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Comparison of the chemical composition of mineralized and unmineralized sandstone and conglomerate samples from the uranium-bearing Chinle Formation of the Colorado Plateau.

By

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COMPARISON OF THE CHEMICAL COMPOSITION OF MINERALIZED AND UNMINERALIZED SANDSTONE AND CONGLOMERATE SAMPLES FROM THE URANIUM-BEARING CHINLE FORMATION OF THE COLOLRADO PLATEAU

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ABSTRACT

This report summarizes the results of chemical and spectrographic analyses of 137 samples of sandstone and conglomerate from primary, tabular-type uranium-vanadium deposits and surrounding unmineralized rock of the Upper Triassic Chinle Formation. The samples came mainly from the Paradox fold belt, White Canyon slope, Henry basin, San Rafael Swell, Monument upwarp, and Defiance and Circle Cliffs uplifts of the Colorado Plateau.

The data were statistically tested to determine which elements were enriched, unchanged, or depleted in the uranium-vanadium deposits compared to unmineralized parts of the host rocks. In addition to U, samples of the Shinarump, Monitor Butte, Moss Back, and other unspecified members of the Chinle Formation are enriched in Al, B, Ba, Be, Ca, Co, Cr, Cu, Fe, Ga, La, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, Y, and Zr compared to unmineralized rocks. No significant enrichment or depletion of K or Ti was found in the mineralized rock. The average amount of Pb present in the deposits is too great to be the product of radioactive decay of the U present; therefore, Pb was either enriched or U was removed from the deposits. The data were inadequate to evaluate As, organic C, S, and Se (elements typically enriched in other tabular uranium deposits). None of the elements studied was found to be depleted in the mineralized rocks.

Many of the elements enriched in the Chinle deposits are also enriched in the tabular uranium-vanadium deposits of the Upper Jurassic Morrison Formation of the Colorado Plateau. This suggests a similar origin for the Chinle and Morrison deposits.

INTRODUCTION

Purpose

This study summarizes previously unpublished chemical data for 137 samples of sandstone and conglomerate from the uranium-bearing Upper Triassic Chinle Formation of the Colorado Plateau. The data, which are stored in the U.S. Geological Survey's Rock Analysis Storage System (RASS), were examined to discern whether the individual chemical elements are enriched, depleted, or show no detectable change in mineralized rock as compared to unmineralized or weakly mineralized rock. This work should provide basic information for studies of the genesis of Chinle uranium deposits as well as for comparison with the chemical characteristics of other sandstone-type deposits on the Colorado Plateau and elsewhere.

Source of samples

The samples were collected mainly from the following Colorado Plateau structural units (Kelley, 1956, fig. 33): Paradox fold belt, White Canyon and Mogollon slopes, Henry basin, San Rafael Swell, Monument upwarp, and Defiance, and Circle Cliffs uplifts. A few samples were taken from the Cameron bench Kaiparowits basin, Acoma sag, and White River, Uncompahgre, and Nacimiento uplifts. Members sampled included the Shinarump, Monitor Butte, Moss Back, and Agua Zarca Members of the lower part of the Chinle Formation.

Samples were collected from 1967 to 1979 by the following U.S. Geological Survey personnel while doing field work on various projects, including NURE (National Uranium Resource Evaluation): R. A. Brooks, A. L. Bush, J. A. Campbell, S. M. Condon, L. C. Craig, A. R. Kirk, R. M. Moxham, F. Peterson, C. T. Pierson, C. S. Spirakis, R. E. Thaden, and K. J. Wenrich.

Previous work

The geology of uranium deposits in Triassic rocks of the Colorado Plateau has been summarized by Finch (1959), and by Isachsen and Evensen (1956). Finch (1955) published a map showing the distribution of uranium deposits and principal ore-bearing formations on the Colorado Plateau. The Triassic deposits discussed in this report are found in fluvial sandstones and conglomerates of the Shinarump, Monitor Butte, and Moss Back Members of the Upper Triassic Chinle Formation.

