UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

Chemical characteristics of roll-type uranium deposits in Wyoming and Texas

by

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Open-File Report 84-366

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1984

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ABSTRACT

Existing geochemical data on roll-type uranium deposits, their host rocks, and some related altered rocks in the Shirley and Powder River Basins of Wyoming and in rocks of the Oakville Formation and Whittset Formation of south Texas indicate differences in composition useful in examining possible modes of origin of the deposits. In addition to U and its radioactive daughter products, the elements enriched in the deposits of the Powder River Basin compared to unmineralized host rock include: Na, K, Ba, Co, ferrous iron, Ga, Al, Pb, Se, As, and V. In the Shirley Basin deposits, Ba, V, Fe, Al, Ga, Cr, Pb, Sr, and Cu are enriched along with U and eU. Ba, Ti, Y, Zr, V, Cr, Co, and Yb are enriched in the deposits in the Oakville Formation compared to nonmineralized rocks downdip of the ore. In the ores in the Whittset Formation, Na, K, Ca, Sr, Co, Ni, Mo, Y, Al, and radioactive decay products are enriched with U. The variation in the chemical characteristics of the roll-type uranium deposits probably reflects differences in the processes that formed the deposits and differences in the subsequent alteration of the deposits.

INTRODUCTION

The purposes of this study are to use existing geochemical data to determine which elements are enriched or depleted in various roll-type uranium deposits in Wyoming and Texas compared to background host rocks, and to compare the chemistry of the roll-type deposits in these districts to each other and to the chemistry of the roll-type (secondary or redistributed) deposits in the Ambrosia Lake district of New Mexico. Both the similarities and differences in the chemistry of these deposits are likely to add to our understanding of the genesis of roll-type uranium ores. Granger and Warren (1969) and Harshman (1974) discuss the genesis of roll-type uranium deposits. Harshman's paper also includes some data on the elements associated with roll-type deposits in Wyoming and Texas. Information used to characterize the secondary deposits of the Ambrosia Lake district was taken from Spirakis and others (1981).

Additional chemical data used in this study was taken from published sources (Harshman, 1974; Santos, 1980) and from chemical analyses of samples included in the Survey's Rock Analysis Storage System (RASS); these samples were collected by A. Butler, J. Vine, F. Armstrong, D. Seeland, H. Dodge, K. Dickinson, and R. Reynolds of the U.S. Geological Survey. The only new data produced for this study were uranium analyses of 30 samples to confirm that the samples were not mineralized.

ORGANIZATION OF THE DATA

The data are organized into five groups: rocks of Tertiary age of the Shirley Basin and Powder River Basin of Wyoming, Oakville Formation and Whittset Formation of the Texas gulf coast, and Jurassic rocks of the Ambrosia Lake district of New Mexico. For each of these groups, data for a mineralized set of samples (arbitrarily defined as samples containing greater than 100 ppm uranium) and data for a background (nonmineralized) sample set were compiled. The background set in the Oakville Formation consisted of samples containing less than 100 ppm U and located downdip of the ore. (In table 2, this set is referred to as downdip.) Samples in the other background sets were selected on the basis of containing less than 100 ppm uranium or less than 100 ppm eU (equivalent uranium) for samples which were analyzed for eU but not U. Separate sets of samples were formed from those samples designated as altered by oxidizing solutions. These altered rocks are believed to represent former positions of the migrating, mineralized solution fronts. No data were available on altered rocks in the Ambrosia Lake district, and the number of analyses of altered rock in the Shirley Basin was too small for statistical treatment. The high average eU and selenium contents of our altered sets suggest that the altered sample sets are dominated by samples from very near the roll front; thus their chemical characteristics are not necessarily representative of altered rocks far from the deposits. Some of the samples from the Powder River Basin district were near-surface samples that are believed to have been oxidized by modern surficial processes. These samples were removed from the mineralized, altered, and background sets. Because of the lack of available drill core and the low relief in the Texas Gulf coast uranium district, most of our background samples for the Whittset Formation were taken from outcrops. These samples could have been affected by surficial processes but the extent of the effect on any sample cannot be determined. Consequently the background data set from the Whittset Formation is less than ideal and the results must be viewed skeptically.

NATURE OF THE DATA

The elements considered in this study, the limits of determination for each element and the analytical techniques used are shown in figure 1. Most of the data are from 3-step or 6-step semiquantitative emission spectrographic analysis. These data are presented as midpoints (.15, .3, and .7 for 3-step and .15, .2, .3, .5, .7, and 1.0 for 6-step) of geometric brackets whose boundaries are 0.12, 0.26, 0.56, and 1.2 for 3-step and 0.12, 0.18, 0.26, 0.38, 0.56, 0.83, and 1.2 for 6-step. Thus there are either three or six brackets for every order of magnitude; the boundaries and midpoints for higher or lower values are the same as these except for the position of the decimal. In 3-step data, about 60 percent of the results will be in the correct bracket. The precision of a reported value in 6-step data is approximately plus-or-minus one bracket at the 68-percent confidence level and plus-or-minus two brackets at the 95-percent confidence level (Motooka and Grimes, 1976).

Large sets of spectrographic analytical data, such as these inevitably include results from samples that contain too little of certain elements to permit accurate determinations of their abundances. Data for such samples in

Figure 1--Elements studied

S V 7ppm	S: Analytical technique V: Element symbol 7ppm: Limit of determination

Analytical technique: S, spectrographic; WC, wet chemical;
X, X-ray fluorescence;
DN, delayed neutron;
R, radiometric

Elements designed by small symbols were rarely or never detected in either the Texas or Wyoming deposits at the stated limits of determination

													ORG WC C .01%				
S Li 50ppm	S Be 1ppm											S B 20ppm	MIN WC C .01%				
S Na .05%	S Mg .002%											S Al .001%		S P .08%	WC S .0075%		
S K 0.1%	S Ca .05%	S Sc 2.5ppm	S Ti 2ppm	S V 7ppm	S Cr 1ppm	S Mn 1ppm	WC S Fe .02%	S Co 1ppm	S Ni 1ppm	S Cu 1ppm	S Zn 200ppm	S Ga 5ppm	S Ge 10ppm	WC As 0.5ppm	X Se 0.1ppm		
	S Sr 2ppm	S Y 10ppm	S Zr 10ppm	S Nb 10ppm	S Mo 3ppm				S Pd 1ppm	S Ag 1ppm	S Cd 2ppm	S In 5ppm	S Sn 10ppm	S Sb 150ppm	S Te 2000ppm		
	S Ba 2ppm	S La 30ppm	S Hf 100ppm	S Ta 200ppm	S W 100ppm	S Re 30ppm			S Pt 10ppm	S Au 10ppm	S Hg 1000ppm	S Tl 50ppm	S Pb 10ppm	S Bi 10ppm			

