Preliminary Geochemical Studies in the Capitol Reef Area, Wayne County Utah

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GEOLOGICAL SURVEY BULLETIN 1015-H

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DEPARTMENT OF THE INTERIOR
March 3, 1849

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By LYMAN C. HUFF

A CONTRIBUTION TO ECONOMIC GEOLOGY

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A CONTRIBUTION TO ECONOMIC GEOLOGY

PRELIMINARY GEOCHEMICAL STUDIES IN THE CAPITOL REEF AREA, WAYNE COUNTY, UTAH

By Lyman C. Huff

ABSTRACT

A bleached zone at the base of the Chinle formation near the Oyler mine, Wayne County, Utah, was studied to establish whether there was a chemical relationship between bleaching in the Chinle and uranium mineralization in the Shinarump conglomerate. The preliminary results suggest that the bleaching was accomplished by a slightly reducing acid solution which deposited zinc and copper but no uranium in the bleached zone. A field test for heavy metals which has been devised for geochemical prospecting appears to be satisfactory for detecting and tracing such mineralization effects. It is hypothesized that the solution which bleached the Chinle also deposited uranium in the Shinarump, but more work is needed to clarify this relationship.

INTRODUCTION

Since 1951 the U. S. Geological Survey has had a field party mapping and studying the Capitol Reef area (fig. 35) on behalf of the Division of Raw Materials, U. S. Atomic Energy Commission. A progress report on these geological investigations has been prepared.[1] The

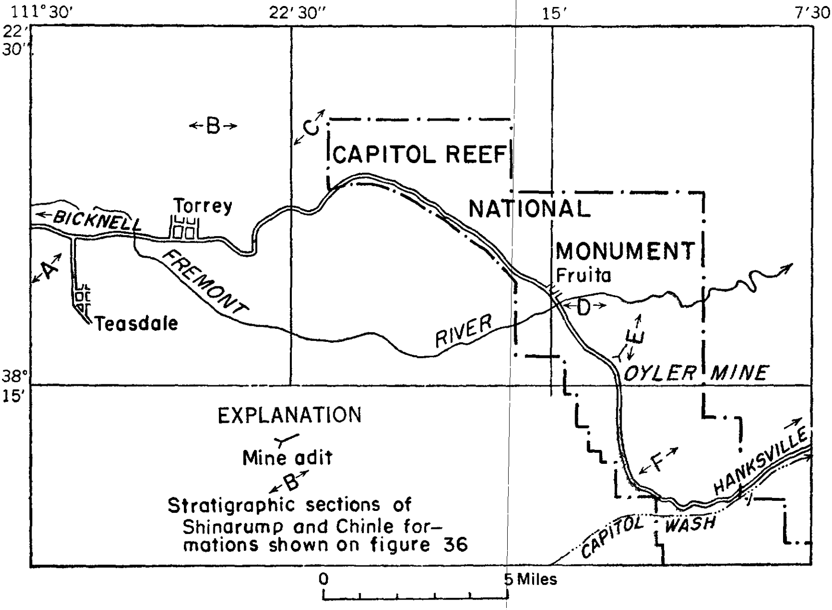

FIGURE 35.—Map of Capitol Reef Area, Wayne County, Utah.