A definitive report on the stratigraphy and origin of the Chinle Formation and related Upper Triassic strata in the Colorado Plateau region has been published by Stewart and others (1972). Various reports deal with the geology and ore deposits of individual Chinle mining areas including: 1) Arizona localities (Peirce and others, 1970); 2) Green River and Henry Mountains districts, Utah (Johnson, 1959); 3) Lisbon Valley, Utah (Wood, 1968); 4) Monument Valley and White Canyon, Utah and Arizona (Witkind and Thaden, 1963; Chenoweth and Malan, 1973; Malan, 1968; Thaden and others, 1964; Dubiel, 1983); and 5) San Rafael Swell, Utah (Johnson, 1957; Hawley and others, 1965, 1968; and Lupe, 1977). Additional general information on the location and geologic setting of Colorado Plateau uranium deposits may be found in the U.S. Geological Survey Geologic Map series (for example: Map I-360 (Williams, 1964), which shows the geology, structure, and uranium deposits of the Moab quadrangle, Colorado and Utah).

Published geochemical data for Chinle ores and unmineralized host rocks are found in Shoemaker and others (1959), Newman (1962), and Hawley and others (1965, 1968). Shoemaker and others (1959) summarize geochemical data for the Upper Jurassic Morrison Formation as well as for the Chinle Formation, and provide an extended discussion of intrinsic (elements whose presence in the ore is unrelated to uranium mineralization) and extrinsic (elements that were introduced by processes related to uranium mineralization) elements. These data (Shoemaker and others, 1959) are mainly from the Temple Mountain area of the San Rafael Swell.

Newman (1962) reports on the distribution of elements in sedimentary rocks of the Colorado Plateau, provides summary data for 97 samples of unmineralized Chinle sandstones taken from 44 localities in Utah and Arizona, and compares the chemical composition of the Chinle sandstones to that of the Salt Wash Member of the Upper Jurassic Morrison Formation.

Hawley and others (1965) discuss the Temple Mountain district on the southeast flank of the San Rafael Swell, while Hawley and others (1968) examine all of the San Rafael deposits, including Temple Mountain. Both reports contain geochemical data as well as discussion of the data.

Published analyses of individual samples of the Chinle Formation of the Colorado Plateau are available in various NURE reports issued by the Department of Energy, for example Peterson and others (1982).

NATURE OF THE DATA AND STATISTICAL TREATMENT

The 28 chemical elements considered in this study, the analytical techniques used, and the limits of determination for each element are shown on figure 1. Most chemical analyses were by semi-quantitative emission spectrographic methods (Myers and others, 1961). Elements determined by other than spectrographic analysis include: U by wet chemical methods or delayed neutron counting (Millard and Keaten, 1982); As by a wet chemical method; and Se by x-ray fluorescence (Wahlberg, 1976). The analyses were done in the analytical laboratories of the U.S. Geological Survey.

In order to compare the chemical characteristics of the mineralized and unmineralized Chinle rocks, the samples used in this study arbitrarily were divided into four groups (table 1). The groups range from strongly mineralized to very weakly mineralized or unmineralized and are defined as: 1) strongly mineralized (containing equal to or greater than 1,000 ppm U); 2) mineralized (containing equal to or greater than 100 ppm U); 3) weakly mineralized (containing less than 100 ppm U); and 4) very weakly mineralized to unmineralized (containing equal to or less than 20 ppm U). Twenty-eight samples contain more than 100 ppm U (G100 group), and 109 samples contain less than 100 ppm U (L100 group). There are 15 samples in the G1000 group and 86 samples in the L20 group.

With the aid of a computer, the geometric means and geometric deviations for each of the elements in the four groups were computed (table 1). The computations are straightforward (Miesch, 1976, p. 18) for all elements for which no qualified values are present. When qualified values are part of the data set, special methods described below were used.

Qualified values are of three types: 1) the element was not detected (N); 2) the element was detected, but was present in an amount less than the lower limit of determination for that element (L); or 3) the element was present in an amount greater than the upper limit of determination for that element (G). For cases where the data are either singly censored on the left (data contain only N or L values), or on the right (data contain only G values) of the normality curve, a method devised by Cohen (1959, 1961) and programmed by VanTrump (1978) was used to calculate geometric means and geometric deviations. In this procedure, log normality for the data is assumed, and the geometric means and deviations (considered as estimates) are calculated from functions of the following quantities for each element: 1) the geometric mean and deviation of the unqualified values; 2) the numerical value of the limit of determination; and 3) the number of qualified values in the set of data for that element. In Cohen's method, N's are not distinguished from L's, and moreover, as the percentage of qualified values increases, the accuracy of the geometric mean and deviation decreases.