S Ce 150ppm	S Pr 100ppm	S Nd 70ppm		S Sm 100ppm	S Eu 100ppm							S Yb 1ppm	
		DN U 1ppm											
		R eU 10ppm											

these results were presented in two categories. One category was for samples with such a low concentration of some element that no evidence for the presence of the element was found (N for "not detected" in the data); the other category was for samples in which the element was present but at too low a concentration to permit an accurate determination (L for "less than the limit of determination" in the data). A technique known as Cohen's method (which is described by Miesch, 1967, and is part of the USGS STATPAC program) was used to estimate most probable values of the means and standard deviations for these censored distributions. The calculation is based on the following factors: (1) the logarithm of the lower limit of analytical sensitivity; (2) the number of concentration values that are below the limit of sensitivity; and (3) the total number of samples. The mean and standard deviation of the analytical values above the limit of sensitivity are computed and then the geometric mean and geometric deviation of the entire distribution, assuming log-normality, are estimated using equations developed by Cohen (1959, 1961). In censored distributions (N's or L's present) where many of the analyses are below the limit of determination, the geometric means obtained by Cohen's method should be considered only as indicating the probable order of magnitude of these means.

In an earlier report (Spirakis and others, 1981), we used a different technique to estimate the values of the samples with too little of certain elements to permit an accurate determination. Consequently, some of the means reported here for the secondary deposits in the Ambrosia Lake area differ slightly from those in the previous paper.

STATISTICAL TREATMENT

Summary statistics shown in table 1 for Wyoming and table 2 for Texas were calculated by computer using the USGS STATPAC programs. A similar presentation of the data for the Ambrosia Lake deposits is included in Spirakis and others, (1981). The geometric deviations provide information on the spread of the data, and the detection ratios reveal how many values had to be estimated in order to arrive at the geometric means for each element in each data set. According to Fisher (1950), the logarithms of geochemical data approach a normal distribution more closely than do the untransformed values in ppm or percent; consequently, geometric means (which are based on the logarithms of the data) are a better measure of the central tendency of the data than are arithmetic means. The geometric means therefore were used to identify differences in the concentrations of the elements among the groups of mineralized, altered, and background samples.

Tests for statistical significance of differences between the above mentioned sample groups for a given element were made with a programmable hand-held calculator utilizing a "t" test described by Natrella (1963, p. 3-36). Summary statistics used in the test are the means and variances of the logarithmic values and the number of samples in each group. A standard table giving percentiles of the "t" distribution was used to determine whether the observed differences were significant at the 95 percent-confidence level. The samples were not collected in anticipation of statistical treatment; consequently, they were not collected in a truly random manner and are not ideally suited for statistical tests. Also, some deposits in any one district are represented by more samples than other deposits thus some deposits may have a disproportionately large influence on the averages.

Table 1.--Statistical summary of Wyoming data

Element or Compound (limit of determination)	Shirley Basin						Powder River Basin								
	Mineralized >100 ppm U			Background <100 ppm U			Mineralized >100 ppm U			Altered			Background <100 ppm U		
	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio
Al% (.001)	6.6	1.20	28/28	5.5	1.55	78/78	4.7	1.31	33/33	4.7	1.38	37/37	3.7	1.65	65/65
As ppm (.5)	---	---	---	---	---	---	4.8	2.79	44/50	1.6	4.39	20/26	3.6	1.30	7/9
Ba ppm (2)	824	1.41	28/28	510	1.93	78/78	648	1.39	33/33	677	1.44	37/37	495	1.88	92/92
Be ppm (1)	*	*	0/28	*	*	8/78	*	*	5/33	*	*	9/37	*	*	26/92
Mineral C% (.0075)	---	---	---	---	---	---	.021	3.72	22/41	.024	6.03	6/12	*	*	1/3
Org C% (.01)	---	---	---	---	---	---	.13	2.96	39/40^G	.05	2.02	11/12	.15	1.94	3/3
Ca% (.005)	.71	2.45	27/28^G	1.09	3.18	27/28^G	.43	1.68	33/33	.60	2.67	37/37	1.21	5.69	59/62^G
Co ppm (1)	*	*	3/28	6.4	1.74	51/78	6.5	1.73	26/33	5.4	1.31	27/37	5.4	1.59	63/92
Cr ppm (1)	53	1.29	28/28	23	2.86	71/78	20	1.60	33/33	23	1.90	37/37	23	1.97	90/92
Cu ppm (1)	46	1.38	28/28	9.3	2.44	78/78	3.3	1.65	32/32	3.4	1.84	37/37	5.9	1.88	92/92
Fe% (.02)	1.36	1.54	28/28	.99	1.84	78/78	.88	1.61	33/33	1.10	2.04	37/37	.97	1.78	92/92
FeO% (.01)	---	---	---	.32	2.74	50/50	1.25	1.89	10/10	.48	2.19	11/11	.31	2.64	27/27
Ga ppm (5)	18	1.22	28/28	9.8	2.12	57/78	12	1.40	32/33	13	1.28	36/37	8.8	1.96	67/92
K% (.7)	3.2	1.34	28/28	3.1	1.51	78/78	2.7	1.20	32/32	2.5	1.29	37/37	1.9	1.87	64/65
La ppm (30)	*	*	4/28	*	*	18/78	*	*	2/33	*	*	7/37	*	*	23/92
Mg% (.002)	.40	1.45	28/28	.46	2.19	28/28	.30	1.78	33/33	.32	1.83	37/37	.47	1.90	65/65
Mn ppm (1)	229	3.16	28/28	199	3.39	78/78	118	1.64	33/33	148	2.40	37/37	213	3.41	92/92
Mo ppm (3)	*	*	0/28	*	*	3/78	*	*	1/33	*	*	33/37	*	*	1/92
Na% (.05)	1.1	1.18	28/28	1.1	2.08	78/78	1.0	1.24	32/32	1.2	1.54	37/37	.55	2.57	64/65
Ni ppm (1)	11	1.87	26/28	11	1.90	66/78	9.8	1.65	32/32	10	1.65	34/37	9.9	1.88	78/92
Pb ppm (10)	30	1.76	28/28	11	2.07	40/78	19	2.28	33/33	16	1.68	33/37	11	1.63	54/92
Sulfide S% (.0075)	---	---	---	---	---	---	.047	3.91	36/38	*	*	3/10	.029	2.56	3/3
Total S% (.0075)	---	---	---	---	---	---	.093	4.22	24/24	.040	5.75	15/15	---	---	---
Sc ppm (2.5)	*	*	15/28	*	*	26/78	*	*	12/33	*	*	16/37	*	*	36/92
Se ppm (.1)	---	---	---	---	---	---	5.0	7.77	61/61	18.4	7.24	36/36	1.6	6.27	8/9
Sr ppm (2)	210	1.17	28/28	168	2.25	78/78	95	1.32	33/33	114	1.54	37/37	105	2.08	91/92
Ti% (.002)	.06	1.27	27/27	.10	1.72	78/78	.08	1.67	33/33	.08	2.15	37/37	.11	1.68	92/92
U ppm (1)	1952	4.61	28/28	13	3.37	6/7	1201	4.2	61/61	18	3.20	33/33	11	4.76	25/26
eU ppm (10)	1851	3.64	28/28	38	1.41	7/7	1046	3.94	61/61	60	2.69	36/36	67	1.73	9/9
V ppm (7)	138	2.47	28/28	30	1.85	75/78	77	4.21	33/33	68	2.63	37/37	30	2.09	89/92
Yb ppm (1)	---	---	---	1.8	2.16	25/28	1.6	1.44	17/26	1.1	1.44	23/33	1.5	1.59	46/51
Zr ppm (10)	87	1.48	28/28	116	1.74	78/78	86	1.71	32/32	83	2.03	37/37	114	1.89	90/92

