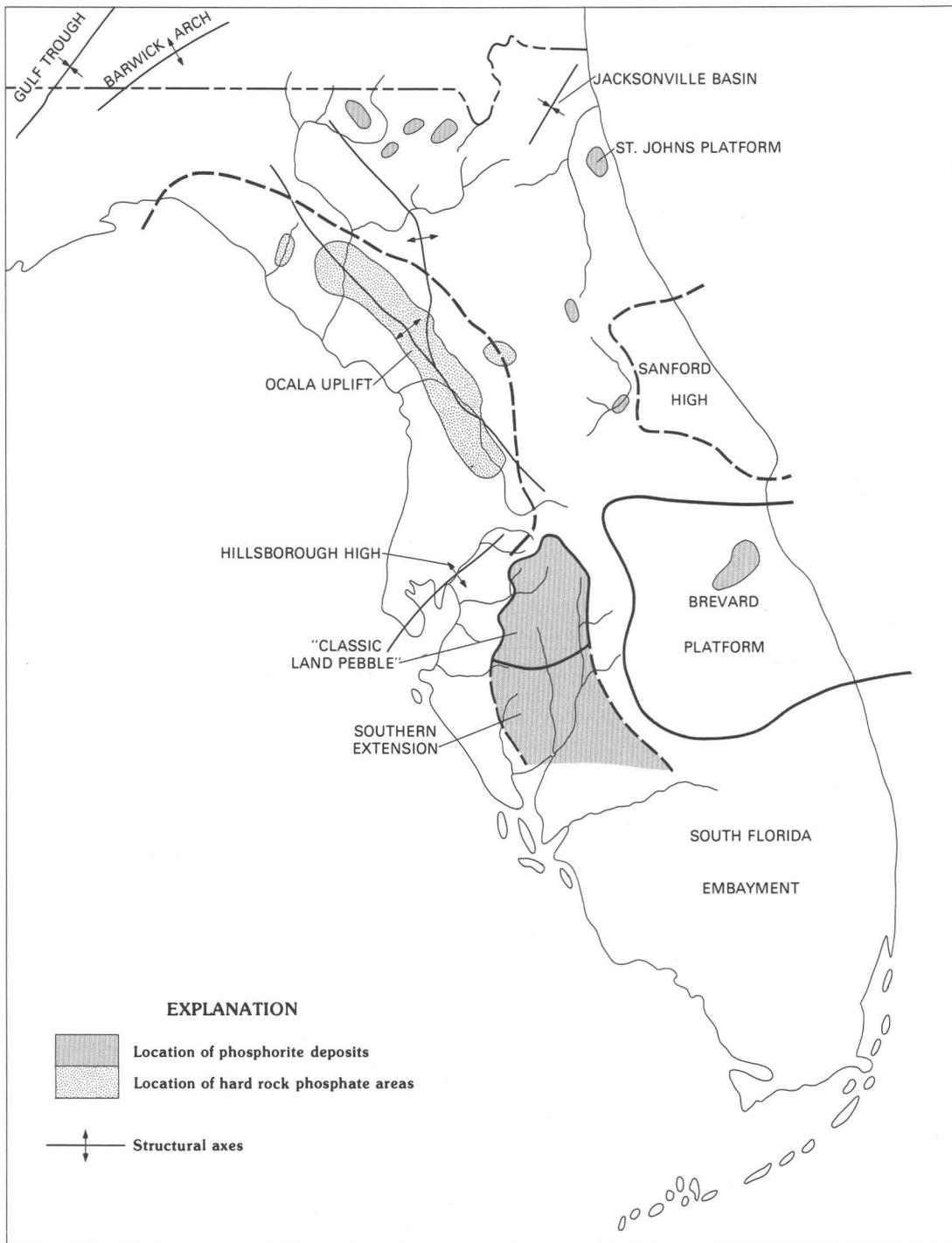


Figure 2. Location of major structural features and known phosphate areas in Florida.

# Organic Matter and Uranium in Solution-Collapse Breccia Pipes of Northern Arizona and San Rafael Swell, Utah

By Karen J. Wenrich<sup>1</sup> and James G. Palacas<sup>2</sup>

## INTRODUCTION

Organic matter is commonly associated with uranium orebodies throughout the Colorado Plateau. Extensive studies have been done on such associations because many authors believe that the organic matter played a major role in the ore-forming process, particularly in the San Juan Basin (Squyres, 1980; Leventhal, 1980; Hatcher and others, 1986). According to Hatcher and others (1986), humic acids were important in the formation of the San Juan Basin ores; the humic-type organic matter presumably acted as a reductant for uranium-bearing oxidizing groundwaters that subsequently deposited uraninite or coffinite.

The uranium-organic matter association is particularly striking in many of the uranium deposits in Arizona. Uranium ore in the Upper Triassic Shinarump Member of the Chinle Formation in Monument Valley (fig. 1A) is restricted primarily to carbonaceous sandstone and conglomerate beds, and similarly in the Cameron area (fig. 1A), to sandstones and conglomerates that contain varying amounts of organic matter, including carbonaceous fossil logs. Along the southern edge of the Colorado Plateau in Arizona at the Promontory Butte deposit, uranium mineralization occurred in coalified plant fossils along bedding planes within the Supai Group (Wenrich and others, 1989).

Nevertheless, not all organic-rich uranium deposits on the Colorado Plateau are believed to have originated from reduction by organic compounds. Breit and Goldhaber (1989)

suggested that vanadium-uranium deposits in the Morrison Formation in southwestern Colorado and southeastern Utah formed by reduction and precipitation that occurred through reaction with localized, strongly reducing (sulfidic) pore waters.

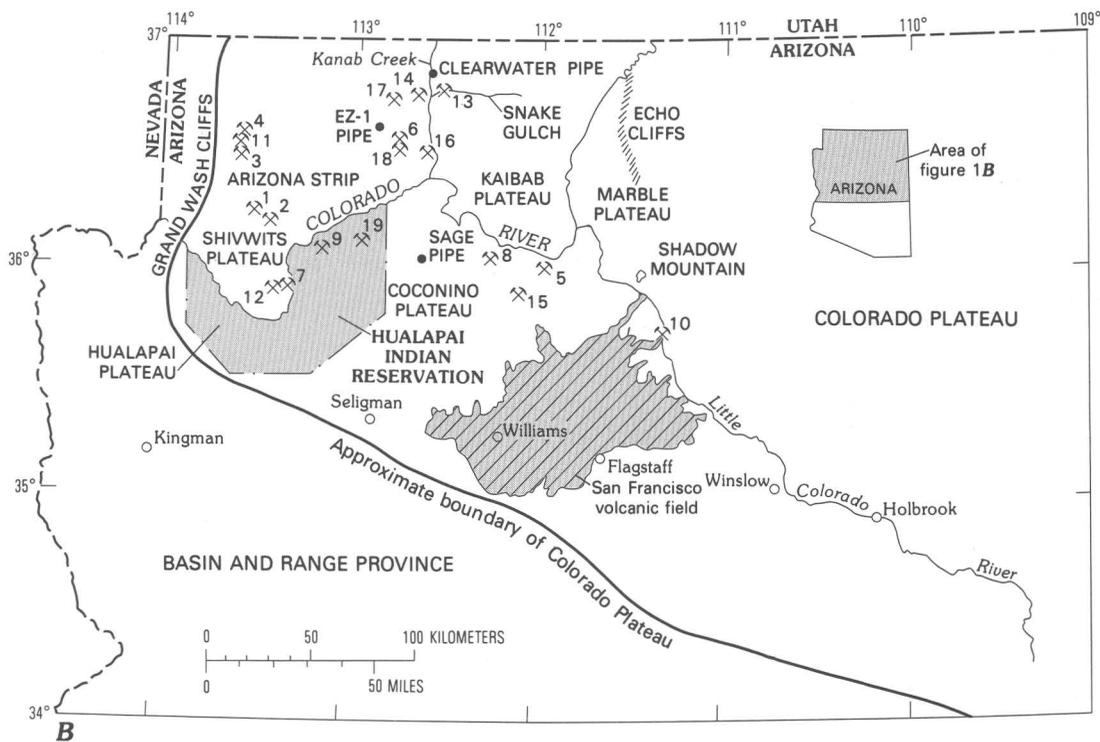
In contrast to more classical sandstone-hosted Colorado Plateau uranium deposits, the uranium orebodies located within solution-collapse breccia pipes in the southwestern corner of the Colorado Plateau do not display any consistent, obvious organic matter-uranium association. These pipes formed by solution collapse into caverns within the Mississippian Redwall Limestone (for stratigraphic column see Brown and others, this volume) and subsequent stoping and brecciation of the overlying Pennsylvanian, Permian, and Triassic strata (Gornitz and Kerr, 1970; Wenrich, 1985; Krewedl and Carisey, 1986; Wenrich and Sutphin, 1989). With the exception of the Upper Mississippian/Lower Pennsylvanian Surprise Canyon Formation and the Lower Permian Brady Canyon Member of the Toroweap Formation, none of the other upper Paleozoic units are known to contain abundant organic matter within northwestern Arizona. The Surprise Canyon Formation fills channels cut into the Redwall Limestone across northwestern Arizona; these channels contain some black shales containing 1 percent organic carbon (K.J. Wenrich, unpub. data). Although breccia pipes that host uranium orebodies do not generally contain any significant amounts of organic matter, several pipes clustered around the Kanab Creek-Hack Canyon area in Arizona (fig. 1B) are known to contain solid bitumen. Because of this association, Landais (1989) studied the effects of biodegradation on these solid bitumens in the Arizona pipes and in the Temple Mountain pipe in Utah; he concluded that biodegraded, migrated, organic material (formerly liquid petro-

