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K/UR-3
Part 5

MASTER

NATIONAL URANIUM RESOURCE EVALUATION PROGRAM

HYDROGEOCHEMICAL AND STREAM SEDIMENT RECONNAISSANCE
PROGRAM IN CENTRAL UNITED STATES

Fourth Quarter FY-1977

July 1 Through September 30, 1977

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Uranium Resource Evaluation

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OAK RIDGE GASEOUS DIFFUSION PLANT
OAK RIDGE, TENNESSEE

prepared for the U.S. DEPARTMENT OF ENERGY under
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Highlights

COOPERATIVE ARRANGEMENTS WITH STATE GEOLOGICAL SURVEYS (Page 8). Letters were sent to representatives of the state geological surveys in the URE Project area of responsibility to solicit interest in contracting ground--water sampling programs. Positive responses were received from 10 states and follow-up visits were made to four of these.

STATUS OF PHASE II RECONNAISSANCE SAMPLING PROGRAM (Page 9). Reconnaissance sampling in the San Antonio, Eau Claire, and Green Bay Quadrangles is essentially complete. Sampling in Seguin, Rice Lake, and Iron Mountain Quadrangles is on schedule.

GROUNDWATER OPERATIONS MANUAL (Page 10). A manual for groundwater sampling was written for use by the Oklahoma Geological Survey in sampling the Oklahoma City Quadrangle.

ANALYSIS OF SEDIMENT EXTRACTS WITH THE INDUCTIVELY COUPLED PLASMA (Page 12). Experiments were conducted for using the Inductively Coupled Plasma Spectrograph to determine major, minor, and trace elements in dissolved sediment samples.

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NATIONAL URANIUM RESOURCE EVALUATION PROGRAM
PROGRESS REPORT
FOURTH QUARTER FY 1977

INTRODUCTION

The National Uranium Resource Evaluation (NURE) Program is being administered by the Grand Junction Office (GJO) of the U. S. Department of Energy (DOE). One part of this program consists of a Hydrogeochemical and Stream Sediment Reconnaissance Program (HSSR) of the United States, including Alaska. The Nuclear Division of Union Carbide Corporation (UCC-ND) is conducting this survey over a 2,500,000-km² (1,000,000 mi²) area of the Central United States. This area includes most of the states of Texas, Oklahoma, Kansas, Nebraska, South Dakota, North Dakota, Minnesota, Wisconsin, Michigan, Indiana, Illinois, and Iowa, and parts of Arkansas, Missouri, New Mexico, and Ohio.

SUMMARY

The reconnaissance sampling program for the Oak Ridge Gaseous Diffusion Plant (ORGDP) Uranium Resource Evaluation (URE) Project continued along the Texas Gulf Coast in San Antonio and Seguin Quadrangles; in Northwest Texas in the Plainview Quadrangle; and in Wisconsin in Eau Claire, Green Bay, Iron Mountain, and Rice Lake Quadrangles.

A summary of URE Project activities for the period from July 1, 1977 through September 30, 1977 is presented. Also included is a listing of plans for the First Quarter FY 1978.

PROJECT STATUS

1. Changes in the objectives of the NURE Program have delayed the ORGDP-URE Program field sampling schedule and completion of the revised URE Program Plan.
2. Operation of the URE Clean Room Laboratory is satisfactory.
3. Quality of the field data remains satisfactory.

FOURTH QUARTER ACCOMPLISHMENTS

1. The URE Project work plan will be revised according to assumptions and guidance provided by DOE-GJO.
2. A preparation of the Phase I reconnaissance survey report on the Plainview, Lubbock, and Big Spring Quadrangles, Texas is nearing completion.

3. Sampling of the Eau Claire and Green Bay Quadrangles, Wisconsin has been completed. Sampling is in progress in the Plainview, Texas Quadrangle and the Iron Mountain and Rice Lake, Wisconsin Quadrangles.
4. A cooperative program was initiated with the Austin Office of Bendix Field Engineering Corporation for the Phase II sampling of the Plainview, Oklahoma City, and Wichita Falls Quadrangles. This effort is approximately 20% complete.
5. Follow-up sampling in the San Antonio Quadrangle has been completed.
6. System for automatic processing of URE Laboratory data and direct input into URE Computerized Data Base has been completed and is undergoing testing prior to implementation.
7. Negotiations were started to establish cooperative programs with the state geological survey offices in each state within the ORGDP sampling area for setting up and conducting the well sampling programs. A contract was let to the Oklahoma Geological Survey to establish a network of wells to be completed and sampling of these wells in the Oklahoma City, Quadrangle. Other cooperative agreements are pending.