--- no data
* result not presented because of a low detection ratio
G data contain values greater than the upper limit of determination
G.M. Geometric Mean
G.D. Geometric Deviation

Table 2.--Statistical summary of Texas data

Element or Compound (limit of determination)	Whittset												Oakville								
	Mineralized >100 ppm U			Altered			Background			Downdip			Mineralized >100 ppm U			Altered			Downdip		
	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio	G.M.	G.D.	Detection Ratio
Al% (.001)	6.3	1.44	74/75^G	6.5	1.15	15/15	4.6	1.54	31/31	6.2	1.19	6/6	2.7	1.44	54/54	5.3	1.25	21/21	2.8	1.29	12/12
As ppm (.5)	21.3	1.57	56/56	52.5	2.28	15/15	---	---	---	15.5	2.20	6/6	39.4	1.61	27/27	---	---	---	---	---	---
B ppm (20)	22	1.39	49/75	20	1.00	7/15	20	1.75	17/31	21	3.05	4/6	*	*	16/54	22	1.19	10/21	*	*	1/12
Ba ppm (2)	656	1.32	75/75	701	1.14	15/15	614	1.79	31/31	662	1.15	6/6	687	1.31	54/54	779	1.32	21/21	472	1.26	12/12
Mineral C% (.1)	*	*	3/75	*	*	0/15	---	---	---	*	*	0/6	1.20	1.83	27/27	---	---	---	---	---	---
Org C% (.1)	---	---	---	---	---	---	---	---	---	---	---	---	.023	2.20	23/27	.021	2.16	17/20	.026	2.14	11/11
Ca% (.005)	1.00	1.57	75/75	.89	1.19	15/15	.76	2.24	31/31	.89	1.20	6/6	5.6	1.72	53/54^G	7.4	1.49	17/21^G	6.6	1.62	10/12^G
Co ppm (1)	3.5	1.72	46/75	*	*	0/15	*	*	6/31	*	*	0/6	11.4	1.45	54/54	*	*	6/21	5.2	1.90	7/12
Cr ppm (1)	6.2	1.32	75/75	5.4	1.15	15/15	9.1	1.73	31/31	5.6	1.19	6/6	12.6	1.96	54/54	23.2	2.44	21/21	9.2	1.33	12/12
Cu ppm (1)	3.7	1.24	75/75	5.0	2.69	15/15	5.8	1.42	31/31	3.0	1.00	6/6	8.9	1.47	54/54	5.3	1.53	21/21	9.0	1.97	12/12
Fe% (.02)	.53	1.22	75/75	.51	1.09	15/15	.57	1.52	31/31	.49	1.31	6/6	1.86	1.64	54/54	1.34	1.59	21/21	1.47	1.50	12/12
FeO% (.01)	.39	1.38	68/75	.24	1.24	15/15	---	---	---	.52	1.43	6/6	.96	1.29	27/27	---	---	---	---	---	---
Ga ppm (5)	12	1.29	75/75	14	1.18	15/15	14	1.28	31/31	14	1.18	6/6	6.6	1.33	50/54	10	1.33	21/21	5.3	1.14	12/12
Hg ppm (.01)	.048	1.33	43/43	.042	1.17	10/10	---	---	---	---	---	---	.046	1.12	13/13	---	---	---	---	---	---
K% (.7)	2.2	1.25	75/75	2.2	1.20	15/15	1.8	1.32	31/31	2.0	1.00	6/6	1.8	1.21	54/54	2.3	1.22	21/21	2.0	1.16	12/12
Mg% (.002)	.16	1.25	75/75	.14	1.41	15/15	.14	1.97	31/31	.16	1.43	6/6	.10	2.31	54/54	.13	1.44	21/21	.10	1.24	12/12
Mn ppm (1)	52	1.40	75/75	43	2.17	15/15	88	3.44	31/31	55	1.49	6/6	157	1.59	54/54	188	1.43	21/21	160	1.55	12/12
Mo ppm (3)	12	4.80	68/75	*	*	5/15	*	*	6/31	17	4.48	6/6	16	4.38	52/54	*	*	0/21	57	4.60	11/12
Na% (.05)	1.87	1.25	75/75	2.17	1.18	15/15	1.36	1.33	31/31	2.00	1.00	6/6	.87	1.26	54/54	1.31	1.39	21/21	.84	1.20	12/12
Ni ppm (1)	*	*	29/75	*	*	5/15	*	*	4/31	*	*	1/6	8.6	1.82	52/54	4.8	1.25	11/21	8.1	1.46	12/12
P as P_2O_5 (.08)	0.11	1.83	47/75	0.08	1.95	7/15	---	---	---	*	*	1/6	.16	1.36	27/27	---	---	---	---	---	---
Pb ppm (10)	14	1.25	74/75	14	1.18	15/15	20	1.53	31/31	14	1.31	6/6	14	1.30	52/54	15	1.15	21/21	11	1.20	10/12
Sulfide S% (.0075)	.09	2.45	74/75	.01	1.94	9/15	---	---	---	.10	1.35	6/6	.92	1.44	27/27	.23	1.46	21/21	1.25	1.59	12/12
%S in SO_4 (.0075)	.314	1.84	75/75	.046	2.61	12/15	---	---	---	.502	2.53	6/6	.267	1.46	27/27	---	---	---	---	---	---
Se ppm (.1)	.82	19.2	48/75	78.7	6.33	15/15	---	---	---	.49	1.46	3/6	18.9	4.65	27/27	---	---	---	---	---	---
Sr ppm (2)	489	1.21	75/75	451	1.24	15/15	359	1.71	31/31	500	1.00	6/6	142	1.40	54/54	147	1.57	21/21	124	1.42	12/12
Ti% (.002)	.07	1.16	75/75	.07	1.34	15/15	.11	1.82	31/31	.07	1.25	6/6	.16	1.52	54/54	.18	1.41	21/21	.13	1.22	12/12
U ppm (1)	847	2.48	75/75	20.6	2.04	15/15	4.2	1.89	30/30	42.3	1.38	5/5	1311	2.79	54/54	10.4	2.69	21/21	67.8	1.28	12/12
eU ppm (10)	926	2.14	75/75	274	2.04	15/15	---	---	---	49	1.31	6/6	3139	2.33	27/27	---	---	---	---	---	---
V ppm (7)	23	1.98	75/75	27	1.37	15/15	27	1.73	31/31	12	1.35	6/6	39	1.60	54/54	43	1.52	21/21	31	1.16	12/12
Y ppm (10)	12	1.30	70/75	10	1.12	13/15	10	1.68	16/31	10	1.25	4/6	15	1.39	54/54	18	1.29	21/21	13	1.28	12/12
Yb ppm (1)	1.4	1.41	57/57	1.0	1.11	15/15	1.6	1.41	29/31	1.0	1.21	5/6	1.8	1.41	29/29	2.0	1.26	21/21	1.4	1.21	12/12
Zr ppm (10)	64	1.39	75/75	47	1.47	15/15	92	1.71	31/31	56	1.19	6/6	110	1.71	54/54	136	1.69	21/21	87	1.28	12/12