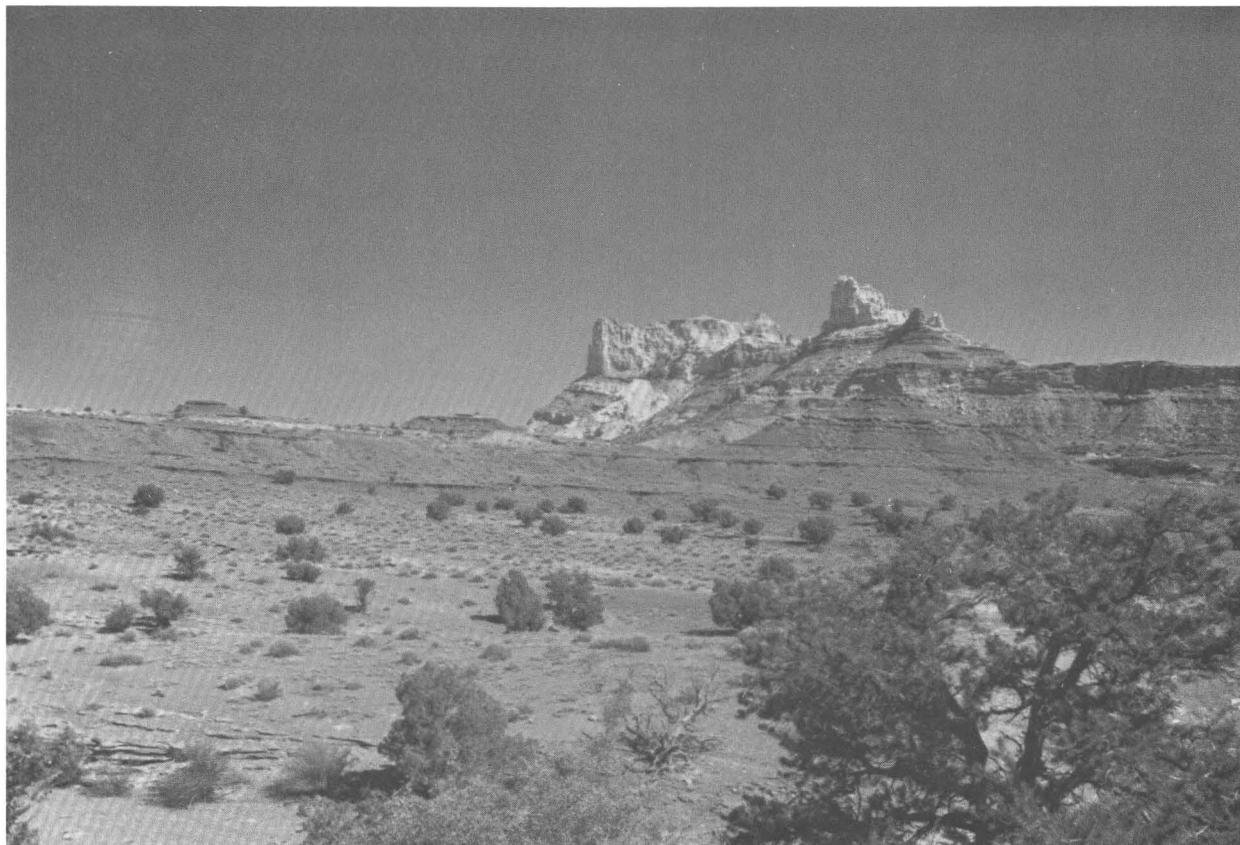
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**Figure 1 (facing page).** A, Index map showing the location of several uranium districts on the Colorado Plateau that contain organic matter. B, Index map of northern Arizona showing the locations of plateaus, Hualapai Indian Reservation, breccia pipes developed into mines, pipes containing bitumen that have not been developed into mines, and the San Francisco volcanic field that buries terrane with high potential for mineralized breccia pipes. Numbers refer to the following mines: (1) Copper House, (2) Copper Mountain, (3) Cunningham, (4) Grand Gulch, (5) Grandview, (6) Hack Canyon (includes old Hack, Hack 1, Hack 2, and Hack 3 mines, and Toroweap source-rock sample HB-821-C83), (7) Old Bonnie Tunnel, (8) Orphan, (9) Ridenour, (10) Riverview, (11) Savannic, (12) Snyder, (13) Pigeon, (14) Kanab North, (15) Canyon, (16) Pinenut, (17) Hermit, (18) Arizona 1, and (19) Mohawk Canyon.





**Figure 2.** The Temple Mountain breccia pipe resides within the north half of Temple Mountain, which is located along the crest of the San Rafael Swell. View is to the northeast. The pipe is dissected and well exposed on the back side of the left-most butte in this photograph.

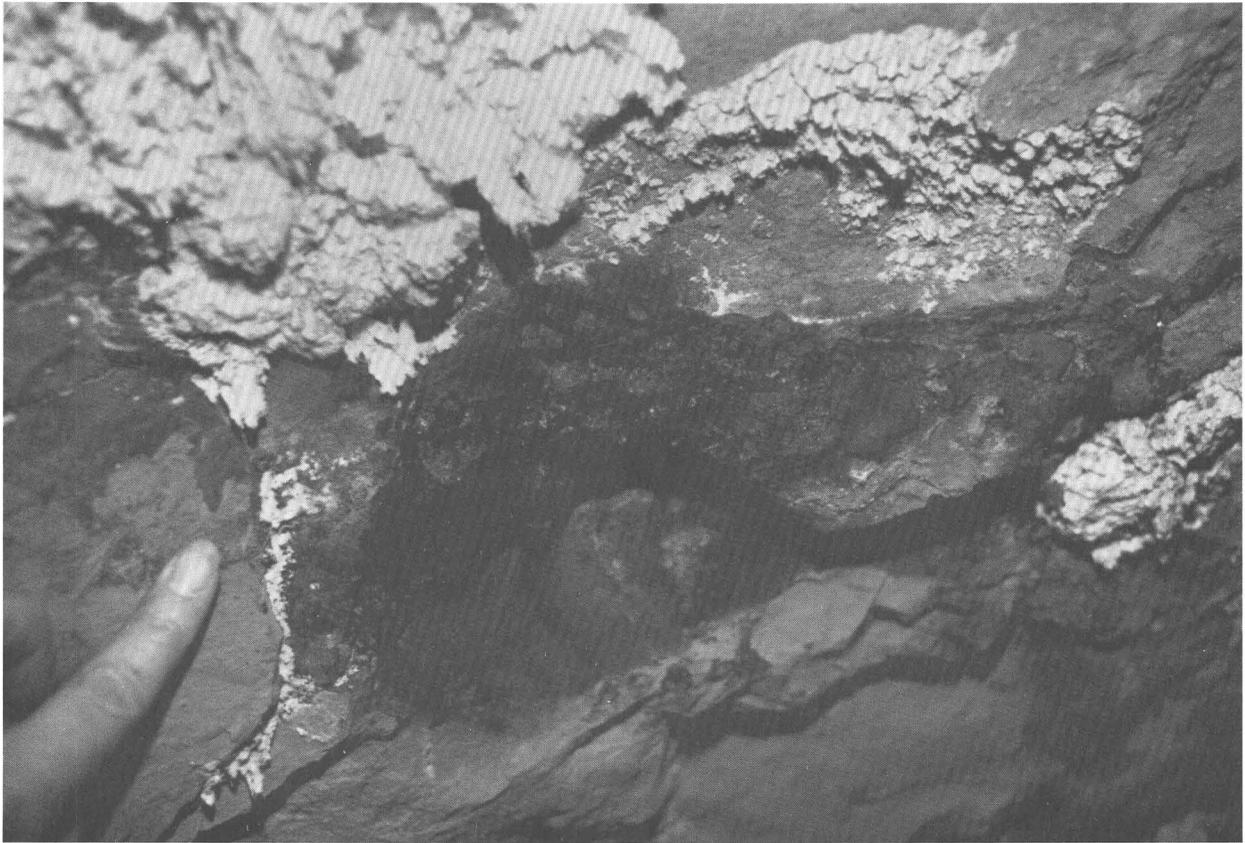
leum) can interact favorably with uranium-bearing solutions to cause deposition of uranium minerals.

Despite the well-documented association of uranium with humic-type organic matter, uranium is not as commonly associated with unaltered hydrocarbon concentrations (commercial oil accumulations). One of the questions addressed in this study was whether the solid bitumens in the northern Arizona breccia pipes and the Temple Mountain pipe were responsible for the associated uranium deposits. Even if bitumen did not influence uranium mineralization, determination of the source of the bitumen is important for exploration and research in uranium-rich breccia pipes. For instance, if the source of oils for the bitumens migrated over long distances, then such permeable channelways may have been available for uranium and base-metal transport. Thus, another objective of the present study was to determine, through comparisons of bulk organic-chemical composition, saturated hydrocarbon distributions, biomarker distributions, and carbon isotopes, whether the solid bitumen and related oils from these two spatially separated breccia pipes are

genetically related. Insights gained from this investigation into the nature of bitumen migration pathways may aid in the understanding of passageways through which uranium and other metals are transported in solution. Information may also be gained concerning the source of these metals. In the past, source rocks for uranium have been assumed to be those that are nearby and contain a volcanic component. For example, Krewedl and Carisey (1986) proposed that the Chinle Formation, with its inherently higher uranium content, was the source rock for the breccia pipe uranium deposits in northern Arizona.

## ORGANIC MATTER AND URANIUM ASSOCIATION

With the exception of a black, glassy, solid bitumen, few carbonaceous fossil logs, coalified plant fossils, or other visually obvious concentrations of organic matter have been



**Figure 3.** “Asphaltite” from a mine in the Temple Mountain breccia pipe.

observed within the Arizona breccia pipes. Apparently unaltered oils have been encountered while drilling in such pipes as the Hack 2. Landais (1989) showed a gas chromatogram for “unaltered oils” from the “Arizona breccia pipes” but did not cite a specific location.

The black, glassy, solid bitumen of the Arizona pipes contrasts with the duller asphaltite collected from the Temple Mountain breccia pipe, Utah (figs. 1A, 2), and the tar sand from Flat Top, Utah (fig. 1A), that was observed to flow down a sun-baked rock surface at or above 75°F (25°C). The Temple Mountain collapse-breccia pipe may have an origin different from that of the Arizona breccia pipes in that the bottom of the pipes may not terminate in Redwall Limestone. The Temple Mountain breccia pipe (fig. 2), which occurs in Jurassic (younger than the uranium mineralization of Arizona pipes) and Triassic rocks, contains abundant solid bitumen (referred to as “asphaltite” by Kerr and others, 1957; fig. 3). According to Hawley and others (1965), “The asphaltite probably contains an average of a few percent uranium\*\*\*.” An analysis of pure asphaltite made during this study showed 809 ppm uranium in the asphaltite, in contrast

to the Arizona bitumen, which generally contains < 10 ppm uranium (table 1). Although the Temple Mountain asphaltite sample appeared as pure as the Arizona bitumen, it is possible that it was not, considering the lower total organic carbon content (table 1). In addition to asphaltite, there is abundant plant debris (fig. 4) at Temple Mountain that also contains anomalously high uranium concentrations. The disparity in results between the Arizona pipes that contain essentially no uranium in the bitumen and the Temple Mountain asphaltite that appears to contain several hundred ppm uranium may be due to plant debris (normally high in uranium) intermixed with asphaltite in the Temple Mountain breccia.

Elemental analyses of 418 surface and subsurface, oxidized and reduced samples collected from mineralized and unmineralized Arizona breccia pipes show no significant correlation between organic carbon and uranium (fig. 5, correlation coefficient = 0.02). The organic carbon-uranium correlation coefficient for 103 samples (a subset of the 418 samples shown in fig. 5) collected from subsurface, reduced rock (much of it mineralized) was -0.07. A down-hole plot through reduced, poorly mineralized rock within the



**Figure 4.** Organic carbon and uranium-rich plant debris from a mine in the Temple Mountain breccia pipe. Horizontal field of view is 3 ft.

Mohawk Canyon pipe (fig. 6) shows little correlation between organic carbon and uranium (correlation coefficient =  $-0.02$ ). Likewise, as discussed above, there is no significant correlation between uranium and organic carbon for samples that contain abundant bitumen material. Indeed, samples of pure bitumen contain less than 10 ppm uranium (table 1).