Table 1 lists the detection ratios (i.e. the number of unqualified values compared to the total number of analyses, including qualified values) as well as the geometric means and deviations for each element studied. Because the accuracy of a geometric mean estimated by Cohen's method decreases with an increase in the percentage of qualified values, an asterisk is appended whenever the percentage reaches 30 percent or more for a given element. Two asterisks are appended and no values for the mean or deviation are reported when the percent of qualified values is greater than 70 percent. The limits 30 and 70 percent were chosen arbitrarily. Three asterisks are appended when the number of samples are insufficient to represent the data set. The usefulness of qualified data varies depending upon the precision and limits of detection of the analytical technique used, as well as upon the variability of element concentrations (geometric deviation) within the group of samples studied.

Because the samples were not collected in a truly random manner, statistical tests made on the results of chemical analyses of the samples must be interpreted with caution. Nevertheless, some useful conclusions may be obtained by identifying statistically significant differences between geometric means of elements among the various mineralized and unmineralized groups. A "t" test (Natrella, 1963) was used for this purpose. The test, which employs the mean and variance of the logarithms of the chemical values as well as the number of samples in each of the two groups being compared, was made at the 95 percent confidence level.

Most of the conclusions concerning enrichment of chemical elements within the mineralized groups (G1000 and G100) as compared to the weakly mineralized to unmineralized groups (L100 and L20) were obtained by statistical comparison of the G100 and L100 groups. In cases where the "t" test between these two groups failed to show a significant difference for a given element, as happened for Al, B, Cu, K, and Ti, a further test of the contrast between mineralized and weakly mineralized to unmineralized sample groups was made by comparing the G1000 and L20 groups. This procedure is regarded as appropriate because the original grouping into G100 and L100 was arbitrary, as is the definition of mineralized and unmineralized samples. As can be seen in table 1, most elements differ more in average concentration when the G1000 group is compared to the L20 group than when the G100 group is compared to the L100 group.

When the G1000 group was compared to the L20 group, Al, B, and Cu were found to have significantly higher concentrations in the G1000 group. These elements are therefore interpreted as being enriched in the strongly mineralized rock. However, K and Ti showed no statistical difference in concentration between the G1000 group compared to the L20 group, and therefore there is no evidence to suggest that either K or Ti is enriched or depleted in strongly mineralized rock.