--- no data
* result not presented because of a low detection ratio
G data contain values greater than the upper limit of determination
G.M. Geometric Mean
G.D. Geometric Deviation

OBSERVATIONS

The results of statistical comparisons of the abundances of elements in mineralized rock to unmineralized rock in the Powder River Basin of Wyoming are displayed in figure 2. The elements found to have a statistically significant enrichment at a 95 percent confidence level are Na, K, Ba, Co, ferrous iron, Ga, Al, Pb, Se, As, V, and, of course, U. Mg, Ca, Y, Ti, Zr, Mn, Cu, were found to be depleted in the ore and Ni, Sr, Yb, total Fe and Cr were unchanged. The elements not shown in figure 2, and on subsequent similar figures, either were not looked for or their abundances were below the limit of determination in too many samples to permit an accurate estimate of the mean abundances of these elements in the sample sets. Figure 3 presents the same type of information for the deposits in the Shirley Basin of Wyoming. The elements enriched along with uranium and its daughter products in the Shirley Basin roll-type deposits include Ba, V, Fe, Al, Ga, Cr, Pb, Sr, and Cu. Those depleted are Ca, Y, Ti, and Zr; Ni, Na, K, Mn, and Mg are unchanged.

In the roll-type ores in the Whittset Formation of Texas, Na, K, Ca, Sr, Co, Ni, Mo, Y, Al, eU, and U were found to be enriched relative to unmineralized rock; Zr, Cr, Cu, Ga, Ti, Mn, and Pb are depleted and Yb, Ba, Mg, V, B, and Fe unchanged (fig. 4). The small number of samples containing enough cobalt, nickel, and molybdenum to yield values above the limits of determination made a rigorous statistical test impossible. The enrichment of these three elements in the ore is inferred by the much higher percentage of values above the limits of determination in the ore samples than in the background samples.

Figure 5 presents chemical contrasts between the mineralized rock in the Oakville Formation and barren rocks downdip of ore. It is possible that some of the chemical characteristics of the barren rocks downdip of ore were affected by processes related to mineralization; no data from rocks distant from ore were available. The results suggest that compared to barren rock downdip of ore, mineralized samples in the Oakville Formation are enriched in Ba, Ti, Y, Zr, V, Cr, Co, Yb, U, and eU. No statistically significant difference in the concentrations of Na, Mg, Ca, Sr, Mn, Fe, Ni, Cu, Ga, Al, organic carbon, and lead were found. Sulfur, potassium, and molybdenum are more abundant in rocks downdip of the ore than in the ore.

A quantitative comparison of the abundances of various elements in the Wyoming, Texas, and Ambrosia Lake ores, can be made by inspection of the geometric means listed in table 3. Figure 6 organizes the results in such a manner that a qualitative comparison can rapidly be made. When examining table 3 and figure 6, the reader should remember that enrichment or depletion is based on comparisons between mineralized rocks and background rocks from each district. These conclusions are not based on comparisons of the abundances of elements among mineralized rocks. Thus the ore with the highest content of some element is not necessarily enriched in that element. The reader should also be aware that the statistical tests consider not only the geometric means of the data but also the spread of the data sets (geometric deviation) and the number of samples in each data set. Consequently there are

Figure 2--Comparison of mineralized rock to unmineralized (background) rock in the Powder River basin.