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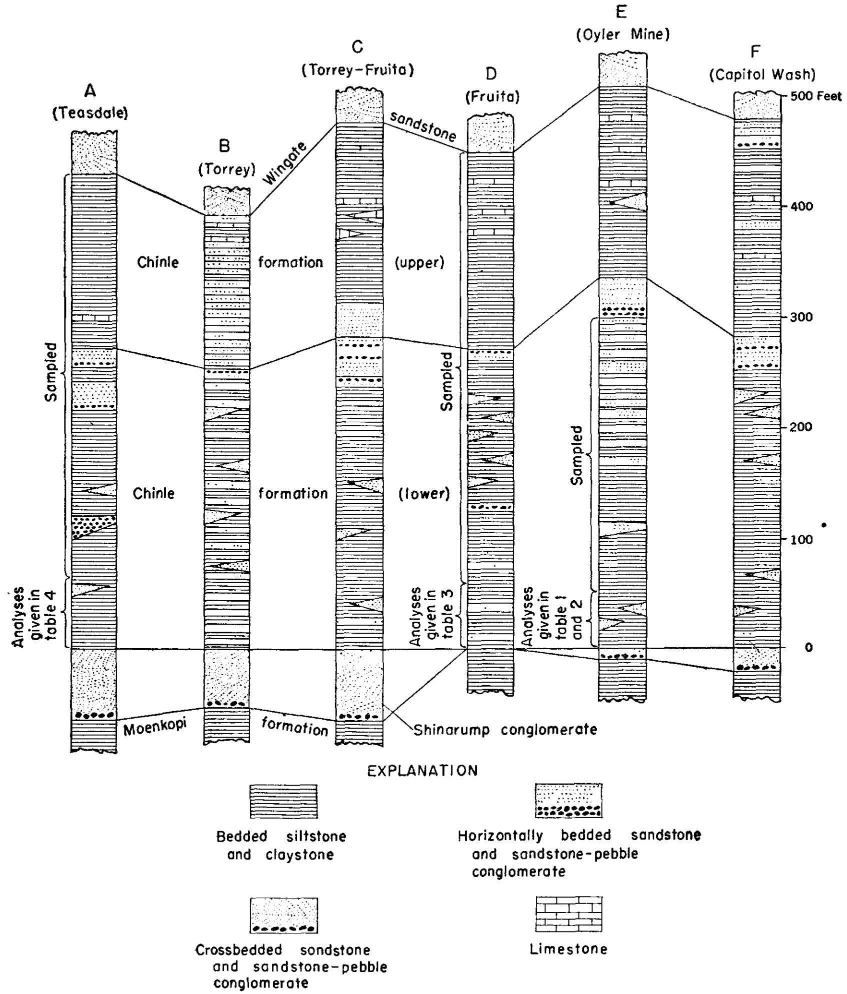
[1] Smith, J. F., Jr., Hinrichs, E. N., Huff, L. C., and Luedke, R. G., 1952, Preliminary report on geologic studies in the Capitol Reef area, Wayne County, Utah: U. S. Geol. Survey Trace Elements Mem. Rept. 538.



Locations of sections shown in figure 35

FIGURE 36.—Stratigraphic sections of the Shinarump and Chinle formations, showing portions sampled for geochemical study.

brief geochemical study herewith described is a part of the geologic investigation.

The Oyler mine [2] is a uranium deposit in the Shinarump conglomerate and is similar in many respects to other Shinarump uranium deposits of the Colorado Plateau. This report describes a chemical study made of the Chinle formation and its possible significance. The chemical study was made to investigate a light-colored bleached zone which is commonly found at the base of the Chinle formation and which is well developed near the Oyler mine. In particular, the

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[2] Smith and others, op. cit.

chemical study was designed to establish whether the bleached zone in the lower Chinle is related genetically to the uranium mineralization of the Shinarump.

SAMPLE COLLECTION

Two suites of samples of the Chinle formation were collected near the Oyler mine and for background data two other suites were collected, at a considerable distance from the mine. The suites collected near the Oyler mine were taken in a traverse across the bottom half of the Chinle formation; the other two suites were taken in a traverse across the entire formation. In all, 188 samples of the Chinle were collected. Figure 36 shows the stratigraphic relationships of these samples. Figure 37 shows in greater detail the location of samples collected near the Oyler mine.

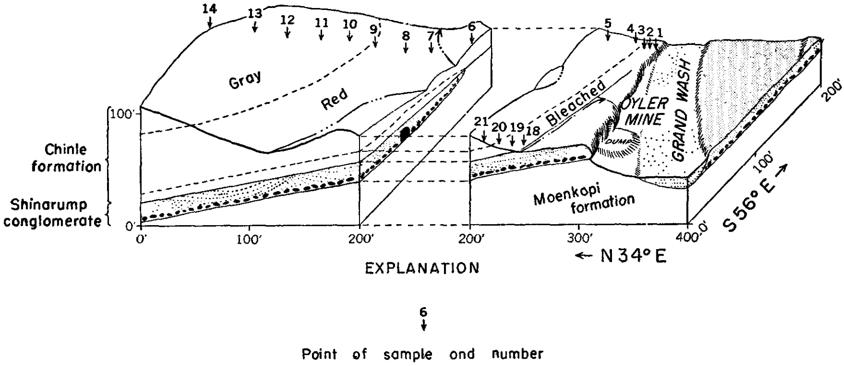

FIGURE 37.—Block diagram showing location of geochemical samples collected near Oyler mine.