## DISTRIBUTION AND GENERAL CHARACTERISTICS OF SOLID BITUMEN

In the northern Arizona breccia pipes, solid bitumen was exceptionally abundant in the Pigeon pipe, now mined out, (fig. 7; fig. 1B, site 13) but was less common at several other breccia pipes. Irregularly shaped pieces of solid, black, glassy bitumen, 4–8 cm in diameter (fig. 8), were found at several mine levels within the Pigeon pipe. They were locat-

ed within the uranium breccia-pipe orebody and were associated with clasts of both the Lower Permian Hermit Shale and Esplanade Sandstone. Significant amounts of bitumen were also found at the Clearwater pipe (located a few miles northwest of the Pigeon pipe; fig. 1B), which, although mineralized, has not yet been delineated as an orebody. Minor amounts of solid bitumen were identified at Pinenut (Reid and Rasmussen, 1990), Kanab North, Hack 2, Hack 3, and Hermit (fig. 1B, sites 16, 14, 6, 6, and 17, respectively) (Pat Hillard, Energy Fuels Nuclear, oral commun., 1990). The EZ-1 pipe, also located near the Pigeon pipe, contains bitumen (D.A. Krewedl, Pathfinder Mines, oral commun., 1988). To date, no solid bitumens have been recognized at the Canyon pipe (fig. 1B, site 15) (Pat Hillard, Energy Fuels Nuclear, oral commun., 1990), yet uranium deposits are present. With the exception of the Sage breccia pipe, located on the South Rim of the Grand Canyon, where very minor amounts of bitumen have been identified (Richard Meade,

**Table 1.** Elemental chemical analyses of samples from the Pigeon and Temple Mountain breccia pipes

[Results were determined by inductively coupled argon plasma emission spectroscopy (ICP) except for: U, determined by delayed neutron analysis; organic C, calculated as (total C) – (carbonate C); SiO<sub>2</sub> and FeTO<sub>3</sub> determined by quantitative X-ray fluorescence (the “T” in FeTO<sub>3</sub> indicates total Fe reported as Fe<sub>2</sub>O<sub>3</sub>); total S determined by combustion with infrared detection; trace metals in pure bitumen sample 455–J–C85 were determined by semi-quantitative emission spectroscopy. Leaders (–) indicate no data]

Element analyzed	Pigeon breccia pipe samples containing varying amounts of solid bitumen		Temple Mountain breccia pipe samples containing varying amounts of asphaltite or carbonaceous plant debris			Pure bitumen samples		
	455-J-C85	455-N-C85	1194-A-C87	1194-C-C87	1194-D-C87	Pigeon breccia pipe		Temple Mtn breccia pipe
						455-J-C85	455-T-C88	1194-M-C87
Ag (ppm)	<2.0	49	6.0	3.0	<2.0	<0.5	<0.5	<0.5
As (ppm)	110	3,500	620	210	2,100	<1,000	<20	64
Organic C (%)	3.26	2.76	61.5	61	31.2	85.6	87.3	77.5
Cd (ppm)	<2.0	23	<2.0	<2.0	170	<50	<4	19
Ce (ppm)	14.2	58	4.0	<2.9	98	<200	<8	<8
Co (ppm)	23.6	310	9.5	20.5	180	<5	<2	78
Cr (ppm)	70	170	12	5.0	210	3	2	6
Cu (ppm)	270	2,600	210	65	32	<1	2	13
FeTO <sub>3</sub> (%)	0.57	14.5 <sup>H</sup>	1.73	0.31	1.4 <sup>H</sup>	<0.01	–	–
Hg (ppm)	<0.14	1.10	0.28	0.08	–	–	0.10	0.70
Mo (ppm)	8.0	820	15	3.0	<2.0	<3	<4	6
Ni (ppm)	170	1,300	11	57	260	50	140	94
Pb (ppm)	49	1,700	170	90	810	50	<8	330
Total S (%)	0.39	12.8	1.95	1.37	2.89	5.74	5.16	2.07
Sb (ppm)	2.55	–	9.32	8.21	–	<200	<100	<100
SiO <sub>2</sub> (%)	87	54 <sup>H</sup>	3.37	1.49	35 <sup>H</sup>	–	–	–
U (ppm)	88.8	9,470	30.5	331	62,800	–	7	809
V (ppm)	41	130	300	110	6,700	100	230	19,000
Zn (ppm)	385	5,600	16.2	230	2,100	15	23	2,900

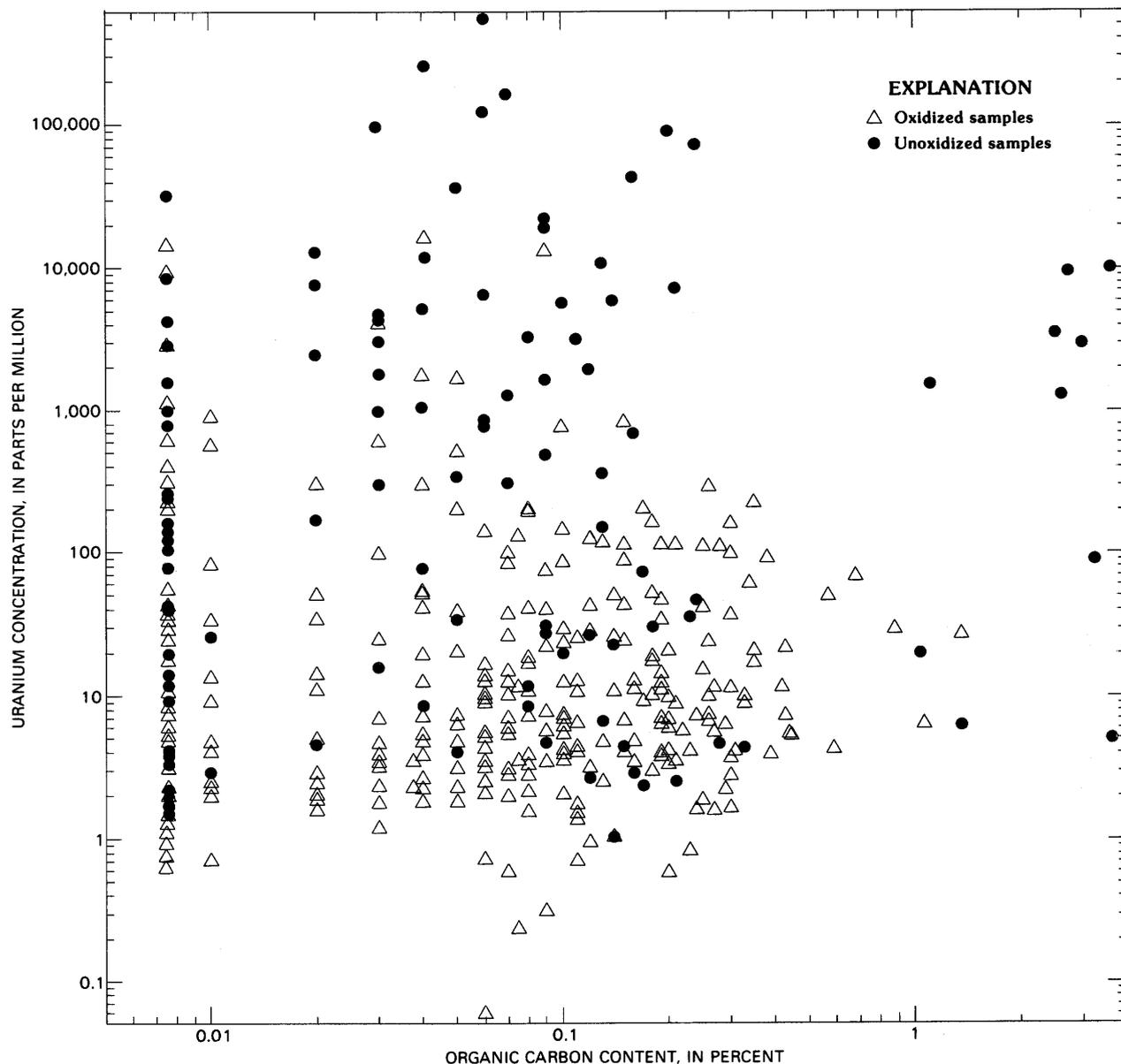
<sup>H</sup> Results are semi-quantitative for this sample due to matrix interferences

Union Pacific Resources, oral commun., 1990), all of the pipes containing significant amounts of bitumen are clustered together near Snake Gulch and Kanab Creek (fig. 1B).

Solid bitumen appears to have been introduced into the pipes late in the paragenetic mineral sequence (Wenrich and others, 1990). Among the sulfides, only some late-stage sphalerite (fig. 9) has been identified as contemporaneous with (or later than) the bitumen. From the paragenetic relations, uraninite appears to have precipitated prior to the bitumen. A large set of U-Pb isotopic analyses from the Hack 2, Hack 3, Pigeon, Kanab North, EZ–1, EZ–2, Arizona 1, Pine-nut, and Canyon pipe orebodies shows that the main uranium-mineralizing event occurred roughly 200 Ma (Ludwig and Simmons, 1988). However, data from the Canyon and Pinenut pipes indicate at least one earlier period of mineralization at about 260 Ma (Ludwig and Simmons, 1988). Fluid inclusion filling temperatures on sphalerite from seven different Arizona breccia pipes range from 80–173 °C; the salinities are high: 70 percent of the salinities are > 19 weight percent NaCl equivalent and the remaining 30 percent range from 9 to 12 weight percent NaCl equivalent (Wenrich,

1985; Wenrich and Sutphin, 1989). Fluorescent orange-yellow petroleum inclusions were observed by Jim Reynolds (written commun., 1985) in sphalerite from the Pigeon pipe—within this sample, petroleum was observed in vugs and microfractures within quartz, indicating that petroleum postdates deposition of the quartz.

The solid bitumen is sulfur rich. Elemental chemical analyses of a pure, solid bitumen sample from the Pigeon pipe yielded 85.6 percent carbon (precision of 1 percent) and 3.74 percent sulfur; the bulk of the remaining fraction is probably hydrogen with minor amounts of nitrogen and oxygen. The bitumen contains few trace elements in concentrations over 3 ppm (table 1); exceptions to this are: Ba (50 ppm), Ni (50 ppm), Pb (50 ppm), V (100 ppm), Zr (15 ppm), and Si (70 ppm). This paucity of trace metals within the bitumen contrasts sharply with the “asphaltite” from the San Rafael Swell discussed by Hawley and others (1965) and shown in table 1. Samples of bitumen from the Temple Mountain pipe contain 1.9 percent vanadium in contrast to 100 and 230 ppm for bitumen from two Pigeon pipe samples. Likewise U, Zn, and Pb are significantly higher in the Tem-