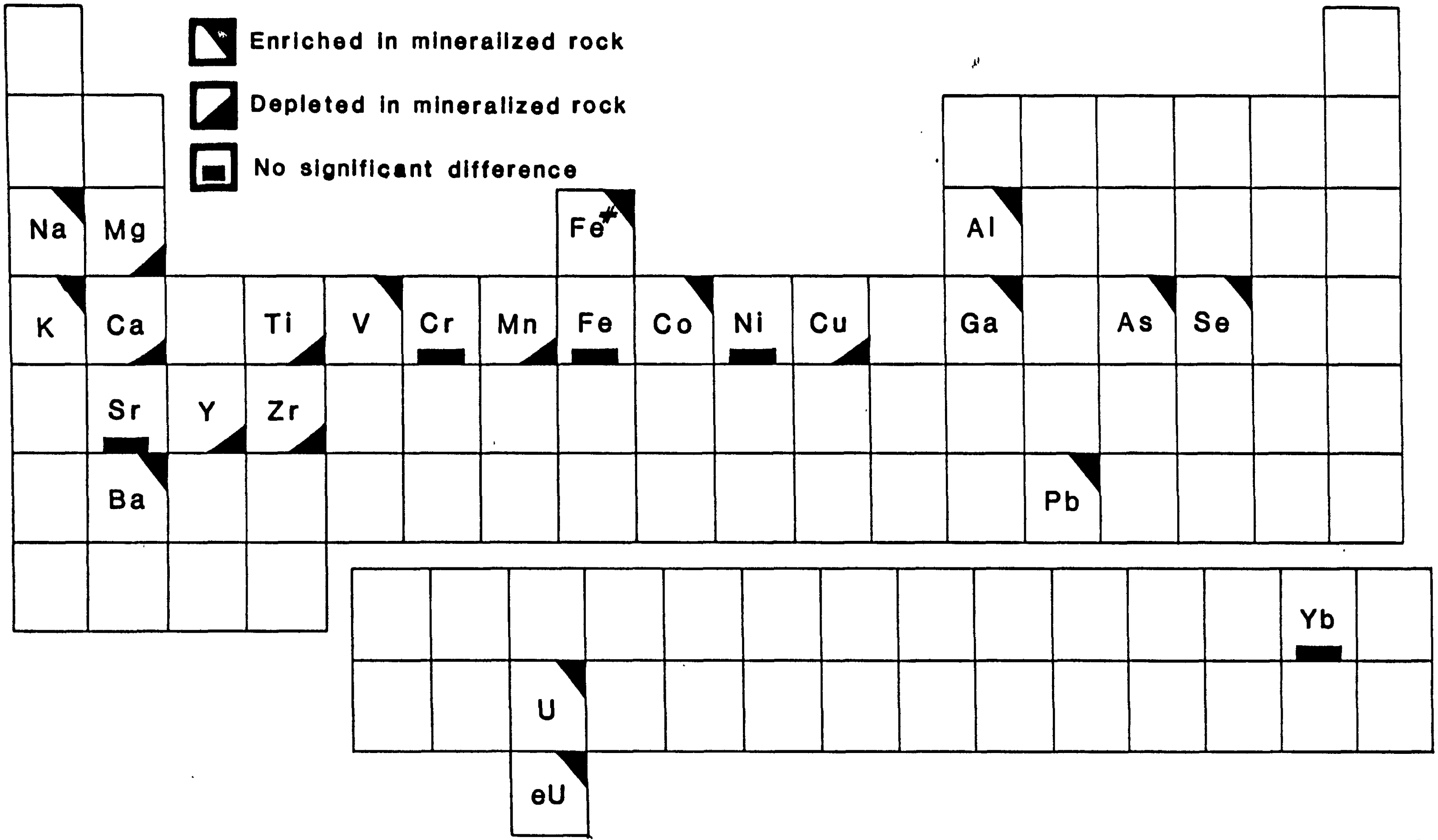


Figure 3--Comparison of mineralized rock to unmineralized (background) rock in the Shirley basin.

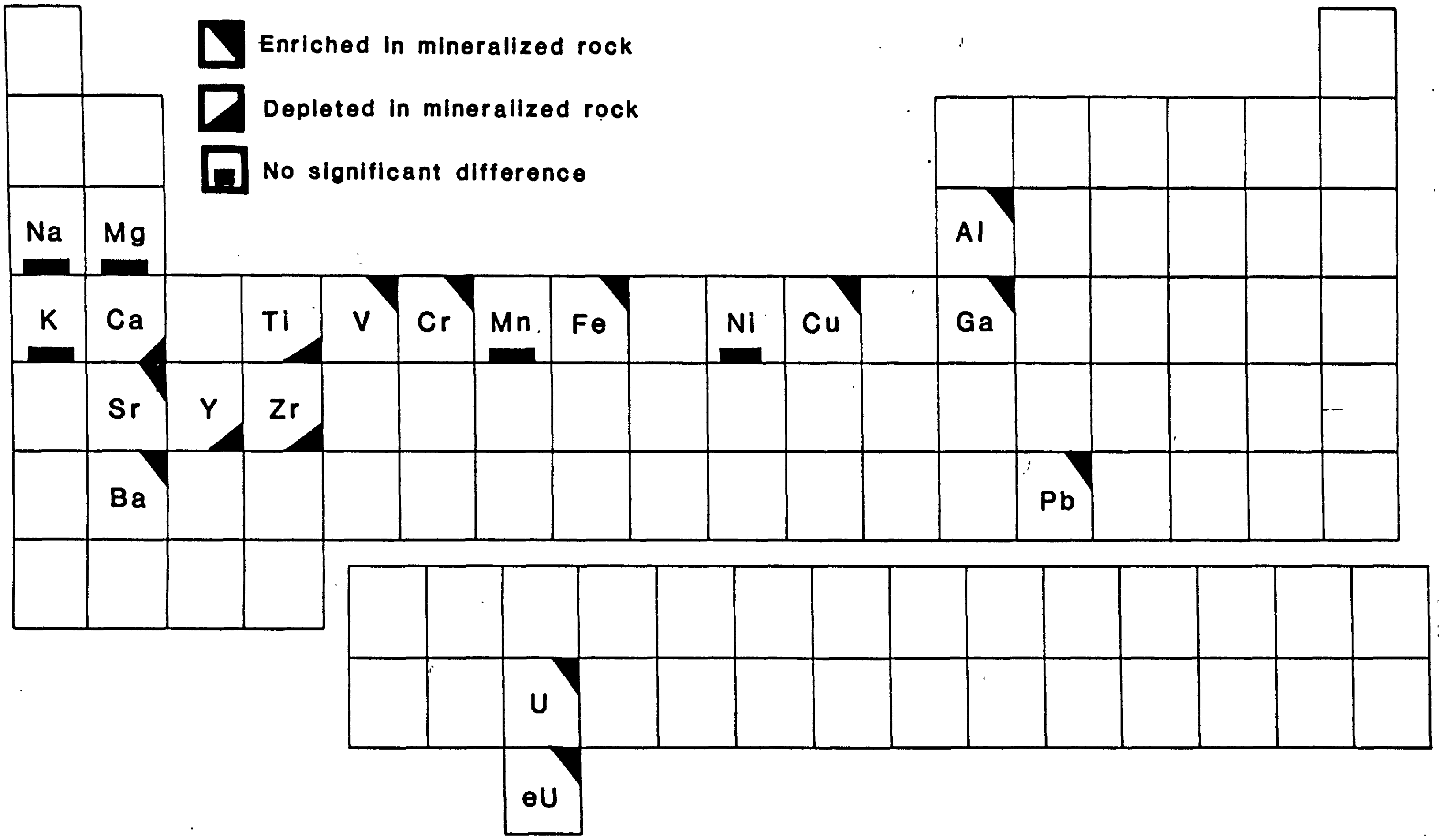
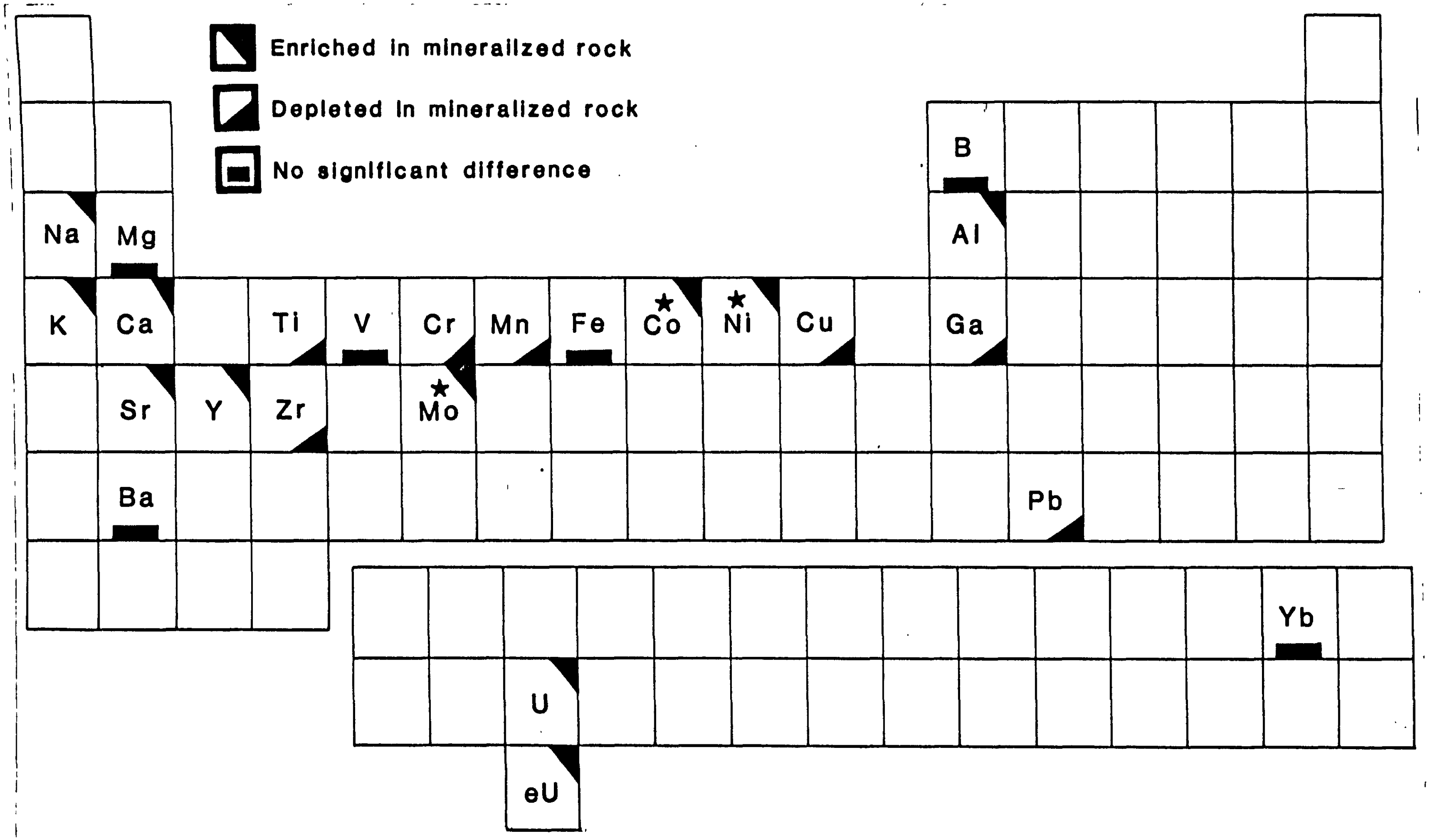