Grab samples of undisturbed Chinle just beneath the land surface were collected with a chisel-edged pick and were stored in cardboard cartons or manila envelopes. Two closely spaced samples were collected at many of the sample sites so that some samples would be available for confirming the results. Most sample sites were marked with numbered wooden stakes and the intervening slope distances measured with a 100-foot tape. This marking system permitted collection of additional samples anywhere along the traverses without error of location. In general, samples were collected at intervals close enough to sample each lithologic type, or where the rock is homogeneous, at 100-foot slope intervals.

A field description of the samples, recorded as they were collected, included sample location, grain-size classification, color according to the rock-color chart (Goddard and others, 1948), presence of calcium carbonate by acid test, and other pertinent features.

METHODS OF ANALYSIS

The Geological Survey analyzed all samples by the total heavy-metal test developed by Huff (1951). The total heavy-metal test is a group test for detecting the presence in trace amounts of any ore metal such as copper, lead, and zinc which react with the reagent dithizone. The heavy-metal test is not affected by uranium, vanadium, iron, or manganese. The test revealed no heavy metals for the bulk of the Chinle samples. Heavy metals were found only in the bleached zone of the lower Chinle, in a very few bleached zones higher in the Chinle, and in the thin bleached zone at the top of the Chinle, below the Wingate sandstone.

Additional analyses were made of samples collected near the base of the Chinle. These samples were analyzed for copper, lead, zinc, and acidity (pH). Acidity was measured by the method used by agricultural scientists for soils (U. S. Bur. Soils, 1951, p. 237). The acidity of a suspension of the ground sample in distilled water was measured with an electric pH meter. The pH measured ranged from about 4.0 (acid) in the bleached zone to slightly over 8.0 (alkaline) in the unbleached Chinle.

The oxidation potential of several samples was investigated with the help of R. M. Garrels and Harold Bloom. Details concerning the measurement of oxidation potentials are given by ZoBell (1946). Oxidation potentials of samples 1 to 6 were measured with a platinum instead of a glass electrode in the pH meter. Nitrogen was bubbled through the sample during measurement to expel oxygen and stir the suspension. The Coleman pH meter used gave stable Eh potentials with the Chinle samples after bubbling nitrogen for about 15 minutes.

Because of the few samples involved the meter used for measuring oxidation potential was not standardized with an oxidation-reduction buffer. The measurements ranged from −354 millivolts in sample 1 to −125 millivolts for sample 6. Expressed in terms of the standard hydrogen cell, the corresponding values would be approximately −108 and +121 millivolts. In simplified terms the range is from reducing conditions in the bleached Chinle to oxidizing conditions in the unbleached Chinle.

Ten samples were analyzed for uranium (table 1) and for equivalent uranium. In addition, the writer made qualitative microchemical tests of representative samples for copper, lead, zinc, iron, manganese, vanadium, uranium, carbonate, sulfate, and phosphate.

ANALYTICAL RESULTS

Analyses of samples collected near the Oyler mine are given in tables 1 and 2. The bleached zone of the lower Chinle near this mine contains several hundred parts per million zinc and about one hundred

TABLE 1.—*Analyses of samples of the Chinle formation, collected along section E at the Oyler mine, Capitol Reef National Monument, Utah*

[Two determinations are listed for analyses of duplicate samples. H. E. Crowe, W. M. Mountjoy, and J. P. Schuch, analysts]

Field no.	Sample description	Total heavy metal (ppm)	Zinc (ppm)	Lead (ppm)	Copper (ppm)	Uranium (ppm)	pH
10	Claystone, sandy and silty, light-olive-gray, 51.0 ft above base of Chinle.	20, 0	10	20	20	4	8.0
9	Siltstone, sandy, grayish-red, 43.2 ft above base of Chinle.	0, 0	10	10	20	3	8.5
8	Siltstone, sandy, grayish-red, 30.9 ft above base of Chinle.	0, 0	10	10	10	1	8.1
7	Sandstone, fine, pale-reddish-brown, 22.3 ft above base of Chinle.	20, 0	10	10	10	2	7.6
6	Sand and siltstone, fine, reddish-brown, 16.7 ft above base of Chinle.	0, 0	10	10	10	2	8.1, 8.2
5	Sand and siltstone, fine, reddish-brown, 11.4 ft above base of Chinle.	0, 0	10	10	10	2	8.3, 8.3
4	Sandstone, fine, clayey, reddish-brown, 5.9 ft above base of Chinle.	90, 30	20	10	20	2	6.1, 6.1
3	Sandstone, clayey, yellowish iron stain, 4.7 ft above base of Chinle.	150, 170	170	10	50	3	4.7, 4.8
2	Claystone, sandy, light-olive-gray, 3.8 ft above base of chinle.	330, 300	300	10	50	5	4.2, 4.2
1	Claystone, light-olive-gray, 1.1 ft above base of Chinle and top of Shinarump.	450, 450	500	10	100	25	4.2, 4.0

parts per million copper. The unbleached beds higher in the Chinle contain a low heavy-metal content.