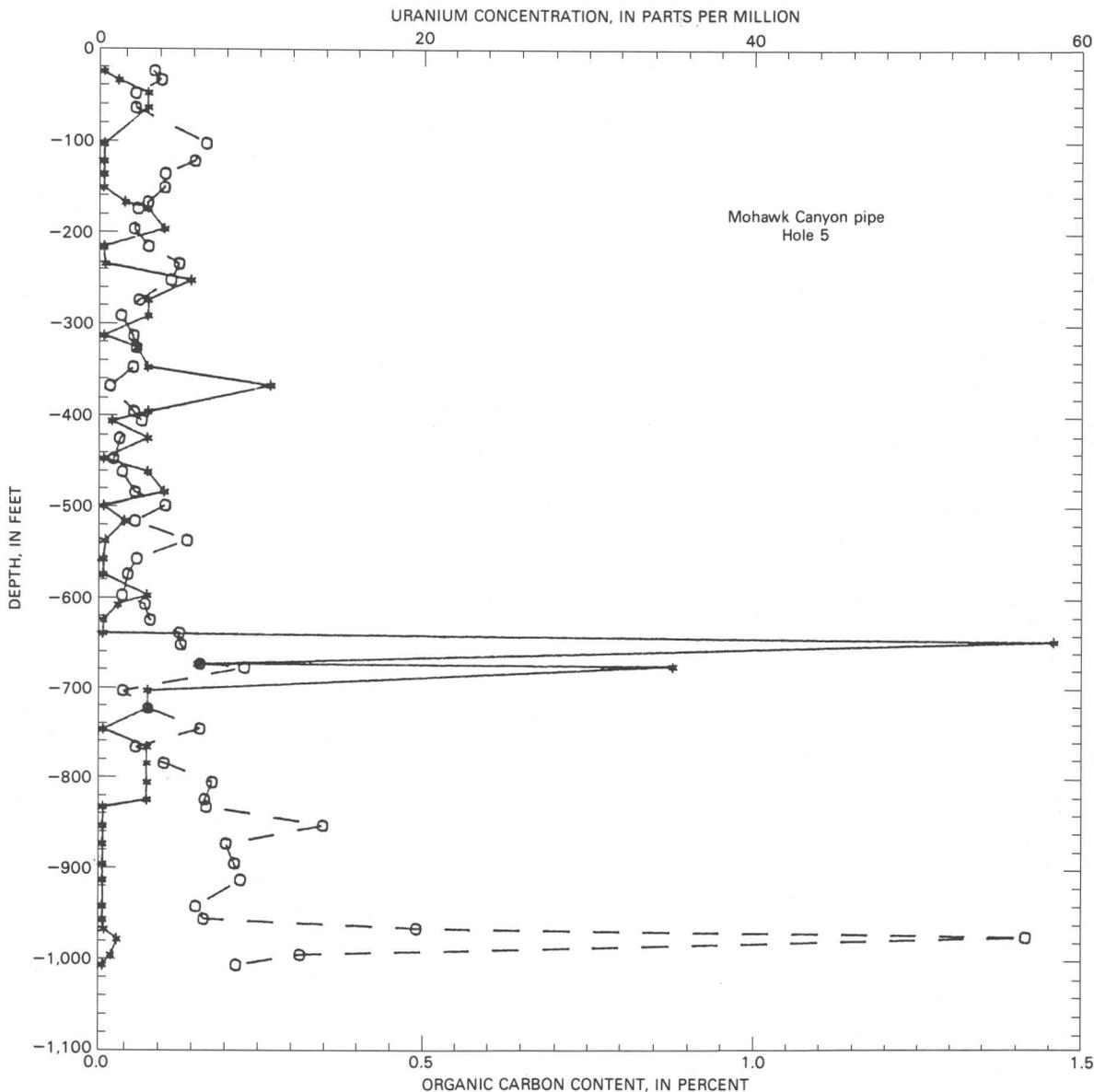
**Figure 5.** Uranium concentration (in ppm) versus organic carbon content (in percent) for 418 surface (oxidized) and subsurface (unoxidized—still in their primary, reduced condition) samples collected from mineralized and unmineralized northern Arizona breccia pipes. Correlation coefficient is 0.02. The 103 subsurface, reduced samples show no more of a significant correlation between uranium and organic carbon than do the 418 mixed group of oxidized and reduced samples.

ple Mountain pipe bitumen than the Pigeon pipe bitumen. Elemental chemical analyses of five bulk rock samples containing varying amounts of solid bitumen and three pure bitumen samples are presented in table 1. The bulk rock samples are provided to illustrate the high metal concentrations that are intimately associated with the bitumen and, hence, should have been available for scavenging by the bitumen. Yet, analyses of pure bitumen (table 1) show that the bitumen did not adsorb or chelate most of these metals. The principal exceptions to this are vanadium and nickel, which are commonly associated with petroliferous substances.

## ORGANIC GEOCHEMISTRY OF SOLID BITUMENS

### Bulk Organic Chemical Characteristics

Gas chromatographic analyses of saturated hydrocarbon fractions (fig. 10) from both Temple Mountain and Pigeon pipe are characterized by a depletion of normal (n)-alkanes and a conspicuous hump of unresolved branched and cyclic alkanes. Such compositional features strongly indi-



**Figure 6.** Down-hole plots of uranium concentration (in ppm, shown by open circles) and carbon content (in percent, shown by asterisks) for drill hole 5 in the Mohawk Canyon pipe. Note the absence of any significant correlation between uranium and carbon (correlation coefficient is  $-0.02$ ).

cate the effects of biodegradation and, to some extent, water washing (Connan, 1984; Landais, 1989). Bulk chemical fractions of chloroform extracts of solid bitumens (J.G. Palacas, unpub. data, 1990) from both areas show some differences. These apparent compositional differences between the Arizona and Utah solid bitumens are probably the result of one or more depositional or post-depositional processes: (1) bacterial degradation (biodegradation), (2) radiation damage, (3) thermal alteration in the presence of sulfur, or (4) derivation from different source rocks.

### Biomarker Distributions

Biomarker distributions of extracts of solid bitumens in breccia pipes from northern Arizona and Temple Mountain, Utah, and tar sands from Flat Top (San Rafael Swell) and Circle Cliffs, Utah (figs. 1A and 1B) are from unpublished data of J.G. Palacas, 1990. These biomarkers include: (1) tricyclic and pentacyclic terpanes ( $m/z$  191), (2) steranes ( $m/z$  217), and (3) combined triaromatic ( $m/z$  231) and monoaromatic ( $m/z$  253) steroids. Figure 11 shows



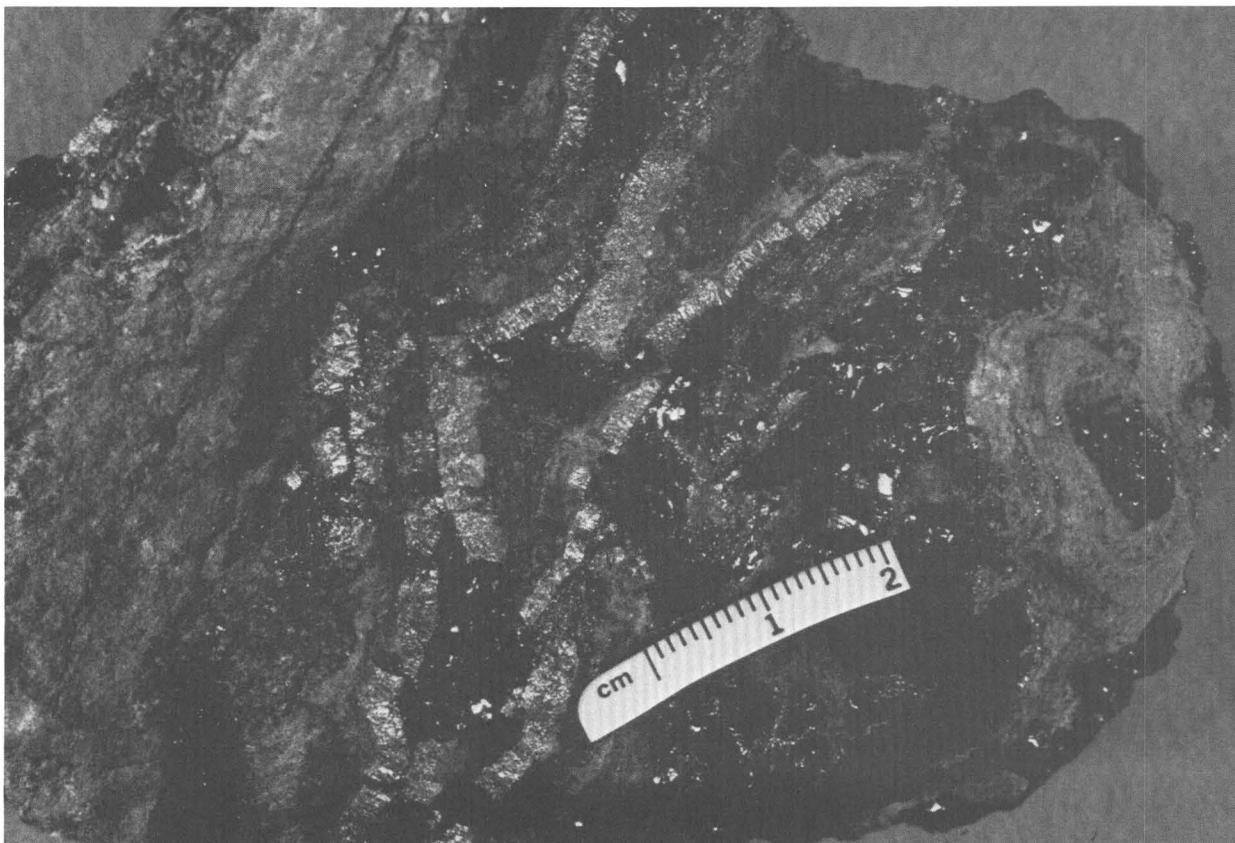
**Figure 7.** Pigeon pipe and mine headframe. Beds on left side of photograph dip inward toward the center of the basin. The collapse basin that has formed over the breccia pipe is about one-half mi in diameter, whereas the Pigeon pipe itself is only 240 ft in diameter.

biomarkers for the terpanes and steranes of samples from some of these areas along with biomarkers of an extract from the Toroweap Formation, which is believed by Landais (1986, 1989) to be a source rock for the solid bitumens in northern Arizona breccia pipes. From this diagram, it can be seen that the Pigeon pipe bitumen, Temple Mountain pipe bitumen, and the Circle Cliffs tar sand have similar biomarker distributions. The only apparent difference is the relatively lower amounts of pentacyclic terpanes in the Pigeon pipe sample—this is attributable to the greater degree of biodegradation (fig. 10). In contrast, the Toroweap rock extract has a low tricyclic to pentacyclic ratio (fig. 11A); this signature is different from any of the other samples. Another disparity may be observed between the sterane distributions (fig. 11B)

in which the Toroweap sample has an abundance of diasteranes relative to regular steranes; in particular, peaks DS and DR have a distribution opposite to that observed in the hydrocarbon deposits from all three of the other areas.

## Carbon Isotopes

Carbon isotopic values ( $\delta^{13}\text{C}$  per mil PDB) of aromatic hydrocarbons and saturated hydrocarbons are similar for the Pigeon pipe and Temple Mountain pipe solid bitumens and Flat Top tar-sand oils (fig. 12). This indicates a similarity of organic chemical composition and, in turn, suggests a similar or common source; this same conclusion is suggested by the



**Figure 8.** Bitumen associated with pyrite in the Pigeon pipe. Note how the pyrite is fractured and offset while the bitumen is not, indicating that the pyrite is older than the bitumen.