Figure 4--Comparison of mineralized rock to unmineralized (background) rock in the Whittset Formation.



★ A low detection ratio precludes statistical testing of these inferred results

Figure 5--Comparison of mineralized rock to unmineralized (downdip) rock in the Oakville Formation.

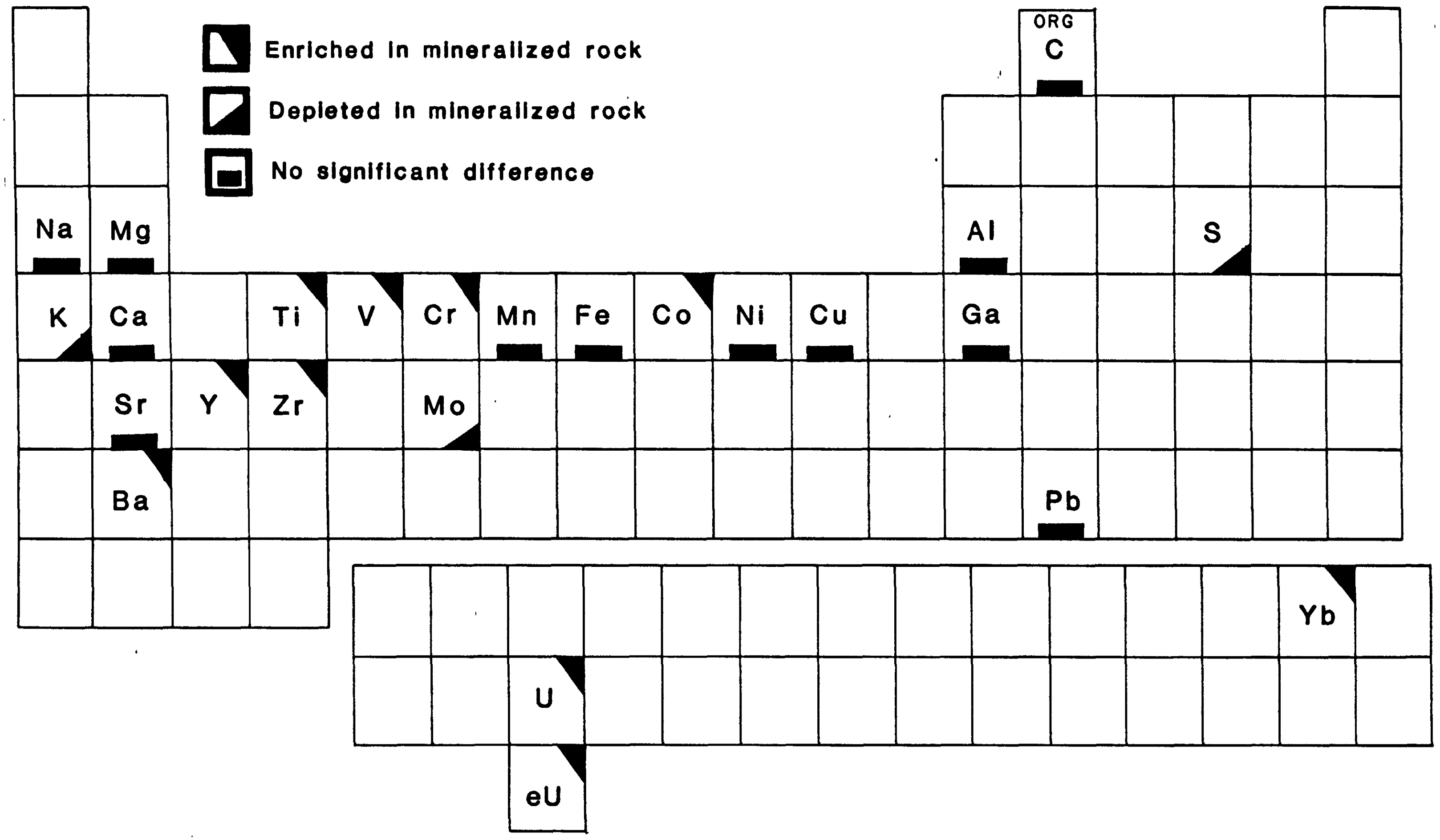


Table 3.--Average abundances (geometric means) of elements in roll-type uranium deposits in the Powder River and Shirley Basins of Wyoming, in the Whittset and Oakville Formations of Texas, and in the Ambrosia Lake area of New Mexico