Figure 1.--Elements studied

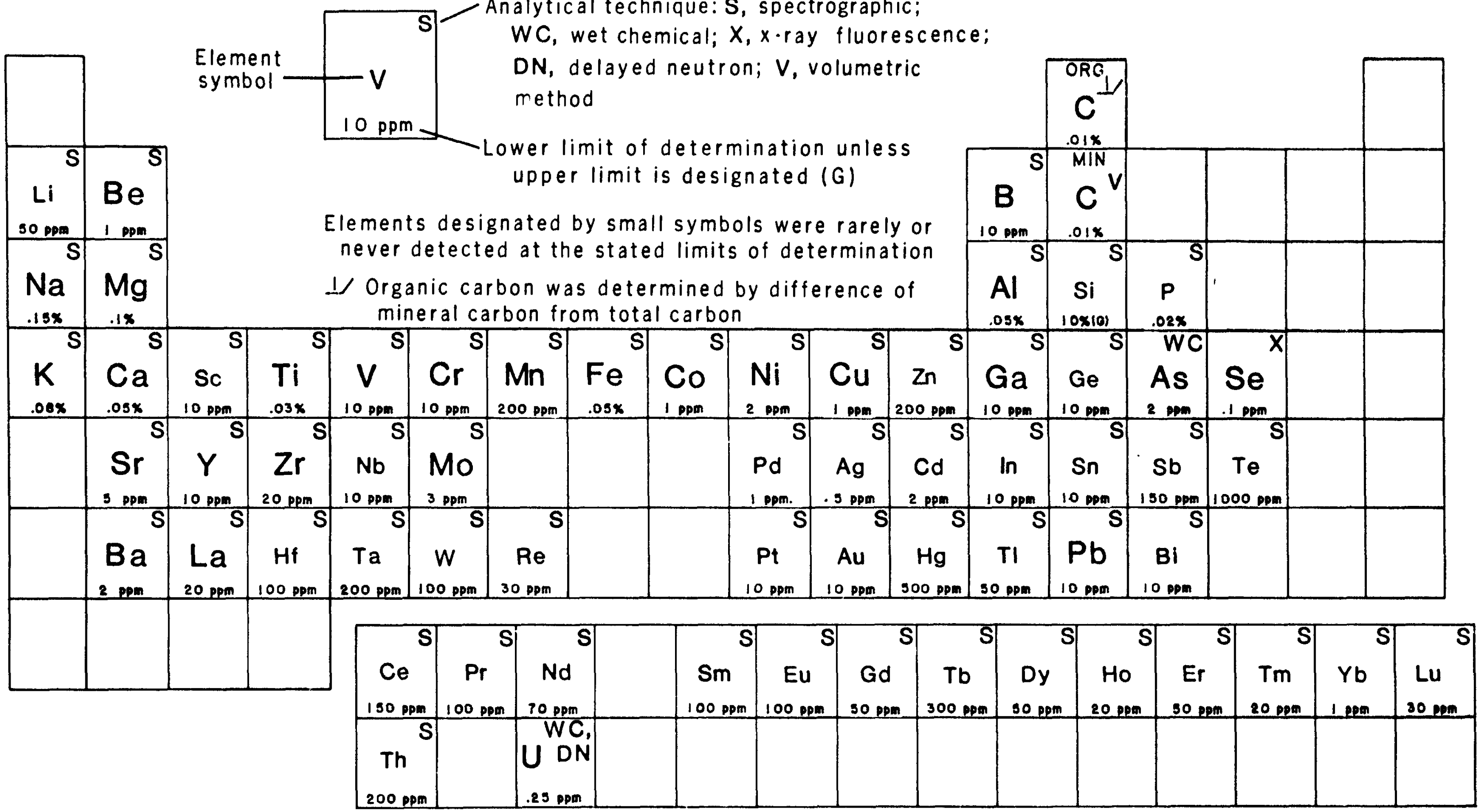


TABLE 1.--Geometric means (GM), Geometric deviations (GD), and detection ratios for Chinle sandstones and conglomerates