FIRST QUARTER FY-78 PLANS

1. The URE Project work plan will be revised according to guidelines from GJO based on a \$3.5 million budget for FY 1978 and FY 1979.
2. The Phase I reconnaissance survey report on the Plainview, Lubbock, and Big Spring Quadrangles will be open-filed.
3. Cooperative programs will be established for the well-site selection and sample collection with the Minnesota, Oklahoma, and Wisconsin Geological Surveys.
4. Sampling will be completed in the Iron River, Rice Lake, Plainview, Oklahoma City, and Seguin Quadrangles.
5. New sampling activities will be initiated along the Texas Gulf Coast and in the Big Bend area in Texas.

ADMINISTRATIVE

COOPERATIVE ARRANGEMENTS WITH STATE GEOLOGICAL SURVEYS

Letters were sent to the State Geologists in each of the 12 states in the URE Project area of responsibility to solicit interest in possible cooperative programs. Two areas of possible effort were discussed.

The first area was the selection of well sampling sites according to the URE Project procedures in specified $1^{\circ} \times 2^{\circ}$ ntms quadrangles. This would involve setting up a grid at 3.2-mi spacings (Phase II) or 10-mi spacings (Phase I) and searching well log records to find a well producing from a known horizon as near to the grid nodes as possible. The well sites would then be entered on a topographic (15 min or 7-1/2 min) or county base maps to be digitized at Oak Ridge. Information required for each well includes surface geologic unit, identity of producing horizon, confidence of producing horizon identity, source of producing horizon identity, type of well, type of casing, depth to top of producing horizon, confidence of producing horizon depth, source of producing horizon depth information, total well depth, confidence of total well depth, source of total well depth information, and owner's name and address. Because this type of information is essential to the success of any groundwater sampling program, it is imperative that high-quality data be obtained. The State Geological Surveys appear to be the best source of this information in each state. The second area of effort in which the State Geological Surveys might become involved is that of sample collection according to the URE Project procedures. The names of the quadrangles to be sampled in each state and the preliminary sampling schedule were indicated.

To date, replies have been received from 10 of the 12 State Geological Surveys. All 10 surveys that replied indicated an interest in becoming involved in a cooperative arrangement. Visits were made to the Oklahoma, Kansas, Minnesota, and Wisconsin State Geological Survey offices to discuss further the well-site identification and well-sampling programs. These arrangements with the State Geological Surveys will benefit the URE Project in providing more reliable information and reducing the cost of sample collection.

GEOLOGY AND GEOCHEMISTRY

NORTHWEST TEXAS PHASE I REPORT

The report on the wide-spaced (Phase I) sampling in the Plainview, Lubbock, and Big Spring Quadrangles, Texas is being drafted. The data are being evaluated. Computer generation of the necessary maps will be available by late October.

FIELD OPERATIONS

STATUS OF THE PHASE II RECONNAISSANCE SAMPLING PROGRAM

Phase II sampling was continued in south Texas with all but 400 sites sampled in the Seguin Quadrangle while sampling was completed in the San Antonio Quadrangle. Difficulties which delayed completion of the sampling included: obtaining access to military bases, poor weather, and difficulty in locating well-sampling sites within the city limits of San Antonio,

Texas. The latter problem was solved through the cooperation of the U. S. Geological Survey (USGS) in providing base maps showing the location of wells which could be sampled.

Ten samplers were loaned to the URE Sampling Program by the Austin Office of the Bendix Field Engineering Corporation, with the objective of sampling the Plainview, Texas; Oklahoma City, Oklahoma; and Wichita Falls, Texas Quadrangles this fiscal year. Technical supervision of the Bendix samplers is being conducted by URE Project personnel while schedule, accomplishments, and administrative matters are the concern of Bendix Field Engineering Corporation. The 10 Bendix samplers and one supervisor, plus new personnel of the URE Project, attended a one-week orientation program at Oak Ridge in July. The general schedule for the orientation is similar to that outlined in Report K/UR-3, Part 4 (GJBX-70(77)).* After office orientation was conducted, the sampling teams were sent to Texas where they were given a field orientation to prepare them for sampling the Plainview Quadrangle. Three additional Bendix samplers were oriented later in the summer.