	Powder River Basin	Shirley Basin	Whittset Formation	Oakville Formation	Ambrosia Lake Area
Al%	4.7	6.6	6.3	2.7	4.2
As ppm	4.8		21.3	39.4	
Ba ppm	648	824	656	687	826
T-C%	2.49	---	---	1.23	.36
Min-C%	.02	---	---	1.21	.40
Org-C%	.128	---	---	.023	.048
Ca%	.43	.71	1.00	5.62	1.93
Co ppm	6.5		3.5	11	
Cr ppm	20	53	6.2	13	5.0
Cu ppm	3.3	46	3.7	8.9	7.6
Fe%	.88	1.36	.53	1.86	.82
FeO%	1.25		.39	.96	
Ga ppm	12	18	12	6.6	3.8
K%	2.7	3.2	2.2	1.8	2.4
Mg%	.30	.40	.16	.10	.16
Mn ppm	118	229	52	157	226
Mo ppm			12	16	3.6
Na%	.96	1.09	1.87	.87	1.19
Ni ppm	9.8	11	1.9	8.6	
Pb ppm	19	30	14	14	12
T-S%	.09		1.24	1.20	
Se ppm	5.00		.82	18.9	15.4
Sr ppm	95	210	489	142	196
Ti%	.08	.06	.07	.16	.09
U ppm	1201	1952	847	1311	1253
eU ppm	1046	1851	926	3139	1103
V ppm	77	138	23	39	1517
Y ppm	6.2	2.0	12	15	12
Yb ppm	1.5		1.4	1.8	
Zr ppm	86	87	64	110	83

Figure 6 -- Qualitative comparison of the behavior of elements in various roll-type uranium deposits

	V	Se	Fe	Mo	Cu	Pb	Sr	Ba	Na	K	Ca	Mn	Mg	Al	Ga	Cr	Yb	Y	Ti	Zr
Powder River basin	+	+	u	ND	-	+	u	+	+	+	-	-	-	+	+	u	u	-	-	-
Shirley basin	+	ND	+	ND	+	+	+	+	u	u	-	u	u	+	+	+	ND	-	-	-
Whittset Formation	u	ND	u	+	-	-	+	u	+	+	+	-	u	+	-	-	u	+	-	-
Oakville Formation	+	ND	u	-	u	u	u	+	u	+	u	u	u	u	u	+	+	+	+	+
Ambrosia Lake	+	+	+	u	+	+	+	+	+	u	+	+	u	+	-	-	ND	u	u	-

+ Enriched relative to background (downdip in the case of the Oakville deposits)

- Depleted relative to background (downdip in the case of the Oakville deposits)

u Unchanged relative to background (downdip in the case of the Oakville deposits)

ND Not determined due to inadequate data cases where a relatively large difference in geometric means is not statistically significant while a smaller difference in geometric means may be statistically significant. The statistically significant results suggest relationships with possible geochemical significance.

POSSIBLE REASONS FOR DIFFERENCES IN THE CHEMICAL CHARACTERISTICS OF THE ORES

Comparisons of figures 2, 3, 4, and 5 indicate that there is a great deal of variation in the behavior of elements among the various roll-type uranium deposits. One major cause of this variation is the variety of genetic processes that may produce roll-type ores. Although reduction of uranium from surface-derived solutions is widely believed to the be the precipitation mechanism for uranium and for some of the other elements associated with roll-type deposits, the nature of the reductant is not the same for all deposits. In some deposits, such as in the Shirley Basin, organic carbon disseminated throughout the host rock is believed to be the reductant (Adler, 1974). The observations that organic carbon is often highly mineralized, that it is removed from altered rocks updip of the deposits, and that there is an enrichment of organic carbon in some deposits compared to background rocks (Files, 1970) indicate that organic carbon was an active reductant at the time of mineralization. In certain roll-type deposits, such as some in the southern part of the Powder River Basin, organic matter is believed to have been concentrated at a change to a finer-grained facies (Dahl and Hagmaier, 1974). Some difference between elements associated with deposits in fine-grained facies and elements associated with coarse-grained facies is likely.

The nature of the process of reduction by organic carbon, and consequently the elements precipitated with uranium by organic carbon, changes with the length of time between sedimentation and the formation of an ore deposit. With sufficient aging, reduction by organic carbon becomes a kinetically slow process and the efficacy of reduction by organic carbon diminishes greatly. Consequently, there is an increase in the amount of reductant required to decrease the redox potential of a surface-derived solution to a level at which uranium precipitates. Therefore, in sandstones of similar organic contents, a mineralizing solution that forms long after sedimentation will migrate a greater distance through a sandstone before precipitating uranium than will an identical mineralizing solution that forms shortly after sedimentation. A study of a roll that formed long after sedimentation (Day and others, 1983) showed that the zone of molybdenum enrichment formed much farther from the uranium ore than in deposits that formed shortly after sedimentation. This larger distance between the uranium and molybdenum zones is believed to be a reflection of the low efficiency of aged organic carbon as a reductant.

In some roll-type deposits, reduction is believed to be the result of interactions between an oxidizing solution and pyrite (Granger and Warren, 1969). Studies by Goldhaber and others (1978) suggest that such reactions precipitated the deposits in the Oakville Formation of south Texas. The secondary deposits in the Ambrosia Lake district may be another example of deposits that formed by the interaction of pyrite with an oxidizing solution. The secondary deposits at Ambrosia Lake, however, differ from other deposits included in this study in that they are believed to have been derived from pre-existing primary uranium deposits (Granger, 1968; Adams and Saucier, 1981).

Adams and Saucier (1981) also suggest that mobile organic matter, rejuvenated from the organic matter in the precursor deposits, may have been present in the mineralizing solutions that formed the secondary deposits. If correct, the presence of mobile organic carbon in some mineralizing solutions but not others may be another cause for variation in the elements associated with different deposits; in particular, mobile organic carbon may affect the solubility of aluminum (Lind and Hem, 1975).

Some of the variability in the elements enriched or depleted in various roll-type deposits may be a reflection of differences in the availability of certain elements. The very strong enrichment of vanadium in the Ambrosia Lake secondary deposits, for example, may be due to a readily available source of vanadium in the primary deposits of the Ambrosia Lake district.

Postmineralization alteration of the deposits is an additional source of variability. A study of the thermoluminescence of calcite (Spirakis and others, 1977) indicates that calcite in one deposit in the Oakville Formation precipitated after the ore and was superimposed on both the ore and host rock. In other deposits (Shirley Basin and Powder River Basin), acid generated by reactions in the ores is believed to have caused calcite to migrate ahead of the redox front (Harshman, 1974).