Element (limit of determination)[3]	(G1000) More than 1000 ppm U[1] G.M.	G.D.	Detection Ratio[2]	(G100) More than 100 ppm U[1] G.M.	G.D.	Detection Ratio[2]	(L100) Less than 100 ppm U G.M.	G.D.[2]	Detection Ratio[2]	(L20) Less than 20 ppm U G.M.	G.D.	Detection Ratio[2]
Al % (.05)	4.7	2.0	15/15	3.8	2.0	28/28	3.1	1.8	109/109	3.0	1.8	86/86
As ppm (2)	***	***	0/0	***	***	0/0	10	2.3	35/37	10	2.4	32/34
B ppm (10)	60	2.3	14/15	26	3.6	20/28	11[*]	3.3[*]	56/109	11[*]	3.5[*]	44/86
Ba ppm (2)	584	1.6	15/15	618	2.1	28/28	382	2.9	108/109[G]	318	2.6	85/86[G]
Be ppm (1)	5.2	2.1	14/15	3.6	2.1	27/28	1.5	1.6	84/109	1.4	1.6	62/86
Organic C % (.01)	--	--	0/0	***	***	2/2	0.14	2.2	44/44	0.15	2.1	41/41
Mineral C % (.01)	--	--	0/0	***	***	2/2	0.02[*]	17.1[*]	26/44	0.02[*]	21.6[*]	23/41
Ca % (.05)	2.2	2.8	15/15	1.8	4.3	27/28[G]	0.5	6.8	105/109[G,L]	0.5	6.6	82/86[G,L]
Co ppm (1)	49	3.4	15/15	31	3.4	28/28	8	2.5	108/109	7	2.3	85/86
Cr ppm (10)	24	1.6	15/15	22	1.7	27/28	17	2.0	87/109	16	2.1	67/86
Cu ppm (1)	34	3.5	15/15	44	7.1	27/28[G]	24	6.1	107/109[G,L]	17	4.3	85/86
Fe % (.05)	2.0	1.7	15/15	1.5	3.1	27/28	0.4	6.8	84/109	0.3	7.4	64/86
Ga ppm (10)	12	1.5	12/15	10[*]	1.6[*]	14/28	**	**	28/109	**	**	23/86
K % (.08)	1.00	4.4	13/15	1.00	3.0	26/28	0.83	2.1	108/109	0.79	2.1	85/86
La ppm (20)	36[*]	3.2[*]	9/15	39	2.4	21/28	26[*]	2.0[*]	67/109	24[*]	2.0[*]	50/86
Mg % (.1)	0.5	3.2	13/15	0.4	3.4	23/28	0.1[*]	4.5[*]	66/109	0.2[*]	4.3[*]	55/86
Mn ppm (200)	337	1.8	13/15	387	2.4	23/28	161[*]	4.9[*]	46/109[G,L]	138[*]	5.2[*]	33/86[G,L]
Mo ppm (3)	**	**	3/15	**	**	7/28	**	**	6/109	**	**	4/86
Na % (.15)	0.4	2.3	12/15	0.3[*]	3.4[*]	17/28	**	**	26/109	**	**	20/86
Ni ppm (2)	32	2.8	15/15	27	2.6	28/28	14	2.1	109/109	13	2.0	86/86
Pb ppm (10)	270	2.6	15/15	102	5.4	25/28	**	**	22/109	**	**	15/86
Se ppm (.1)	---	---	0/0	---	---	0/0	0.08[*]	2.6[*]	15/40	0.07[*]	2.5[*]	13/36
Sr ppm (5)	253	1.5	15/15	232	2.1	28/28	117	2.8	109/109	105	2.9	86/86
Ti % (.03)	0.15	1.9	14/15	0.15	2.0	27/28	0.13	2.4	105/109	0.12	2.5	82/86
U ppm (.25)	7,800	4.3	15/15	1,500	8.2	28/28	9	2.6	109/109	6	1.9	86/86
V ppm (10)	1,750	3.9	15/15	580	6.0	28/28	36	2.6	99/109	31	2.3	76/86
Y ppm (10)	42	1.9	15/15	39	2.0	27/28	22	1.9	100/109	20	1.8	77/86
Zr ppm (20)	249	2.0	15/15	229	2.1	27/28[G]	99	3.7	90/109	90	3.9	69/86

[1]Spectrographic analyses of uranium (as substitutes for missing delayed neutron or wet chemical analyses) were used to determine grouping into the G100 and G1000 groups for 9 samples, as well as to calculate geometric means and deviations for uranium in these two groups.

[2]Detection ratios are reported as the number of unqualified values (numerator) and total number of analyses, including qualified values (denominator). Detection ratios of less than one and not followed by "G" indicate data sets that contain values below the limit of determination.

[3]Only lower detection limit is given. For calculation of geometric mean and geometric deviation, G's in the data were replaced by the value of the next midpoint higher in the six-step semiquantitative spectrographic series (Myers and others, 1961). Also note that the geometric mean calculated by Cohen's (1959) technique may be less than the lower limit of determination when there is a large proportion of N's or L's in the data, e.g. Mn in the L100 and L20 groups.

G denotes that values greater than the upper limit of determination are present in the data.

G, L denotes that values both above and below the limits of determination are present in the data.

* 30-69 percent qualified values are present.

** 70 or more percent qualified values are present; geometric mean and deviation are not reported.

*** Number of samples are insufficient to represent the data set.

-- No data are available.

When more than 70 percent qualified values are present, the "t" test was not used. Rather, judgment as to the relative enrichment or depletion was made on the basis of the percentages of qualified values present in the groups being compared. For example, Ga has percentages of unqualified values of 80, 50, 26, and 27 percent in the G1000, G100, L100, and L20 groups respectively. In this case, no statistical tests were made between mineralized and unmineralized groups because both the L100 and L20 groups contain more than 70 percent qualified values. Ga, however, was judged to be enriched in the mineralized sandstone as compared to the unmineralized sandstone because the former group contains a much greater percentage of samples in which Ga is found in amounts above the detection limit of the analytical method used. Similar logic was used to judge enrichments for Mo, Na, and Pb.