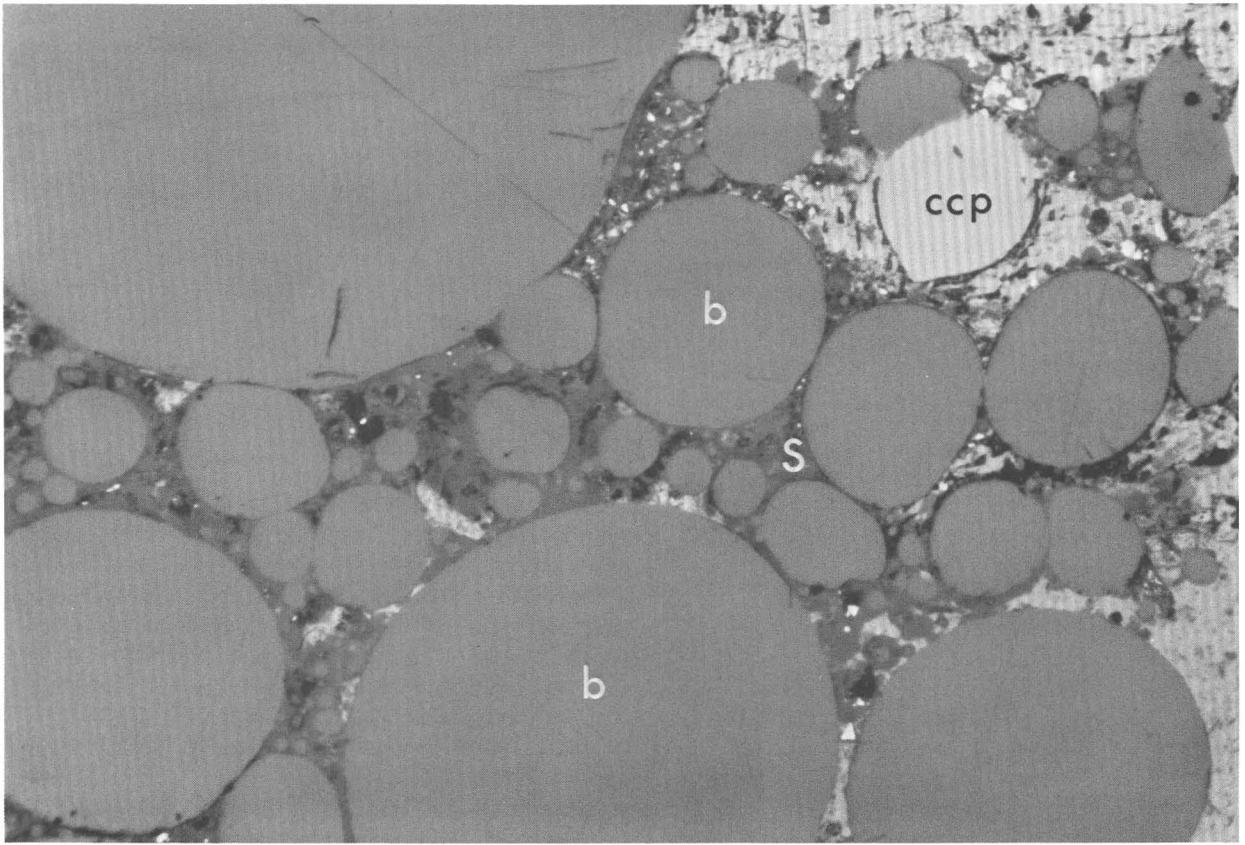
biomarker correlations. Although the Toroweap Formation has the potential to be a local source rock for northern Arizona solid bitumens, no obvious carbon isotope correlation seems to exist between the Toroweap source rock and the Pigeon pipe bitumens.

## SOURCE OF SOLID BITUMENS

Similar  $\delta^{13}\text{C}$  values and (or) biomarker distributions of Pigeon pipe and Temple Mountain pipe solid bitumens to those of the tar-sand oils at Flat Top and other parts of the San Rafael Swell, Circle Cliffs, and Tar Sand Triangle (fig. 1A) indicate that most, if not all, of these hydrocarbon substances were derived from the same source or from similar

source facies either through long-distance or short-distance migration. The distinctly lighter  $\delta^{13}\text{C}$  values (fig. 12), somewhat dissimilar biomarker distributions (fig. 11), and lower maturity levels of the Toroweap Formation hydrocarbons from northern Arizona indicate that the bitumens associated with breccia pipes in northern Arizona do not have their source in either the local Permian Toroweap Formation or in stratigraphically younger, less mature formations.

If the source of bitumen involved local vertical migration, then older, more deeply buried, and more mature rock than the Permian Toroweap might qualify as an alternative source. If this scenario is viable, then the question arises: Can either Paleozoic rocks older than the Pennsylvanian or Precambrian rocks be possible source rocks? To date, based

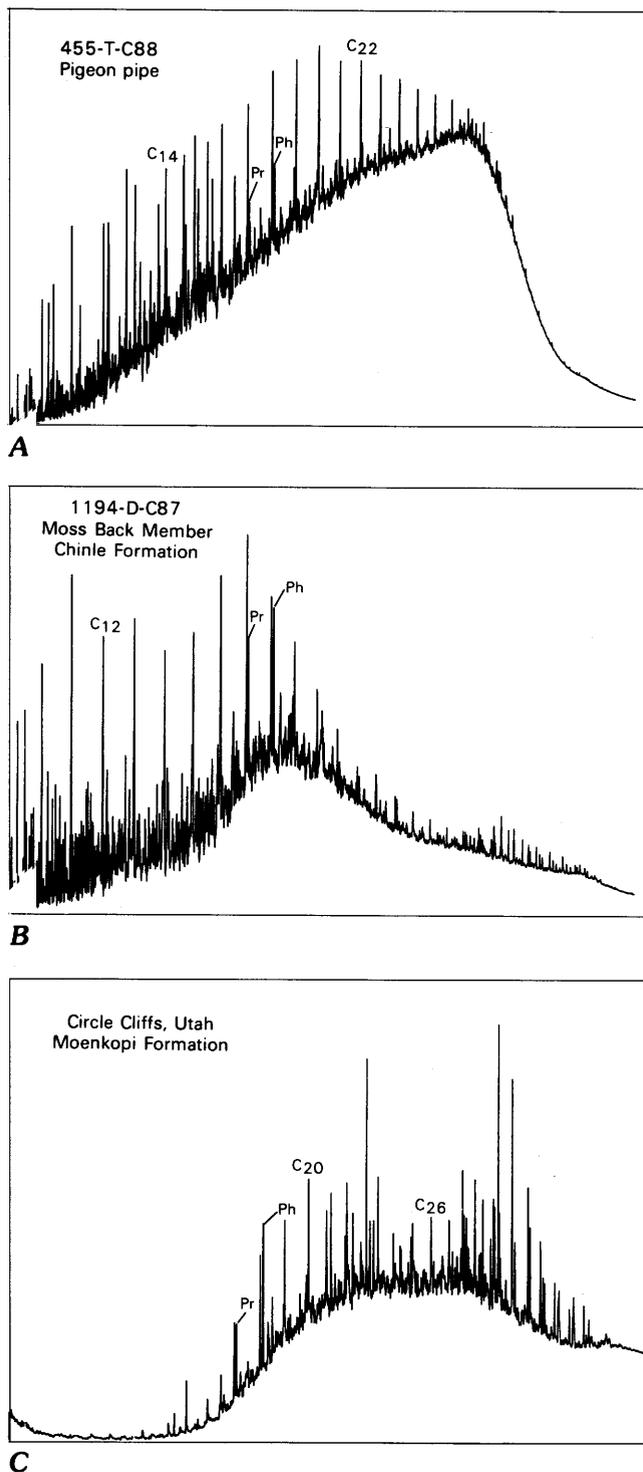


**Figure 9.** Reflected light photomicrograph of chalcopyrite (ccp) and globules of bitumen (b) surrounded by later sphalerite (S). Horizontal field of view is 1.29 mm.

on published data and unpublished information gleaned from field work by one of the authors and from other geoscientists who have worked in the Grand Canyon area, there is no evidence for the presence of viable petroleum source rocks of Paleozoic age older than the Toroweap Formation in the vicinity of the pipes; the only exception to this is the Upper Mississippian/Lower Pennsylvanian Surprise Canyon Formation channels that cover less than 1 percent of the Grand Canyon region (in plan view). Reynolds and others (1988) and Palacas and Reynolds (1989) recently discovered that a 5,300-ft section of unmetamorphosed Late Proterozoic Chuar Group rocks exposed in the eastern part of the Grand Canyon, Arizona, has good to excellent oil source-rock potential. More than 1,000 ft of dark gray, organic-rich mudstones and siltstones contain as much as 9 weight percent organic carbon. This area of the eastern Grand Canyon lies within the Arizona breccia pipe province. These Chuar Group rocks are believed to be present beneath some of the plateaus (Coconino, Kaibab, Kanab, Marble, and Shivwits)

that are known to contain collapsed breccia pipes to the south and north of the Grand Canyon in northern Arizona; Chuar Group rocks are also likely to exist into the subsurface of southern Utah (M.W. Reynolds and J.G. Palacas, unpub. data, 1990; Chidsey and others, 1990). Preliminary organic geochemical analyses (J.G. Palacas and M.W. Reynolds, unpub. data, 1990) show some faint similarities to the breccia pipe bitumens in saturated hydrocarbon and biomarker distributions, but no clear-cut source rock–solid bitumen correlations have been ascertained. However, approximately the upper 450 ft of the Chuar (upper half of the Walcott Member of Kwagunt Formation), also considered to be organic rich, have not yet been sampled. Until these Precambrian rocks are fully evaluated, they cannot be completely excluded as possible sources for the breccia pipe bitumens.

In summary, particularly in south-central Utah, the confinement of tar-sand oils and solid bitumens principally to a stratigraphically narrow interval (Lower Permian White Rim Sandstone Member of the Cutler Formation to Lower and



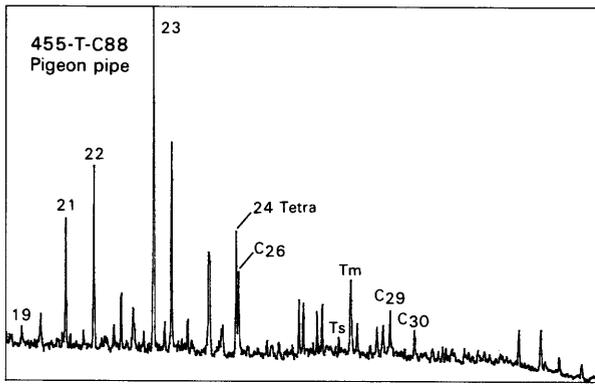
**Figure 10.** Gas chromatograms of saturated hydrocarbons. All chromatograms are  $C_{9+}$  saturated hydrocarbon fractions. Pr, pristane; Ph, phytane; numbered peaks are n-alkanes. *A*, Solid bitumens in the Pigeon uranium-bearing breccia pipe, northern Arizona; *B*, Solid bitumens in the Chinle Formation at the Temple Mountain uranium-bearing breccia pipe, south-central Utah; *C*, Bitumen or "heavy oils" of tar sands in Moenkopi Formation, Circle Cliffs, Utah.

Middle(?) Triassic Moenkopi Formation), similar biomarker signatures, and similar molecular maturity indices ( $T_m/T_s$ ,  $S/R$  ratios of  $C_{29}$  steranes and ratios of triaromatic to monoaromatic steroids; J.G. Palacas, unpub. data, 1990) suggest that these widely separated surface to near-surface hydrocarbon deposits are genetically related. Hence, they are derived from either a single, extensive, organically rich source-rock facies through long-distance migration or from various, similar, local source-rock facies. In any case, whatever hydrocarbon source rock is responsible for these deposits, it must have been one capable of generating huge amounts of petroleum. Estimated present combined oil-in-place reserves within the San Rafael Swell, Circle Cliffs, and Tar Sand Triangle areas amount to at least 8 and possibly as much as 18 billion barrels of tar-sand oils (Ritzma, 1973; Campbell and Ritzma, 1982)—the estimated volume of heavy oils and bitumens prior to alteration and destructive processes totals about 16 to perhaps as much as 35 billion barrels of oil. However, source rocks capable of generating such an enormous volume of oil have not, as yet, been identified in this area.

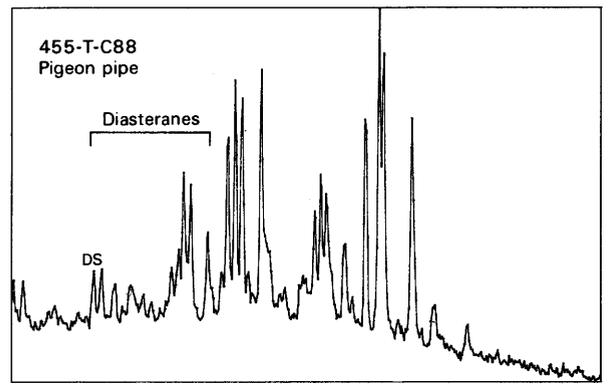
## CONCLUSIONS

Comparisons of saturated hydrocarbon gas chromatograms, biomarker distributions, and carbon isotope data for (1) extracts of solid bitumens from solution-collapse breccia pipes at Temple Mountain, Utah, and (2) bitumens or "heavy oils" in tar-sand deposits from Flat Top, Circle Cliffs, and Tar Sand Triangle, Utah, indicate that the solid bitumens of Temple Mountain are definitely genetically linked to the pervasive tar-sand oils located throughout south-central Utah. Although a similar link can be made to the northern Arizona Pigeon pipe, such a conclusion is somewhat more tenuous because of the degree of biodegradation of its solid bitumens.