Because of problems encountered in maintaining the appropriate level of manpower, and difficult access in Palo Duro Canyon, sampling in the Plainview Quadrangle fell considerably behind the anticipated schedule. At the end of the quarter when six samplers were active, the Plainview Quadrangle was reported 60% complete. No sampling had been conducted in the Oklahoma City or Wichita Falls Quadrangles. On the west side of the Plainview Quadrangle in the Edward's Plateau, only samples of well water were collected. The thick mantle of wind deposited cover sand that makes stream sediment sampling invalid. In the eastern side of the Plainview Quadrangle, samples are being collected of both well water and stream sediment. The area completed for Plainview is shown in Figure 1.

Phase II sampling was continued in Wisconsin at a satisfactory rate. The Green Bay and Eau Claire Quadrangles are essentially complete, except for an anticipated 3 man-weeks of Phase G (General) sampling to supplement the Phase II coverage in order to achieve the targeted sample density of one per 10 mi². Sample collection in the Iron Mountain and Rice Lake Quadrangles is proceeding on schedule. The major problems encountered are difficult access because of a lack of roads and large tracts of swampland with indefinite drainage that complicates the problem of sediment sample acquisition. The area completed is shown in Figure 1.

GROUNDWATER OPERATIONS MANUAL

A 26-page manual for groundwater sampling was written for the Oklahoma Geological Survey to serve as an outline of procedures to be followed in

*Arendt, J. W., *National Uranium Resource Evaluation Program Hydrogeochemical and Stream Sediment Reconnaissance Program in Central United States: Second and Third Quarters FY 1977*, January 1, 1977 through June 30, 1977, UCC-ND, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee, August 12, 1977, (K/UR-3, Part 4).