OBSERVATIONS AND DISCUSSION

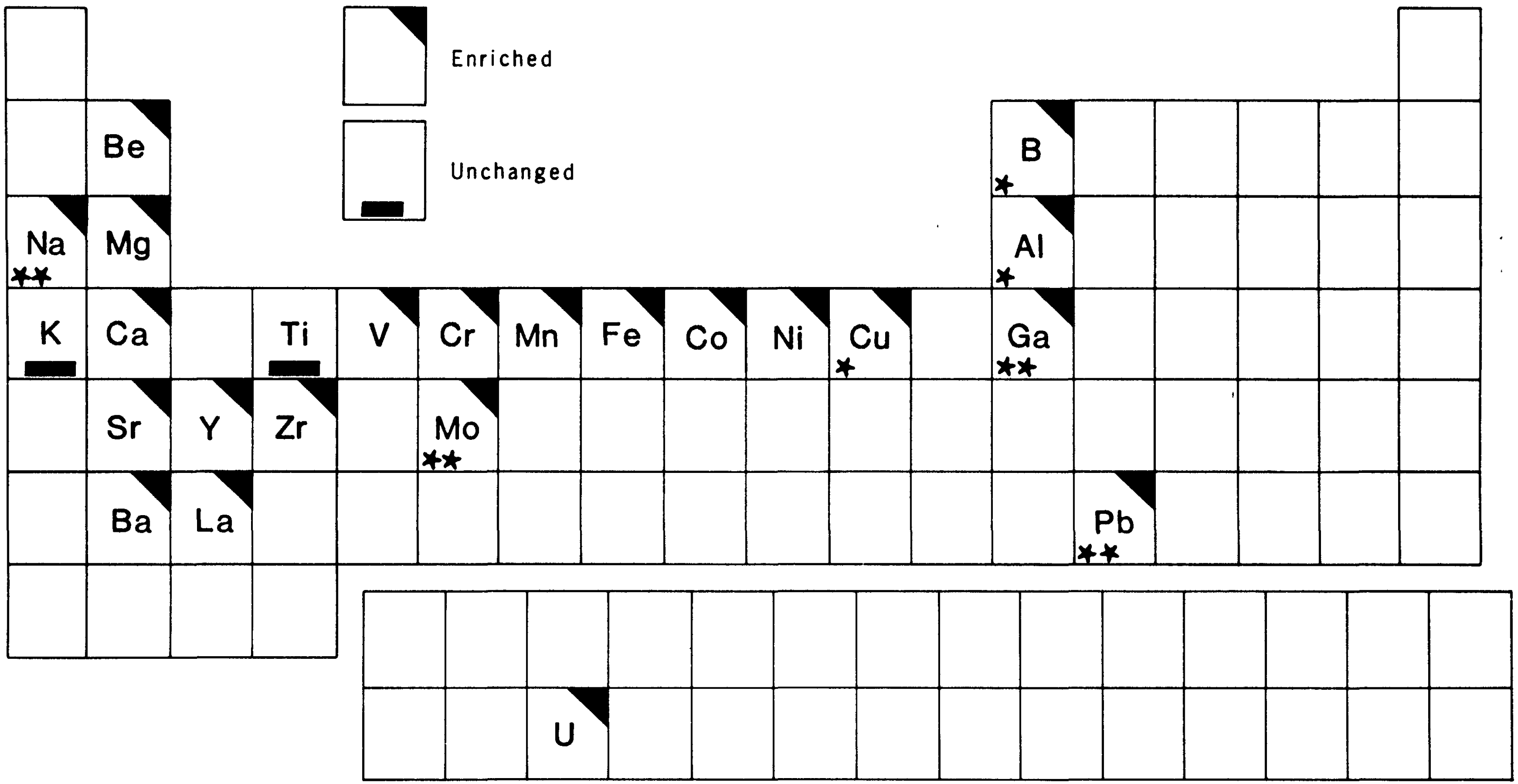
On the basis of statistical tests or the relation of the percentages of qualified values among the groups, the elements Al, B, Ba, Be, Ca, Co, Cr, Cu, Fe, Ga, La, Mg, Mn, Mo, Na, Ni, Pb, Sr, V, Y, and Zr (figure 2) are interpreted as being enriched along with U in the tabular Chinle uranium-vanadium deposits (G1000 and G100 groups) as compared to weakly mineralized or unmineralized parts of the host rocks (L100 and L20 groups). No significant enrichment or depletion of K or Ti was found in the mineralized rocks.