Analyses of samples collected far from the Oyler mine are given in tables 3 and 4. These samples show little or no concentration of zinc or copper at the base of the Chinle formation.

The detection, identification, and tracing of heavy-metal anomalies amounting to only several hundred parts per million has been proven feasible by many geochemical prospecting studies. The duplicate results given under "total heavy metal" and "pH" columns (tables 1 and 3) were obtained from separate samples and give a measure of the reproducibility of the results. In other words, the variations shown are due to both local variation of metal content and to analytical errors. Such a comparison permits evaluation of the ability to reproduce measurements in terms of the amount of natural variations. Although of small magnitude, the presence of a heavy-metal anomaly in the basal Chinle seems fairly well established.

Sample 1, at the base of the bleached zone, contains 25 ppm (parts per million) uranium (table 1). The higher samples, 3 to 10, contain only 1 to 4 ppm uranium. Experiments indicate that 25 ppm uranium is not detectable by the field (bead) test for uranium. Apparently the uranium anomaly is less extensive and not as readily detectable by field tests as the heavy-metal anomaly.

Qualitative microchemical tests on samples listed in table 1 confirmed the presence of abnormal amounts of zinc and copper in the bleached zone. In addition, the microchemical tests indicate that the bleached beds contain more sulfate but less iron and carbonate than the unbleached beds. Microchemical tests revealed no abnormal amounts of lead, vanadium, manganese or phosphate in either bleached or unbleached beds. Apparently, the bleaching removed iron and carbonate and added sulfate, zinc, copper, and uranium.

GEOCHEMISTRY OF SHINARUMP URANIUM DEPOSITS

Before the relation between the bleached Chinle and the uranium deposits can be considered, it might be advantageous to review briefly the behavior of the ore metals of Shinarump-type uranium deposits under different conditions of acidity and oxidation. Krumbein and Garrels (1952) have shown that metals such as iron, uranium, copper, and zinc are appreciably soluble in slightly reducing acid solutions and can be precipitated either by additional reduction or by neutralizing the acid. If precipitation is caused by additional reduction, the minerals formed contain ions in their reduced form such as U^{4+}, V^{3+}, Cu^{1+}, Fe^{2+}, and S^{2-}. Pitchblende, pyrite, and chalcopyrite are examples of minerals in this assemblage which have been identified at the Oyler mine. If precipitation is caused by neutralization, the minerals formed contain ions in their oxidized form such as U^{6+}, V^{5+}, Cu^{2+}, Fe^{3+}, and S^{6+}. Zippeite $(UO_2)(SO_4)(OH)_2 \cdot 4H_2O$, metatorbernite $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$, johannite $Cu(UO_2)_2(SO_4)_2(OH)_2 \cdot 6H_2O$, gypsum, alunite, and malachite are examples of minerals in this assemblage at the Oyler mine. Although there may be many complicating factors, such as the effects of temperature and pressure, the writer believes that it would be helpful in understanding the chemistry of the uranium deposits such as those in the Oyler mine if the minerals present are classified in two broad groups: (1) Minerals precipitated by reduction and (2) minerals precipitated by neutralization or oxidation.

Both chemical and mineralogical evidence are needed to decipher the history of the Shinarump-type deposits. With the ore minerals classified as they are above the writer interprets the genesis of the Shinarump ore as follows: Precipitation of minerals of the reduction assemblage in the vicinity of organic materials, and later alteration of some of the ore with slight migration of its constituents to minerals of the oxidation assemblage. It is inconceivable, on the basis of chemistry and textural relationships, that minerals of both assemblages could have been deposited together. The alteration from reduced to oxidized minerals can be attributed to the effects of ground water, which is normally slightly alkaline and has a slight tendency to oxidize. The original precipitation of the ore minerals is conjectural but, unless it took place under abnormal conditions of pressure and temperature, the ore solutions were probably mildly reducing and acid in character. As suggested by Krumbein and Garrels (1952), it is only solutions of this type which can carry significant quantities of the ore metals in solution. Such solutions must have been quite different chemically from most present-day ground water.