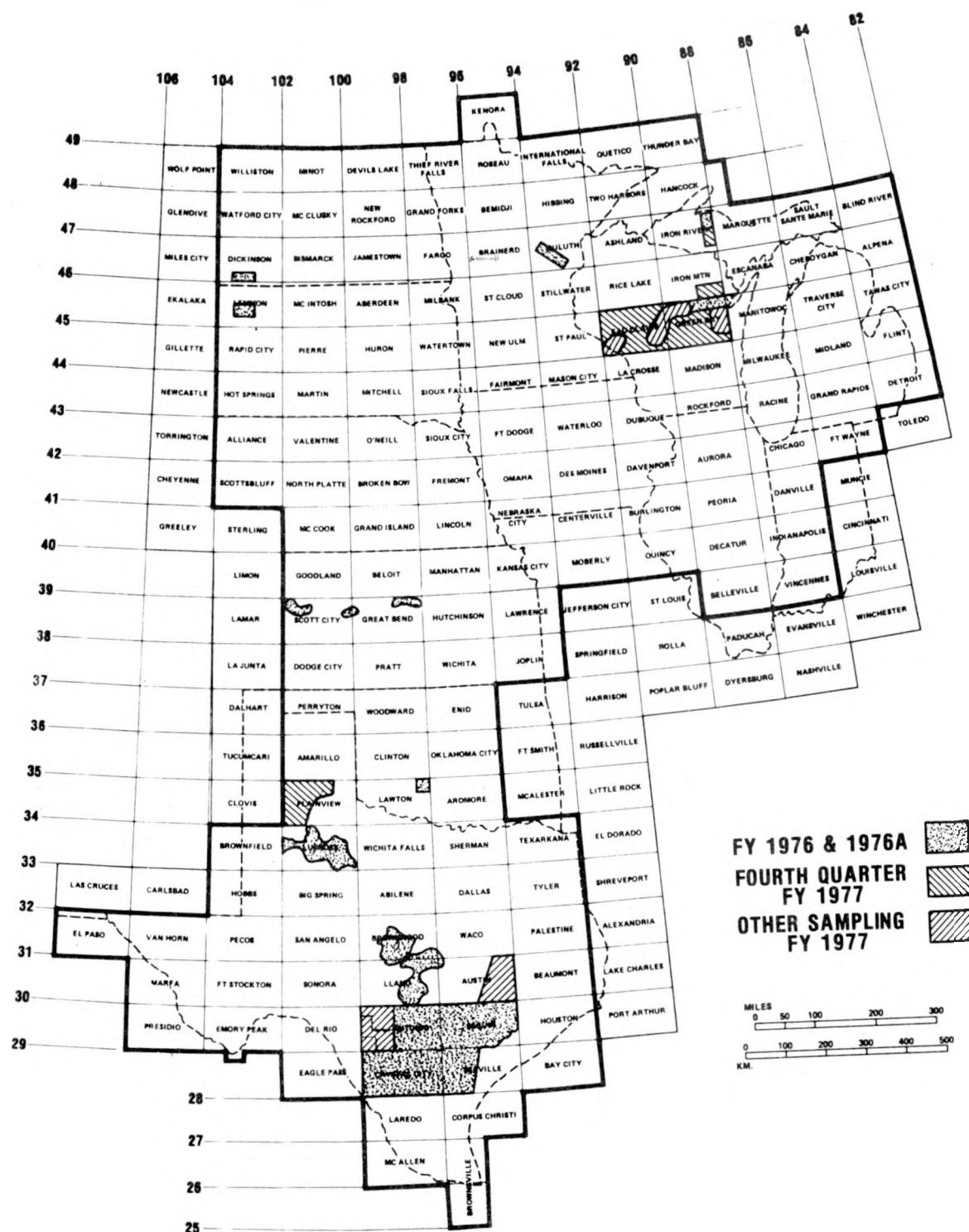


Figure 1
PHASE II AREA SAMPLED

the contract for well-water sampling in the Oklahoma City Quadrangle. The manual emphasizes procedures for sample collection, field measurements, field form completion, evaluation of contamination, and sample shipment. It also includes a section on general procedures for data control, which is designed to eliminate potential errors incurred while selecting alternate sample sites. An orientation to URE Project field and sampling procedures was given to members of the Oklahoma Geological Survey on September 27 and 28, 1977 in Norman, Oklahoma.

ANALYTICAL CHEMISTRY

ANALYSIS OF SEDIMENT EXTRACTS WITH THE INDUCTIVELY COUPLED PLASMA

Initial investigations into the feasibility of using the inductively coupled plasma (ICP) direct reading spectrometer for the analysis of the URE stream sediment extracts for major, minor, and trace constituents have been performed. Sediment extracts are presently prepared using a hot HNO_3 -HF leach for the determination of soluble arsenic, selenium, and uranium. The remaining portion of the extract (~25 ml) appears suitable for analysis with the ICP.

The procedure described in an earlier part of this report series (K/UR-3, Part 3)* for analyzing water samples with the ICP spectrometer was used to analyze the sediment extracts. Detection limits calculated on a dry sediment basis are compared for DC arc and ICP spectroscopy in Table 1. These limits and all the data discussed were obtained with the instrument calibrated at the beginning of a run and operated under normal automated operating conditions except for wavelength scanning for thorium.

NBS Coal Fly Ash (SRM No. 1633) and the URE sediment controls were used for a study of the accuracy and precision of the proposed method. An additional seven sediment samples which had been analyzed by neutron activation analysis (NAA) were also analyzed with the ICP. Preliminary results obtained from the S-2 sediment control are compared to results by DC arc analysis and NAA in Table 2.

Based on results which have been evaluated to date, the following comparisons between to the present DC arc method and the proposed ICP method can be made:

1. The overall agreement with the NAA results is better for the ICP method than the DC arc. Reasonable agreement of ICP results with

*Arendt, J. W., *National Uranium Resource Evaluation Program Hydrogeochemical and Stream Sediment Reconnaissance Program in Central United States: First Quarter FY 1977, October 1, 1976 through December 31, 1976, UCC-ND, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee, February 15, 1977 (K/UR-3, Part 3)*.

Table 1

LIMITS OF DETECTION COMPARED DC ARC AND ICP SPECTROGRAPHY

DETECTION LIMITS, ppm OF DRY SEDIMENT

<u>1-2</u>		<u>3-5</u>		<u>6-10</u>		<u>11-50</u>		<u>> 50</u>	
ARC	ICP	ARC	ICP	ARC	ICP	ARC	ICP	ARC	ICP
Ag	Li		Ag	Cr	Ba	Ba	P	P	
Cu	Ni	Co	Be	V	Mo ^(a)	Mn	Pb ^(a)	Th	
Mo	Sc		Co ^(a)	Y		Nb	Ti	Ti	
Y	Li	Cr			Zr			Zn	
Zr	Ni	Cu							
	Sc	Mn							
	Pb	Nb							
		Th							
		V							
		Zn							

(a) New line is being installed.