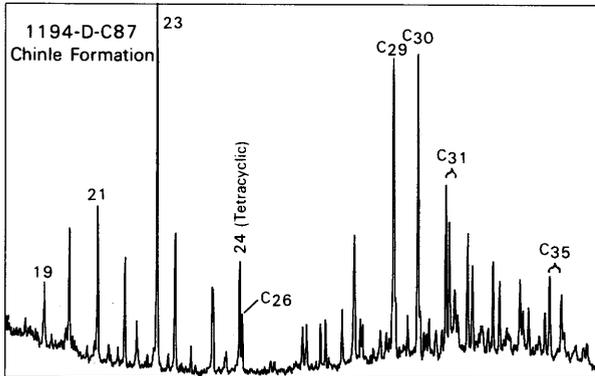
Because uranium ores in these Colorado Plateau solution-collapse breccia pipes are sometimes associated with solid bitumen, uranium as well as the other associated metals (Ag, Co, Cu, Mo, Ni, Pb, Zn, and V) in these orebodies may well have followed the same migration path as the oils. Most of the solid bitumen found in northern Arizona breccia pipes occurs in pipes clustered together near Snake Gulch and Kanab Creek (fig. 1*B*), suggesting a local source. Yet one of the most likely source-rock candidates, according to Meyer and others (1989) and Landais (1989), in the nearby vicinity—the Brady Canyon Member, Toroweap Formation—is dissimilar in hydrocarbon distributions and is less thermally mature than the pipe bitumens, suggesting that the local Toroweap is not the source of the bitumens. With the exception of the localized Surprise Canyon Formation, most of the remaining rock in the Paleozoic section in the nearby vicinity below the Toroweap contains no obvious organic-rich source-rock units. However, another possibility



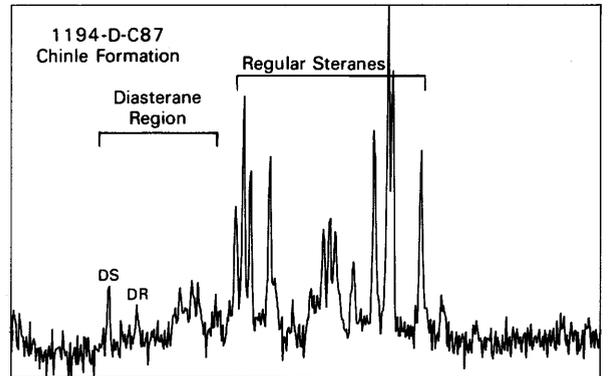
**A1**



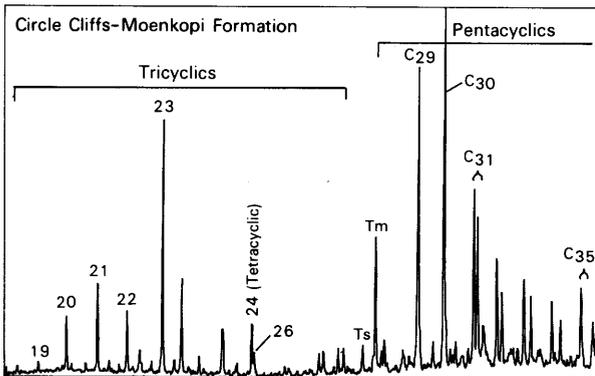
**B1**



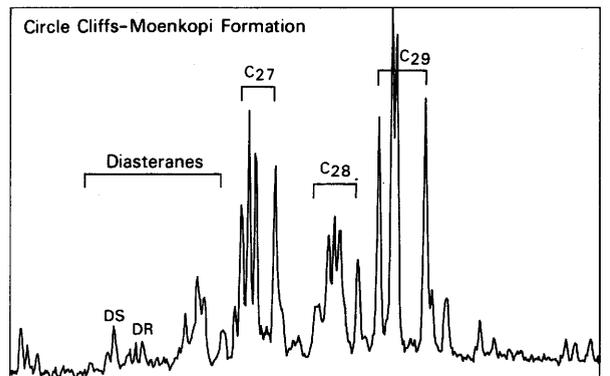
**A2**



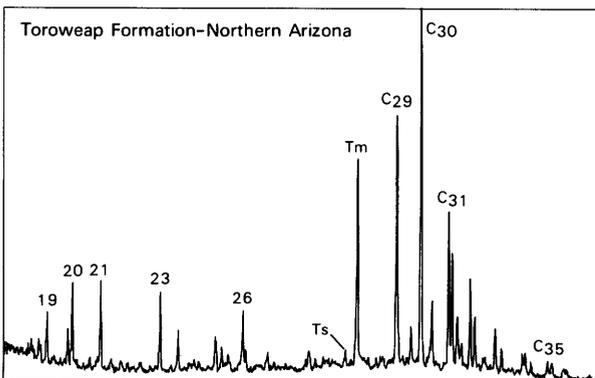
**B2**



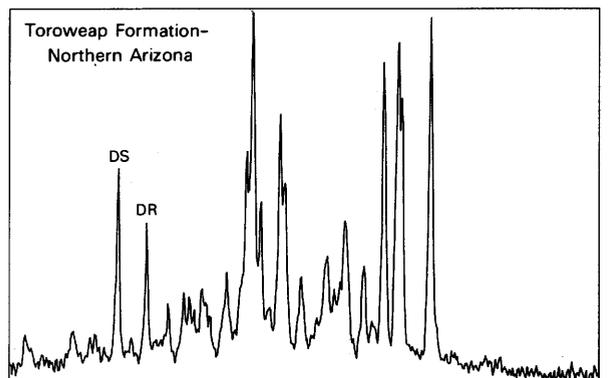
**A3**



**B3**



**A4**



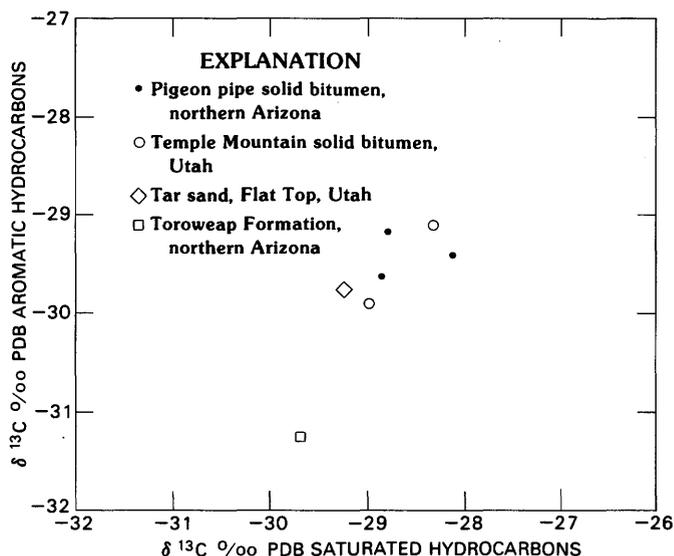
**B4**

**Figure 11 (facing page).** A, Tricyclic and pentacyclic terpanes ( $m/z$  191); B, Sterane ( $m/z$  217) distributions. A1 and B1, Solid bitumens in Pigeon breccia pipe, northern Arizona; A2 and B2, Solid bitumens in Chinle Formation at Temple Mountain breccia pipe, Utah; A3 and B3, Bitumens or "heavy oils" of tar sands in Moenkopi Formation, Circle Cliffs, Utah; A4 and B4, Toroweap Formation extract. Peaks 19–29 are tricyclic terpanes; peaks Ts to C<sub>35</sub> are pentacyclic terpanes; Ts = 18 $\alpha$ (H) trisnorneohopane; Tm = 17 $\alpha$ (H) trisnorhopane. DS and DR are C27 13 $\beta$ (H), 17 $\alpha$ (H) 20S and 20R diasteranes, respectively.

is that long-distance lateral migration was responsible for transporting the hydrocarbons that eventually formed the bitumen deposits. If this were so, then a more mature Toroweap or comparable source-rock facies under greater burial depth or under higher geothermal gradients located west and northwest of the breccia pipes could be the probable source. An alternative to long-distance lateral migration is vertical migration: If the source were local, then an older, more deeply buried, more mature local rock unit might be an alternative source. A good candidate might be the Late Proterozoic Chuar Group, which has been shown to have good to excellent oil source potential by Reynolds and others (1988) and Palacas and Reynolds (1989). Some similarities exist between the Chuar Group and the breccia pipe bitumens, but they were not striking enough to conclude that the Chuar Group rocks were the source for the breccia pipe bitumens. Because the source rock for the oils is not a local source such as the Permian Toroweap or younger rocks, the same scenario may well exist for the uranium and associated metals in the breccia pipe orebodies. There is no firm evidence to suggest that the oils and other metals followed the same migration path and had the same source rock, but, if they are related, the best uranium source rock is not the nearby Triassic Chinle Formation as proposed by Krewedl and Carisey (1986).

## ACKNOWLEDGMENTS

The authors wish to thank Benny Law for his constructive review and suggestions that improved the manuscript. Bradley Van Gosen compiled the uranium and organic carbon geochemical data for the 418 samples from breccia pipes in Arizona as well as the down-hole data for the Mohawk Canyon breccia pipe. David Detra assisted in providing a rapid, accurate, inorganic geochemical analysis of the pure bitumen samples, and Eric Michael, Paul Lillis, David King, Ted Daws, and Augusta Warden provided the organic



**Figure 12.** Plot of  $\delta^{13}C$  values of saturated hydrocarbons versus aromatic hydrocarbons for solid bitumen samples from Pigeon pipe, northern Arizona and Temple Mountain breccia pipe, Utah. For comparative purposes, isotope values are also plotted for one tar-sand sample (Flat Top, Utah) and for one Toroweap Formation possible source-rock sample (northern Arizona).

geochemical analyses. Thanks also go to Harry Dembicki, Marathon Oil Company, for providing metastable ion monitoring data.

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# Gold-Bearing Collapse-Breccia Pipe, Copper Mountain, Northwestern Arizona

By Paul Adamek,<sup>1</sup> H.J. Behr,<sup>2</sup> and Edmund von Pechmann<sup>3</sup>

## INTRODUCTION

The Grand Canyon region of the Colorado Plateau is the site of hundreds of collapse-breccia pipes that commonly contain anomalous amounts of U, base metals, and Ag. These pipes became targets for an extensive exploration program carried out during the 1970's and 1980's, resulting in the discovery of a number of uranium orebodies. Out of hundreds of pipe occurrences presently known, only one, the Copper Mountain pipe, contains gold in amounts as high as 150 ppm. Although attempts to mine gold at Copper Mountain were made during the 1950's, the occurrence was not mentioned in the literature until done so by Wenrich and Silberman (1984) and Wenrich (1985). The Copper Mountain pipe was explored by Uranerz U.S.A., Inc. between 1985 and 1987. The results of the Uranerz program are briefly outlined in the first part of this paper.

Because Uranerz has been engaged in a regional exploration of collapse-breccia pipes, it was only natural to ask whether other pipes on the southwestern Colorado Plateau might host significant gold accumulations. To answer this question, gold abundances in several pipes were investigated and fluid inclusions were studied to determine if the mineralizing fluids active in the collapse-breccia pipes were likely to have transported and deposited gold. Results of these studies are described in the latter parts of this paper.