BLEACHING AT BASE OF CHINLE FORMATION

No ore minerals have been identified in the basal, bleached zone of the Chinle. The composition and nature of the solution which caused the bleaching must be inferred from the chemical changes involved in the bleaching. The bleaching involved removal of iron and carbonate and addition of sulfate, zinc, copper, and uranium (tables 1, 2 and fig. 37). Only an acid solution, except at abnormal temperatures, would be expected to deposit zinc and copper as it is neutralized by carbonate. Moreover, only a slightly reducing acid solution would be

TABLE 2.—*Analyses of supplementary series of samples of the Chinle formation, collected near section E and the Oyler mine, Capitol Reef National Monument, Utah*

[H. E. Crowe, analyst]

Field no.	Sample description	Total heavy metal (ppm)	Zinc (ppm)	Lead (ppm)	Copper (ppm)	pH
28	Silt, clayey, light-olive-gray, 103.0 ft above base of Chinle.	0	20	20	10	8.4
27	Silt, clayey, light-olive-gray, 73.0 ft above base of Chinle.	0	20	10	10	8.1
26	Claystone, light-olive-gray, 59.0 ft above base of Chinle.	0	20	20	10	6.6
25	Claystone, silty, light-olive-gray, 46.4 ft above base of Chinle.	0	20	10	10	6.7
24	Siltstone, reddish-brown, 35.8 ft above base of Chinle.	0	20	10	20	7.9
23	Siltstone, reddish-brown, 21.8 ft above base of Chinle.	0	20	10	10	8.2
22	Silt, sandy, reddish-brown, 14.2 ft above base of Chinle.	0	20	10	20	7.9
21	Siltstone, clayey, reddish-brown, 8.8 ft above base of Chinle.	0	20	10	20	7.6
20	Siltstone, yellowish-orange, 6.0 ft above base of Chinle.	250	300	10	50	4.8
19	Claystone, light-olive-gray, 3.6 ft above base of Chinle.	300	700	20	150	3.5
18	Claystone, light-olive-gray, 0.5 ft above base of Chinle and top of Shinarump.	350	350	50	100	3.7

expected to dissolve iron. Thus, the known geochemical behavior of these elements indicates a slightly reducing acid solution was responsible for the bleaching.

At the locality where the Shinarump conglomerate is lacking, the basal Chinle formation has no heavy-metal anomaly or bleached zone (table 3). At another locality where unmineralized Shinarump conglomerate lies beneath the Chinle formation, the basal Chinle is bleached but shows only a small metal anomaly (table 4). At count-

TABLE 3.—*Analyses of samples of the Chinle formation, collected along section D near Fruita, about 2 miles from the Oyler mine*

[Two determinations are listed for analyses of duplicate samples. H. E. Crowe, analyst]

Field no.	Sample description	Total heavy metal (ppm)
160	Claystone, silty, grayish-red-purple, 55.1 ft above base of Chinle	0, 0
159	Claystone, silty, dusky-yellow, 49.6 ft above base of Chinle	0, 0
158	Claystone, silty, dusky-yellow, 46.1 ft above base of Chinle	0, 0
157	Claystone, silty, dusky-red-purple, 41.1 ft above base of Chinle	0, 0
156	Claystone, silty, greenish-gray, 34.1 ft above base of Chinle	0, 0
155	Claystone, silty, dusky-yellow, 26.6 ft above base of Chinle	0, 0
154	Siltstone, light-olive-brown, 19.1 ft above base of Chinle	0, 0
153	Siltstone, dusky-red-purple, 12.0 ft above base of Chinle	0, 0
152	Claystone, pale-purple, 6.1 ft above base of Chinle	0, 0
151	Claystone, pale-purple, 2.0 ft above base of Chinle and top of Moenkopi	0, 0

TABLE 4.—*Analyses of samples of the Chinle formation, collected along section A, near Teasdale, about 14 miles from the Oyler mine*

[H. E. Crowe, analyst]