Interpretation of the patterns of elements enriched or depleted in various roll-type deposits is complicated further by the drastic changes in the nature of the mineralizing solutions during the ore-forming processes. Prior to reaching the site of mineralization, the ore-forming fluids are believed to be carbonate-rich and oxidizing with respect to Fe, U, V, Se, and Mo (Harshman, 1974). As Granger and Warren (1969) point out, the interaction of oxidizing solutions with pyrite in the ores will consume oxygen, produce partly oxidized sulfur species and generate acidic conditions. Both the oxidizing, carbonate-rich solution and the more reducing, acidic solution containing partly oxidized sulfur species will effect the distribution of elements in roll-type uranium deposits. Some elements enriched in the ores may be transported to the deposits in the oxidizing solution; others may be derived from the detrital minerals in the host rock. In the latter case, reactions in the ore may mobilize elements which then migrate with or, as in the case of calcite, ahead of the deposits.

Elements that are soluble under oxidizing conditions but not under reducing conditions, such as uranium, vanadium, molybdenum, and selenium, were probably transported to the ore in the oxidizing solution. Barium is another element that is likely to be transported in the oxidizing solution. Our data indicate that barium is enriched in all of the roll-type ores included in this study except for those in the Oakville Formation. In the case of the Oakville deposits, barium was found to be enriched in the altered rock just updip of the deposits. Thus, barium is associated with all of the deposits. Barium has a very low solubility in the presence of sulfate. According to Granger and Warren (1969), sulfate is generated by the oxidation of pyrite in roll-forming processes. Reaction of this newly formed sulfate with barium in the mineralizing solution is a likely means of precipitating barite associated with these ores.

One surprising result of this study is the enrichment of aluminum in the ores. (Again the Oakville group is an exception but aluminum is enriched in the altered rock just updip of the Oakville ores.) In the case of the Powder River Basin deposits, the enrichment in Al (as well as Ga and possibly Na and K) may be due to the higher clay content of the fine-grained facies associated with the ore. The other deposits, however, do not occur in finer-grained portions of the host rocks, so some other factor must be responsible for the enrichment in Al. In most natural solutions, the solubility of aluminum without organic complexing is low, but in the presence of certain organic complexing agents, the solubility of aluminum may increase by a factor of 100 (Lind and Hem, 1975). This suggests that mobile organic matter may have been involved in the transport of aluminum and other elements to these roll-type uranium deposits. Files (1970) presents evidence that mobile organic material was concentrated in some roll-type deposits.

The variability in the suites of elements enriched or depleted in roll-type uranium deposits is probably not an artifact of the data or of the statistical treatment of these data. Instead, the variability is probably a reflection of the variety of processes that form roll-type uranium deposits, of the complicated chemistry of the ore-forming processes, and of the post depositional alteration of the deposits.

REFERENCES

Adams, S. S., and Saucier, A. E., 1981, Geology and recognition criteria for uraniferous humate deposits, Grants uranium region, New Mexico: Department of Energy Report GJBX-2(81), 225 p.

Adler, H. H., 1974, Concepts of uranium-ore formation in reducing environments in sandstones and other sediments, in Formation of uranium ore deposits: International Atomic Energy Agency, Vienna, p. 141-168.

Cohen, A. C. Jr., 1959, Simplified estimators for the normal distribution when samples are singly censored or truncated: Technometrics, v. 1, no. 3, p. 217-237.

Cohen, A. C. Jr., 1961, Tables of maximum likelihood estimates; singly truncated and singly censored samples: Technometrics, v. 3, no. 4, p. 535-541.

Dahl, A. R., and Hagmaier, J. L., 1974, Genesis and characteristics of the southern Powder River Basin uranium deposits, Wyoming, USA, in Formation of uranium ore deposits: International Atomic Energy Agency, Vienna, p. 201-218.

Day, H. C., Spirakis, C. S., Zech, R. S., and Kirk, A. R., 1983, Distribution of trace elements in drilling chip samples around a roll-type uranium deposit, San Juan Basin, New Mexico: U.S. Geological Survey Open-file Report 83-56.

Files, F. G., 1970, Geology and alteration associated with Wyoming uranium deposits: Unpublished Ph. D. Thesis, University of California, Berkeley, 113 p.

Fisher, R. A., 1950, Statistical methods for research workers: New York, Hafner Publishing Co., 354 p.

Goldhaber, M. B., and Reynolds, R. L., and Rye, R. O., 1978, Origin of a south Texas roll-type uranium deposit: 2. Petrology and sulfur isotope studies: Economic Geology, v. 73, no. 8, p. 1690-1705.

Granger, H. C., 1966, Analytical data on samples collected at Ambrosia Lake, New Mexico - 1958 through 1962: U.S. Geological Survey open-file report, 485 p.

Granger, H. C., 1968, Localization and control of uranium deposits in the southern San Juan Basin mineral belt, New Mexico - An hypothesis: U.S. Geological Survey Professional Paper 600-B, p. 60-70.

Granger, H. C., and Warren, C. G., 1969, Unstable sulfur compounds and the origin of roll-type uranium deposits: Economic Geology, v. 64, no. 3, p. 160-171.

Harshman, E. N., 1974, Distribution of elements in some roll-type uranium deposits, in Formation of uranium ore deposits: International Atomic Energy Agency, Vienna, p. 169-183.

Lind, C. J., and Hem, J. D., 1975, Effects of organic solutes on chemical reactions of aluminum: U.S. Geological Survey Water Supply Paper 1827-G, 83 p.

Miesch, A. T., 1967, Methods of computation for estimating geochemical abundance: U.S. Geological Survey Professional Paper 574-B.

Motooka, J. M., and Grimes, D. J., 1976, Analytical precision of one-sixth order semiquantitative spectrographic analysis: U.S. Geological Survey Circular 738, 25 p.

Natrella, M. G., 1963, Experimental statistics: U.S. National Bureau of Standards Handbook 91.

Santos, E. S., 1980, Analytical data on uranium ore-bearing samples collected in the southern part of the Powder River Basin, Wyoming--1972-1979: U.S. Geological Survey Open-File Report 81-83, 72 p.

Spirakis, C. S., Goldhaber, M. B., and Reynolds, R. L., 1977, Thermoluminescence of sand grains around a south Texas roll-type deposit: U.S. Geological Survey Open-file Report 77-640, 13 p.

Spirakis, C. S., Pierson, C. T., Granger, H. C., 1981, Comparison of the chemical composition of mineralized and unmineralized (barren) samples of the Morrison Formation in the Ambrosia Lake uranium area, New Mexico: U.S. Geological Survey Open-File Report 81-508, 42 p.