Table 2 compares the results of the present study with conclusions reached by Spirakis and others (1984) and Spirakis and Pierson (1983) for tabular uranium-vanadium deposits in the Upper Jurassic Morrison Formation of the Henry Mountains, Utah and the Grants uranium region, New Mexico. Although there is some variation in the chemistry of the deposits, many of the elements enriched in the Chinle deposits are also enriched in most of the other tabular deposits. This similarity suggests that the tabular uranium-vanadium deposits in all of these areas were formed by similar processes.

The enrichment of Pb in tabular-type deposits in the Morrison Formation of the Henry Mountains and Grants areas was thought to be the product of radioactive decay of U (Spirakis and others, 1984; Spirakis and Pierson, 1983). For the Chinle deposits, however, the average amount of Pb now present in the G100 group is in excess by about 50 ppm of the amount that would be expected from the radioactive decay of U, assuming that mineralization took place about 200 million years ago. This suggests that either Pb was transported to the deposits, or that U has been removed from them. In addition to Pb, the deposits of the Chinle Formation contain much more Co, Cr, Cu, Ni, Y, and Zr than do the tabular-type uranium deposits of the Morrison Formation in the Henry Mountains region or in the Grants mineral belt.

A study by Hawley and others (1968) of the geology, altered rocks, and Chinle uranium deposits of the San Rafael Swell area indicates, that in addition to the elements identified by the present study as enriched in ores of the Chinle Formation of the Colorado Plateau region, Ag, As, Li, Mo, Zn, and rare earth elements are also enriched in the ores compared to unmineralized rocks of the Chinle Formation. The same authors suggest that the degree of enrichment of various elements in the ores in the collapse structure at Temple Mountain differs from the degree of enrichment of the same

Figure 2.--Elements enriched or unchanged in abundance in mineralized sandstone and conglomerate of the Chinle Formation compared to unmineralized rock.



* One asterisk indicates that interpretation of enrichment was based on statistical comparison of G1000 and L20 groups.

** Two asterisks indicate element interpreted as enriched on basis of higher detection ratios in mineralized (G1000, G100) group than in weakly mineralized or unmineralized group (L100, L20). All other enrichments based on statistical comparison of G100 and L100 groups.

Table 2. -- Comparison of element enrichments and depletions in tabular uranium-vanadium deposits in the Chinle and Morrison Formations

Formation	Chinle	Morrison				
Area	This Study	Henry Mts[a]	Mariano Lake[b]	Ruby Deposit[b]	Ambrosia Lake[b]	Jackpile Deposit[b]
Element						
Al	+	+	o	+	o	*
As	*	*	+	+	+[3]	*
B	+	o	*	*	*	*
Ba	+	o	+	+	+	+
Be	+	+	+	o	+	*
C org.	*	+	+	+	+	*
C min.	*	-	*	o	+	*
Ca	+	o	+	+	+	+
Co	+	+	+[1]	+	*	*
Cr	+	+	-	*	-	+
Cu	+	+	+	+	+	+
Fe	+	+	+	+	+	o
Ga	+	+	+	+	-	*
K	o	+	+	o	o	*
La	+	*	*	*	*	*
Mg	+	+	o	+	+	+
Mn	+	o	+	+	+	+
Mo	+	+	+	+[2]	+	*
Na	+	+	+	o	+	*
Ni	+	+	*	+	*	*
Pb	+	+	+	+	+	+
S	*	+	+	+	+[3]	*
Se	*	+	+	+[2]	+[3]	*
Sr	+	+	+	+	+	+
Ti	o	+	o	-	o	o
V	+	+	+	+	+	+
Y	+	+	+	+	+	*
Zr	+	+	+	+	-	o

Explanation

[a] Spirakis and others, 1984
[b] Spirakis and Pierson, 1983

+ enriched
o unchanged
- depleted
* no or inadequate data

[1]Because of the high proportion of L values in the data, the behavior of the element is uncertain.
[2]sporadically enriched
[3]based on limited data

elements in other deposits of the Chinle Formation of the San Rafael Swell.

Austin (1957) studied the Chinle ores in the Petrified Forest Member of the Chinle Formation in the Cameron area of Arizona and presented data that suggest that Co, Cu, Mo, Ni, Pb, and Y are at least twice as abundant in the ore of the Cameron area than in the Chinle deposits included in the present study.

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