Field no.	Sample description	Total heavy metal (ppm)	Zinc (ppm)	Lead (ppm)	Copper (ppm)	pH
210	Claystone, silty, light-olive-gray, 63.2 ft above base of Chinle.	0	10	10	10	7.9
209	Claystone, light-olive-gray, 42.0 ft above base of Chinle.	70	70	10	20	8.0
208	Claystone, silty, light-olive-gray, 38.2 ft above base of Chinle.	0	10	10	10	8.1
207	Claystone, silty, light-olive-gray, 32.7 ft above base of Chinle.	0	20	10	10	8.1
206	Claystone, dark-reddish-brown, 24.7 ft above base of Chinle.	0	10	10	20	7.6
205	Claystone, dark-reddish-brown, 11.0 ft above base of Chinle.	0	10	10	10	4.7
204	Claystone, dark-reddish-brown, 9.7 ft above base of Chinle.	0	10	10	10	4.7
203	Claystone, silty, light-olive-gray, 7.2 ft above base of Chinle.	30	50	10	20	4.5
202	Claystone, silty, light-olive-gray, 6.0 ft above base of Chinle.	120	70	20	10	5.4
201	Claystone, silty, light-olive-gray, 2.5 ft above base of Chinle and top of Shinarump.	100	50	10	20	7.4

less other localities examined but not sampled the basal Chinle and uppermost Moenkopi are bleached if Shinarump conglomerate is present. If the Shinarump conglomerate is absent so is the bleaching. The bleaching, therefore, seems to have been accomplished by solutions in the permeable Shinarump conglomerate.

The relationship between the ore deposition and the bleaching is significant because the correct interpretation of this relationship may lead to better understanding of the ore genesis. Three possibilities present themselves: Bleaching preceded ore deposition, bleaching accompanied ore deposition, and bleaching followed ore deposition.

If the bleaching preceded ore deposition the Shinarump conglomerate must have been saturated with a slightly reducing acid solution prior to ore deposition. The bleaching solution must have contained copper and zinc because these metals were deposited in the bleached zone. Such a solution would have to have been similar to the ore-bearing solution except for the absence of uranium. Explaining the successive appearance of two slightly reducing acid solutions differing only with respect to their uranium content presents many difficulties.

If the bleaching accompanied ore deposition they were probably both effects of the same solution. Both effects were caused by a slightly reducing acid solution. The simplicity of this explanation lends it support.

If the bleaching followed ore deposition the bleaching was probably caused by normal ground water in the zone of oxidation. Normal ground water which has come in contact with oxidizing sulfides could readily acquire the slightly reducing acid character requisite for iron solution. Some bleaching near uranium deposits is undoubtedly of this type (Alice Weeks, oral communication, 1954).

The samples collected near the Oyler mine were all collected close to the land surface and undoubtedly have been subjected to the affect of weathering. However, the bleached zone appears to be related more to the upper contact of the Shinarump conglomerate than it is to the land surface. In other areas, both in Shinarump and Morrison ore deposits, similar bleaching has been noted associated with deep unoxidized ore. In addition, the amount of bleaching is known to increase near ore and has even been used as a guide in prospecting. It is for these reasons, in addition to the chemical evidence mentioned, that the writer believes that most of the bleaching was probably caused by the ore solutions.

In whatever manner the history of the bleached zone is interpreted, the results of this brief chemical study indicate that primary dispersion of heavy metals in the vicinity of the uranium deposits may be more extensive than the primary dispersion of the uranium itself. If this relation can be verified by additional study, field tests for heavy metals might prove to be useful as a prospecting guide. Some ore deposits are characterized by dispersion of an associated element exceeding that of the ore metal of primary economic interest. Warren, DeLavault, and Irish (1952) have investigated the possibilities of using analyses of the associated elements for prospecting and use the name "pathfinder" for the element of great dispersion which is detected by analysis. By this terminology zinc and copper would be pathfinder elements if they can be used to guide the way to the Shinarump uranium deposits.

Besides indicating the chemical conditions of uranium deposition and possible geochemical prospecting applications, geochemical studies also offer some possibility of tracing the solution passageways. The thinness of the bleached zone at the Oyler mine argues against much local downward percolation of reducing acid solutions through the main mass of the Chinle. Extension of the Chinle studies and similar studies of the Moenkopi and the Shinarump formations might yield a three-dimensional picture of solution passageways helpful in determining the source of the uranium.

CONCLUSIONS

Near the Oyler mine a bleached zone at the base of the Chinle formation contains abnormal amounts of zinc and copper. This bleached zone also differs chemically from the bulk of the Chinle formation in respect to acidity, oxidation potential, and iron content. It is hypothesized that the bleaching and associated chemical changes that took place in the lowermost Chinle were caused by the same solutions which deposited the ore in the Shinarump conglomerate. Whether this hypothesis proves to be correct or not it seems evident that chemical studies may help clarify the genesis of the ore and offer promise of application of geochemical prospecting.

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