## THE COPPER MOUNTAIN PIPE

The Copper Mountain collapse-breccia pipe in the lower Andrus Canyon on the Shivwits Plateau is deeply eroded and is exposed at an elevation of 970 m to 1,040 m at the stratigraphic level of the lower part of the Esplanade Sand-

stone and lower formations of the Supai Group. The pipe structure plunges about 45° to the southeast and consists of a polymictic breccia core, approximately 100 m in diameter, surrounded by a zone of severely broken wallrock which includes two isolated lensoidal bodies of polymictic breccia. The outer limit of the pipe structure is marked by hematite-filled ring fractures. Dolomitization of the core is pervasive. Bleached and dolomitized sandstones with anomalous Ag, As, Ba, Co, Cu, Ni, Zn, and U contents surround the pipe, forming an alteration halo up to 250 m wide. Copper and uranium reach peak concentrations in breccias within the southeastern peripheral zone of the pipe core. The central portion of the core is metal poor.

Very strong supergene oxidation affected the pipe down to an elevation of about 920 m to 960 m, causing almost complete replacement of sulfides by limonite and secondary minerals of Cu, Zn, Ag, and Cd.

Anomalous gold concentrations occur exclusively within the limonitic zone and, similar to other metals, are concentrated along the southeast margin of the breccia core in an arcuate body up to 50 m wide (the 0.14 ppm Au isopleth was arbitrarily used for this delineation). Within the partly eroded arcuate body, a zone between elevations of 988 m and 998 m is particularly enriched and contains an average of 4.37 ppm Au and 19.25 ppm Ag; the maximum gold concentration is as much as 150 ppm. Above and below this zone, the average grade is approximately 0.9 ppm Au and 8.7 ppm Ag. The amount of the gold contained within the enriched zone was estimated to be about 300 kg.

In a data set of 52 samples collected from drill cores from holes drilled in the pipe core, Au shows positive correlation at the greater than 95 percent significance level with Ag ( $r=0.760$ ), Zn ( $r=0.677$ ), and Pb ( $r=0.527$ ). Likewise, Ag is significantly correlated with Pb ( $r=0.903$ ) and Zn ( $r=0.901$ ). The mineral assemblage is dominated by a matrix consisting of goethite and lepidocrocite and contains very fine grained particles of disseminated gold associated with acanthite and smithsonite. Gold is mainly hosted by goethite with which it sometimes forms rhythmically grown aggregates. Dendritic grains up to 50  $\mu\text{m}$  long are a characteristic habit of the gold. Other minerals occurring in the gold assemblage at Copper Mountain are Cu-carbonates, covellite, hemimorphite, and greenockite and relics of pyrite, marcasite, chalcopyrite, and bornite.

## STUDY OF GOLD ABUNDANCE IN NON-OXIDIZED COLLAPSE-BRECCIA PIPES

More than 300 samples from 12 uranium-bearing pipes in the Grand Canyon region were collected and assayed for Au (samples from Hack 1, 2, and 3, Pigeon, Kanab North, and Canyon pipes collected courtesy of Energy Fuels Corp.; see fig. 1).

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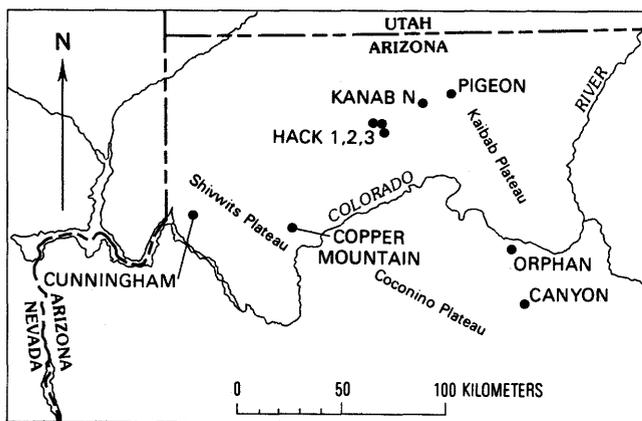


Figure 1. Map of northwestern Arizona showing locations of collapse-breccia pipes mentioned in this paper.

Disregarding some values that occur close to the analytical limit, only one pipe, the Orphan, was found to more consistently contain gold in enhanced amounts. Out of 18 nonoxidized samples analyzed from the Orphan, 10 contained identifiable Au (> 5 ppb). Because all samples were collected from dumps, no details can be given about their position within the pipe. The four samples with the highest gold content contain 0.010 ppm to 0.045 ppm Au, 3 ppm to 44 ppm Ag, 0.55 percent to 1.615 percent U, Pb+Zn+Cu between 0.67 percent and 8.55 percent, and As 0.10 percent to 1.35 percent. No correlation between Au and other elements has been established, nor does there appear to be a special relationship between Au and certain lithological types. All gold-bearing samples show a variable degree of silicification; however, this is also a common feature of nonauriferous pipes. Quartz overgrowths on detrital quartz grains were determined to be one of the oldest mineral phases in the breccia pipes.

## FLUID INCLUSION STUDIES ON COLLAPSE-BRECCIA PIPES

Fluid inclusion studies on samples from Orphan, Hack 2, Kanab North and Cunningham pipes (fig. 1) were carried out by one of the authors (H.J. Behr) at the University of Goettingen, Germany. Results of these studies have been used to determine whether the collapse-breccia pipes are likely to host significant gold accumulations. On the basis of more than 100 determinations of fluid inclusion characteristics, the following fluid systems were distinguished (fig. 2):

System (a) is a hypersaline (melting temperature,  $T_m$ ,  $-28$  to  $-35$  °C), higher temperature (homogenization temperature,  $T_h$ , 250 to > 350 °C) fluid system that contains  $CO_2$ . The fluid occurs in healed microfractures formed after

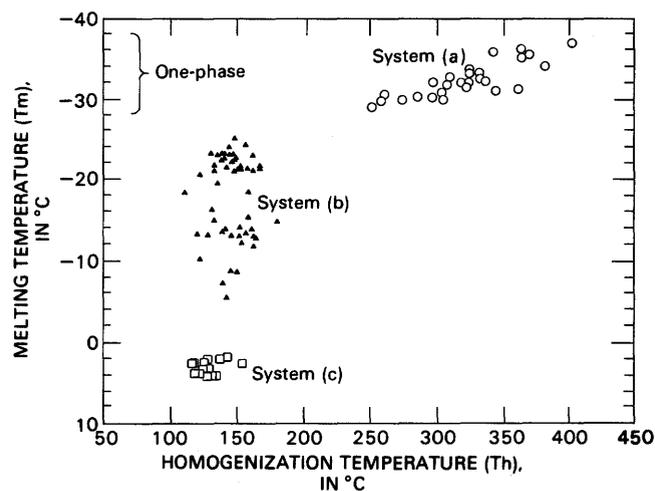


Figure 2. Measured homogenization temperature ( $T_h$ ) versus melting temperature ( $T_m$ ) for inclusion fluids from collapse-breccia pipes, northwestern Arizona

the emplacement of detrital grains in pipes and as inclusions in the quartz overgrowths. Some of the fluid inclusions show critical homogenization conditions and boiling phenomena, in the course of which the  $CO_2$  phase separated completely from the solution. The fluids have a complex composition characterized by a combination of NaCl+KCl+CaCl<sub>2</sub>. System (a) was the earliest occurring fluid system in the breccia pipes.

System (b) is a medium-salinity fluid system ( $T_m$ ,  $-10$  to  $-23$  °C) with  $T_h$  between 120 and 160 °C (fig. 2). These fluids were identified in primary inclusions in dolomite and sphalerite, in secondary inclusions in quartz, and in microfractures. The fluids have a simple composition characterized by NaCl. System (b) appears to be the most volumetrically significant and the most persistent fluid system in the breccia pipes.

System (c) is a late, low-salinity fluid system ( $T_m$ , 0 to 3 °C) with  $T_h$  between 50 and 120 °C (fig. 2).

System (d) is a pure  $CO_2$  system that has been released by the  $H_2O-CO_2$  fluids (this system is not shown on fig. 2).

Mixed systems consisting of fluids (b) and (c) and  $CO_2$  are located at the intersections of microfractures and at the margins of grains.

## DISCUSSION AND CONCLUSIONS

There is little doubt that the present enrichment in gold at Copper Mountain has been caused by multiphased supergene processes similar to those described in western Australia by Butt (1989) and Mann (1984). Nothing, however, is known about the initial abundance of gold in this pipe. Even

if it is assumed that most of gold that is presently concentrated in the enriched zone was remobilized from the eroded parts of the Copper Mountain pipe, pipe volume calculations imply that the initial gold endowment of this pipe had been higher than that observed in the Orphan mine.

The complex salinity composition of the earliest fluid system distinguished in the pipes of the Grand Canyon region suggests that the high salt component of the mineralizing fluids was derived from deep basinal brines that were seated immediately above the basement or in fractures within the basement. These brines were probably activated by and intermixed with a deeper, higher temperature, lower salinity, CO<sub>2</sub>-rich system. The rising fluids may have carried both gold and base metals. However, due to high salinity, their pH was relatively low regardless of CO<sub>2</sub> content, and consequently, the gold solubility was low as well (Hedenquist and Henley, 1985). If the results of our fluid inclusion studies are characteristic for all collapse-breccia pipes in the Grand Canyon region, it may be concluded that these pipes do not represent a likely host for gold deposits. The Copper Mountain pipe may be an exception in which the ore-form-

ing solutions had somewhat different characteristics better suited for gold transfer and concentration.

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# Relationship Between Collapse History and Ore Distribution in the Sage Breccia Pipe, Northwestern Arizona

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The Sage breccia pipe is located on the Coconino Plateau approximately 90 miles northwest of Flagstaff, Arizona (fig. 1). The pipe is exposed on the eroded surface of the Kaibab Limestone just above the Fossil Mountain Member–Harrisburg Member contact and manifests itself as a bowl-shaped depression several hundred ft in diameter with inwardly dipping Harrisburg sedimentary rocks encircling the collapse area.

Pipe formation began during or shortly after deposition of the Supai Group and caused 50 ft of thinning in the upper part of the Esplanade Sandstone on the northern side of the pipe and a corresponding thickening of the Hermit Shale section. Pipe formation continued, probably intermittently, through the Permian, as evidenced by secondary brecciation of pre-existing sandstone flows. However, one of the most active periods of stoping and pipe formation occurred during the deposition of the Lower Permian Kaibab Limestone. Breccia fragments from the Fossil Mountain Member have been observed in core at depths as great as 1,560 ft; this indicates a vertical displacement of over 1,000 ft. The Sage pipe is similar to other collapse breccia pipes in northern Arizona that have their roots in cave systems in the Redwall Limestone. Stopping of successively younger units caused the upward propagation of the pipe and provided the pipe-filling breccia. The Sage pipe extends at least 2,500 ft (762 m) vertically; the horizontal dimensions range from 100 to 300 ft (30.5 to 91 m), depending on variations in host-rock stratigraphy (fig. 2).