Table 2

COMPARISON OF RESULTS FROM THE S-2 SEDIMENT CONTROL
OBTAINED BY ICP AND DC ARC SPECTROSCOPY AND BY
NEUTRON ACTIVATION ANALYSIS

Concentration (ppm unless specified)

<u>Element</u>	<u>ICP</u>	<u>DC ARC</u>	<u>NAA</u>
Al	6.96%		6.78%
Ba	441	332	380
Ca	0.47%		0.49%
Cr	64	56	69
Cu	50	39	
Fe	3.26%		3.56%
Mg	0.52%		1.1%
Mn	848	522	760
Mo	32	18	15
Na	0.30%		0.24
P	923		
Sc	15	14	14
Th	26 ^(a)		13
Ti	0.29%	0.56%	0.48%
V	174	121	174
Y	45	28	
Zr	117	151	290
Zn	116		

(a) Inadequate correction for calcium stray light.

the neutron activation results was obtained for aluminum, barium, calcium, chromium, iron, manganese, sodium, scandium, and vanadium. Reasonable agreement between the ICP and DC arc is found for barium, chromium, copper, manganese, lithium, nickel, and yttrium.

2. The major constituents, aluminum, calcium, iron, magnesium, and sodium are readily determined by the ICP method but not by the present DC arc method.
3. The ICP method determines only the fraction of the element which is extracted with the HNO_3 -HF procedure. Therefore, low values for titanium and zirconium are found with the proposed method because of the relatively low solubility of the refractory oxides of these elements.
4. Several elements are not presently determined by the proposed method. Boron is not determined due to a substantial memory effect. Lead, niobium, and cobalt are not determined due to large spectral interferences. Alternate analytical lines for cobalt and lead should improve the situation especially for cobalt.
5. The lower detection limits for phosphorous and zinc with the ICP should make possible their determination in most (if not all) sediment extracts.
6. In the present ICP procedure, thorium measurements are biased upward by stray light from calcium. With suitable background correction techniques, it should be determinable down to about 3 ppm. A comparison of ICP results, using wavelength scanning, to NAA is given in Table 3. Background problems also cause a positive bias in the molybdenum results, but this will be helped with the addition of another analytical line for molybdenum.
7. Analysis time by the ICP method is projected to be ~3 min/sample for the prepared extract. The present DC arc method requires ~10-15 min/sample.

URE SAMPLE SUMMARY

A summary of the samples collected and analyzed in the fourth quarter FY 1977 is given in Table 4.

Table 3

ICP THORIUM RESULTS USING BACKGROUND CORRECTION
BY SCANNING COMPARED TO NAA RESULTS

<u>SAMPLE IDENTIFICATION</u>	THORIUM, ppm	
	<u>ICP</u>	<u>NAA</u>
SRM 1633	29 \pm 2	24 (NFS)
600019	5	6
600089	4	6
600193	5	5.7
700350	5	4.9
750021	5	3.5
750425	11	11.3
S-2	15	13
S-2	15	13
R-2	10	13

Table 4

URE Sample Summary for Fourth Quarter FY 1977

	<u>Samples Collected</u>	<u>Samples Analyzed</u>
July	1,337	185
August	1,881	319
September	<u>979</u>	<u>299</u>
Total	4,197	803

DATA MANAGEMENT

REMOTE TERMINAL SUBMISSION OF COMPUTER OUTPUT REQUESTS

A system to submit requests for all computer output directly from the URE Project Office has been completed. Currently, all plots, data listings, and statistical analyses can be requested via a computer terminal in the URE Project Office. Geologists complete 1 of 12 computer output request forms and submit the request to the data clerk. This system is organized so that it can be completely run by a data clerk rather than computer personnel. The requested output material is generally delivered the following morning. This terminal request system not only enables quick, efficient processing of computer output, but also frees computer personnel for developmental work.

IMPROVEMENTS IN URE COMPUTER PLOTTING CAPABILITY

The URE plotting/contouring system is undergoing a major upgrading process. Added options include the capability of contouring over a large area (up to six quadrangles) and plotting any subarea at any scale. This procedure will provide matching contour lines for large-scale maps. Also, it is possible to contour and simultaneously plot the location of sample points using the Canadian symbol system. Finally, the contouring algorithm has been substantially improved by the addition of a new weighting function.

GEOSTATISTICAL DEVELOPMENTS

Statistical work has concentrated on evaluating the necessity of separating different geologic populations in statistical analyses. Using chi-square tests and graphical displays, it is possible to determine what geologic populations are different with regard to any element.

Also, work has been completed for the automation of ordered correlation matrices. These displays can be used to access variable interrelationships and formulate models in which groups of elements are associated. An example of an ordered correlation matrix for the Northwest Pilot Survey is presented in Figure 2. Groups of variables such as the uranium/uranium ratio (total uranium/extractable uranium), zirconium, arsenic, boron, and lithium group are immediately apparent. Additionally, single-element groups such as barium and copper are not shown to be appreciably related to the other variable groupings.

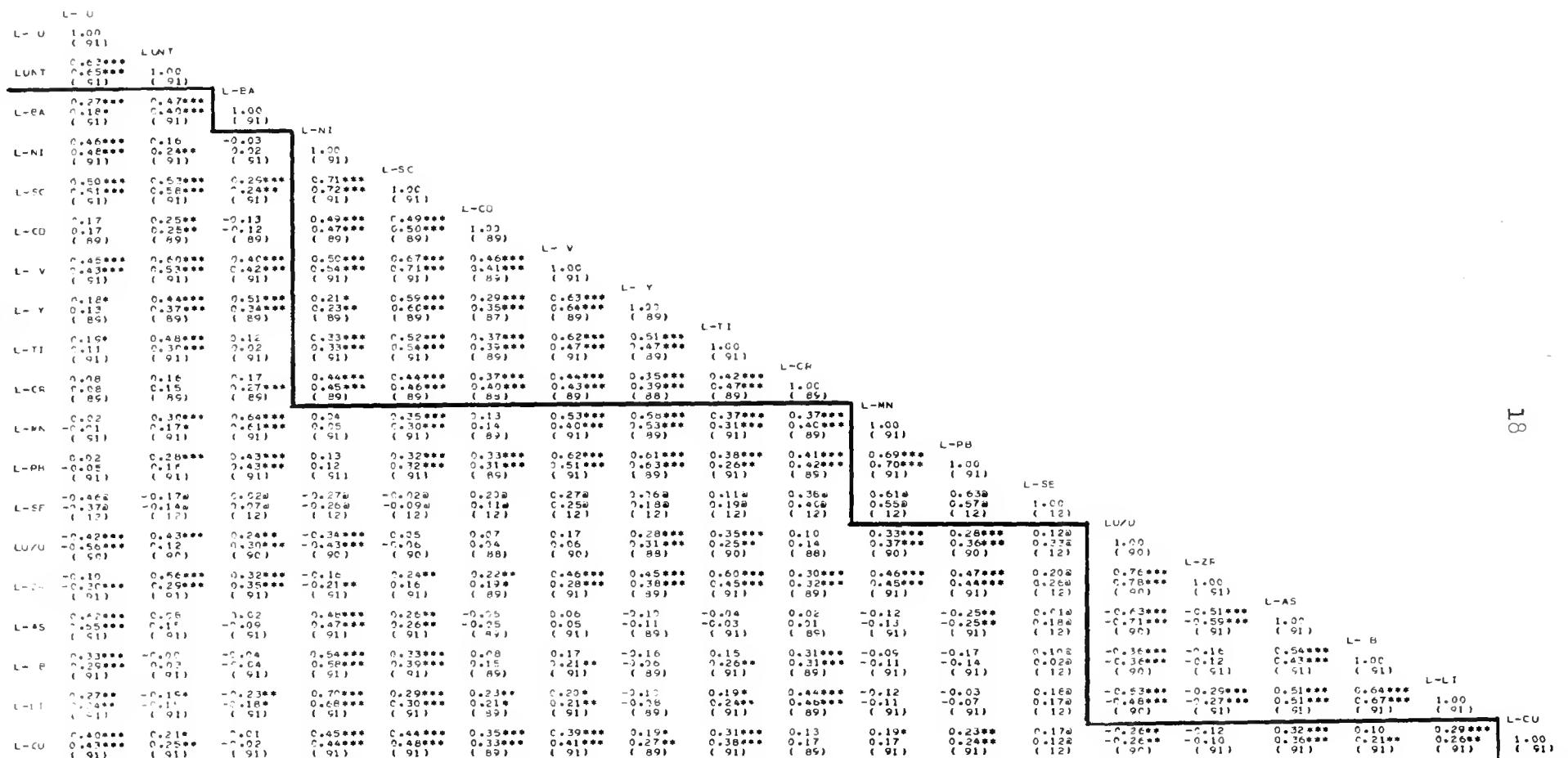


Figure 2

NORTHWEST TEXAS PILOT SURVEY STREAM SEDIMENTS
ORDERED CORRELATION MATRIX

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