Acidic, reducing solutions migrated laterally through the Redwall cave system until they encountered fault or frac-

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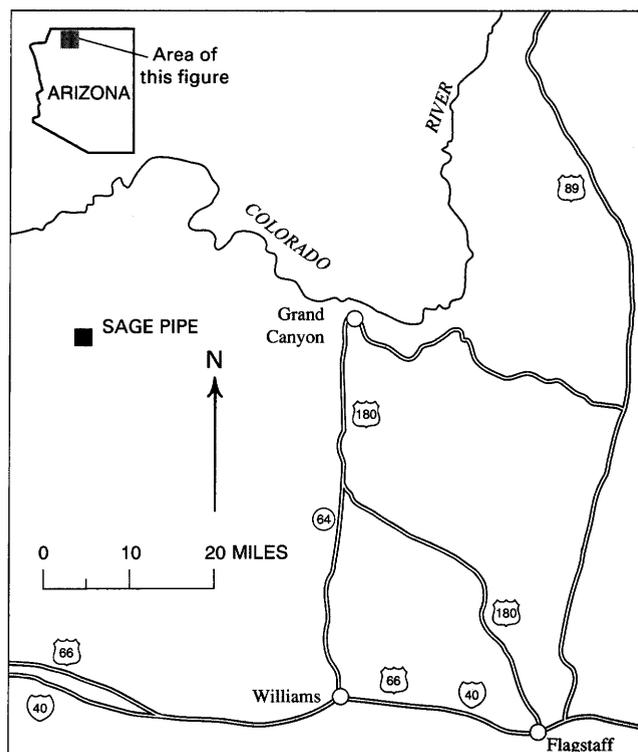
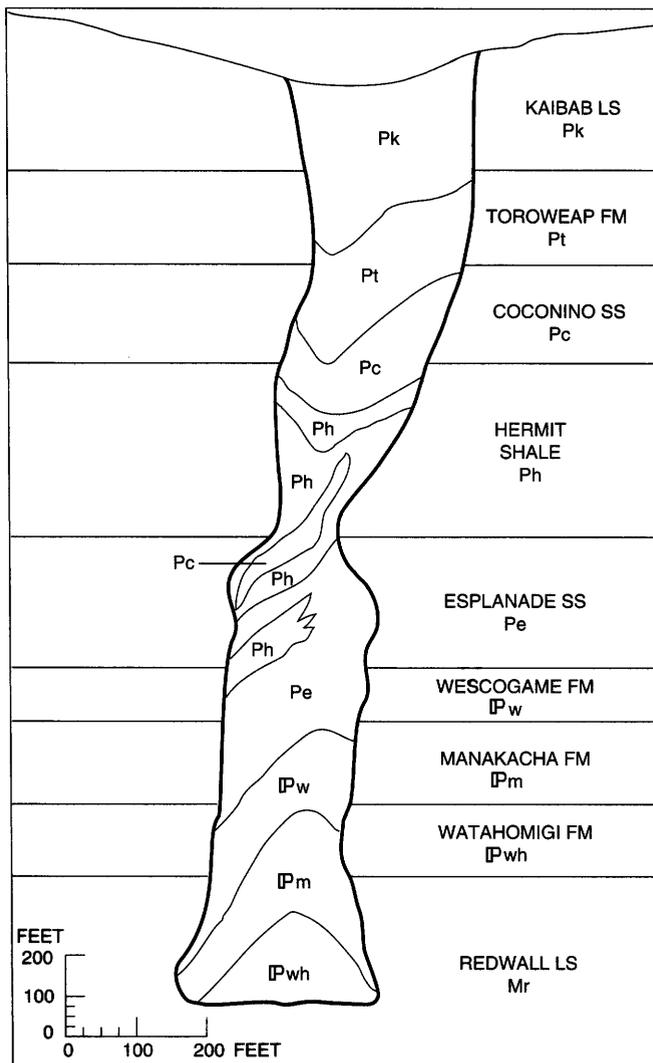
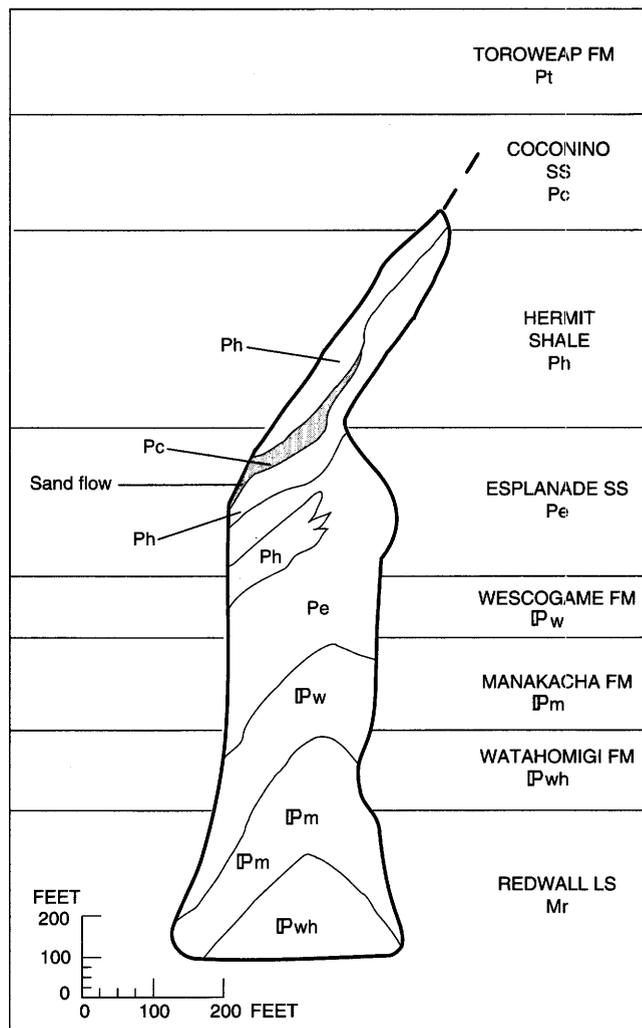


Figure 1. Index map showing a portion of northwestern Arizona and the location of the Sage pipe.

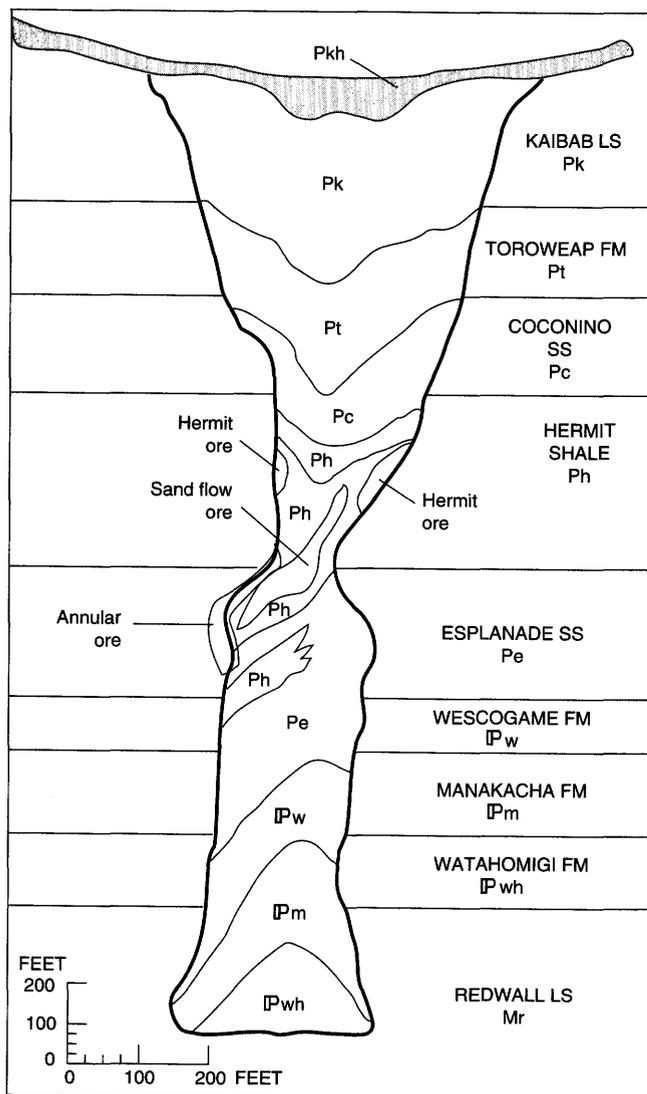
ture zones that provided vertical pathways for upward stoping and caused decementation of carbonate-cemented grains and iron reduction and removal. At Sage, the 80° SW. plunge of the pipe is believed to be related to the fracture or fault on the northern side of the pipe along which the solutions ascended. The ascending solutions dissolved the carbonate cement in Supai sediments resulting in collapse and deposition of sand and silt breccias and flows on the underlying breccia pile. The stoping processes involved both chemical disaggregation and mechanical failure of roof and wall rocks. This combination produced a complex mixture of rock types observed in the Sage core: these rock types include purely mechanical breccias, silty-sandy slurries, and flows resulting from chemical disaggregation or decementation of sandstones and siltstones. The solutions eventually stopped upward through the Hermit Shale, depositing a blanket of Hermit-derived siltstone breccias and flows on the growing debris pile at the bottom of the pipe. Due to the



**Figure 2.** Schematic cross section of the Sage pipe showing constriction through the Hermit Shale interval, expansion through the Esplanade Sandstone interval, and internal geometry of the breccia zones. Rock types in the pipe below the Watahomigi Formation are inferred. The representation depicts pipe geometry near the end of Permian time.



**Figure 3.** Schematic cross section of the Sage pipe showing the Coconino-derived sand flow (Pc) encased in impermeable silstone breccias derived from the Hermit Shale.



**Figure 4.** Schematic representation of the Sage pipe at the end of the Permian showing overthickening of the Harrisburg (Pkh) in the pipe and the location of the Hermit ore, sand flow ore, and annular ore zones.

plunge of the pipe, the debris pile became asymmetrical and created long continuous breccia zones and flows, resembling talus piles, that dip to the southwest. As stoping progressed upward into the Coconino Sandstone, the sand was decompacted and poured down into the underlying void and was deposited as a permeable wedge-shaped sand flow in the lower Hermit-derived level of the pipe (fig. 3). Subsequent stoping attacked the Hermit Shale on the hanging wall side of the pipe and deposited a large impermeable silt breccia pile on top of the Coconino-derived sand flow. Ensuing stoping then dissolved and brecciated Toroweap and Kaibab rocks.

Bedded sandstones of the Harrisburg Member in the upper 60 ft of the pipe are thicker than equivalent units outside the pipe. These overthickened, unbrecciated units were deposited in a paleodepression centered over the pipe and indicate that stoping within the pipe had stopped by middle Harrisburg time (fig. 4).

Uranium mineralization at Sage occurs primarily within the portion of the pipe at the Hermit and Esplanade horizons. Ore-grade mineralization occurs vertically for nearly 700 ft. Uranium ore occurs in three distinct environments (fig. 4) including: (1) upper Hermit ore, (2) sand flow ore, and (3) annular ore.

The upper Hermit ore generally occurs near the pipe contact with the surrounding unbrecciated Hermit Shale. This ore is hosted in Coconino-derived sand flow and breccia that was deposited above the main sand flow ore zone. The sand flow ore zone accounts for 60 percent of the ore reserves at Sage. Nearly all of the sand flow "encased" between the two silt flows (labeled "Ph" on fig. 4) is ore bearing. Annular ore occurs along the pipe contact with the Esplanade Sandstone similar to the Orphan pipe occurrences. The best annular ore grade and maximum thickness generally occurs near the shoulder of the pipe as it flares out into the Supai Group.

Uranium was deposited in permeable breccias and flows that were strongly reduced and contained minor hydrocarbon. In conclusion, the mineral distribution at Sage is directly related to the permeability of the internal breccias and flows and, to a lesser extent, to the ring fracture zone.





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