



UNITED STATES  
DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY  
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Division of Raw Materials  
U. S. Atomic Energy Commission  
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We are asking Mr. Hosted to approve our plan to submit this report for publication in Economic Geology.

Sincerely yours,

for W. H. Bradley  
Chief Geologist

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GEOLOGICAL SURVEY

PROGRESS IN RADIOACTIVE IRON OXIDES INVESTIGATIONS\*

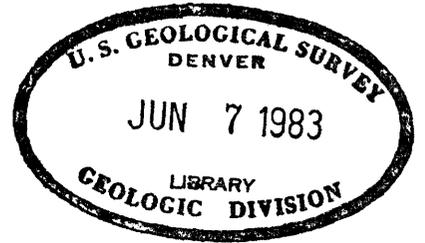
By

Tom G. Lovering

June 1954

Trace Elements Investigations Report 276

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## PROGRESS IN RADIOACTIVE IRON OXIDES INVESTIGATIONS

By Tom, G. Lovering

## ABSTRACT

The compilation of data on uranium and thorium deposits in various western states has shown that many of these deposits are closely associated with zones of secondary radioactive iron minerals. A study of these radioactive "limonites" was therefore undertaken in an attempt to find out in what form the radioactive material is present in the limonite, how it was introduced, and whether a field study of leached ferruginous cappings over uranium and thorium deposits might yield information about the depth, distribution, size, and grade of underlying ore bodies. This investigation consisted largely of a detailed study and analysis of many samples generously contributed by others--samples within the range 0.001 to 0.7 percent uranium, 0.003 to 5.3 percent equivalent uranium, and  $< 0.001$  to 4.16 percent  $\text{ThO}_2$ .

It is concluded that uranium minerals in an oxidizing sulfide environment go into solution in acid sulfate waters as uranyl sulfate in the presence of ferric sulfate. When these acid waters are neutralized, ferric sulfate hydrolyzes to form colloidal ferric oxide hydrate. This adsorbs the uranyl ion and thus removes most of the uranium from solution. As the colloidal ferric oxide hydrate ages, it crystallizes to form goethite; in this process most of the uranium is expelled to form secondary uranium mineral particles in the resulting limonite. Most thorium minerals are resistant to weathering and remain in their original form in thorian limonites.

## INTRODUCTION.

In western United States secondary radioactive iron oxides commonly occur in association with deposits of uranium and thorium. This association has been noted with a wide variety of radioactive source materials--with hydrothermal pitchblende-bearing veins in pre-Cambrian igneous rocks, with thorite deposits in metamorphic rocks, and with deposits of uranium vanadates and phosphates in sedimentary rocks.

Some secondary iron oxides that are apparently unrelated to uranium or thorium deposits, however, also show appreciable radioactivity. The presence of radioactive limonites near uranium and thorium deposits has long been used as a field guide by geologists and prospectors in various districts, but few people realize how common the association really is. Radioactive limonite has been found over uranium and thorium deposits, but many of these occurrences of radioactive limonite have not been shown to be related to such deposits. This poses a major question: do these radioactive limonites have any characteristics that will enable a field geologist to determine whether they are genetically related to nearby deposits of uranium or thorium ore? The problem of establishing criteria for the interpretation of radioactive limonites entails several related questions: 1) how is the radioactive material held by the iron oxides; 2) what chemical processes are responsible for the combination; 3) can a study of the iron oxide capping over a uranium or thorium deposit yield any information about the depth, distribution, size, and grade of ore bodies beneath?

"Limonite" is used in this report to mean any secondary iron minerals in the zone of oxidation; "limonite" commonly consists of mixture of goethite and hematite with minor amounts of jarosite or siderite, and rarely of lepidocrocite. "Gossan" is used to mean the limonite-rich outcrop over an oxidizing sulfide ore body.

#### ACKNOWLEDGMENTS

The data presented in this paper are almost entirely based on a review of the available literature and on analytical results furnished by X-ray, spectrographic and chemical analyses of selected samples. The author is indebted to the capable technicians and scientists in the Denver and Washington laboratories of the U. S. Geological Survey for their invaluable services. Thanks are also due to the many geologists

who took the time and trouble to collect samples for the author. This work was done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

## RESULTS OF INVESTIGATION

Following initial library work, a number of grab samples of radioactive and nonradioactive iron oxides were analyzed and the analytical data were compiled. Most of these samples were submitted by geologists of the U. S. Geological Survey and came from various places in western United States. The information obtained on each specimen varies with the nature and size of the sample, but in the more detailed studies it included: the location, environment and hand specimen description, petrographic description of thin and polished sections, autoradiographs, analysis for radioactivity, semi-quantitative spectrographic analyses for 36 elements, quantitative chemical analyses for FeO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Cu, Pb, Zn, MnO, and S, differential thermal analysis, and X-ray (powder-diffraction photograph) studies.

Sixty-two limonite samples from forty localities in eight states were received during 1952 and the first six months of 1953. Analyses of radioactivity are now available on forty of these samples; twenty of them contain more than 0.01 percent uranium and ten contain more than 0.01 percent thorium.

A study of spectrographic and chemical analyses of 25 samples showed no element consistently associated with uranium. Thirteen of these samples contained 0.01 percent or more of uranium; of this group nine were high in arsenic, seven in zinc, seven in cobalt, six in molybdenum, five in copper, and five in vanadium. (In this report a sample is defined to have a "high concentration" of an element if the element is present in amounts equal to or more than 10 times the average of all samples analyzed in the group.) Of the 12 samples that did not show significant concentration of uranium, six were high in arsenic, five in cobalt, three in molybdenum, three in zinc, three in vanadium and two in copper. Data on arsenic

—/ Spectrographic analyses were made by P. J. Dunton; chemical analyses by Harold Levine, Jesse Meadows, and E. C. Mallory, Jr.

are not available on three of the high uranium samples; data on molybdenum are not available on four of them; and molybdenum assays are not available on three of the low uranium samples. This information is summarized in table 1.

These data are admittedly insufficient to furnish a basis for reliable conclusions on the usefulness of any of these elements as a guide to uranium. From the available evidence it seems possible that in some districts the concentration of some elements may show a close correlation with that of uranium whereas in other districts such correlation may be lacking.

Table 1. --Percent of samples tested, containing at least 10 times the average concentration of the specified element: 1/.

High concentrations	A $> 0.01 U^{2/}$	B $< 0.01 U^{2/}$	Ratio A/B
Arsenic	90 (10 samples)	50 (12 samples)	1.8
Zinc	54 (13 samples)	25 (12 samples)	2.2
Cobalt	54 (13 samples)	42 (12 samples)	1.3
Molybdenum	67 (9 samples)	33 (9 samples)	2.0
Copper	38 (13 samples)	17 (12 samples)	2.2
Vanadium	38 (13 samples)	25 (12 samples)	1.5

1/ Concentrations determined by semiquantitative spectrographic analyses, P. J. Dunton, analyst.

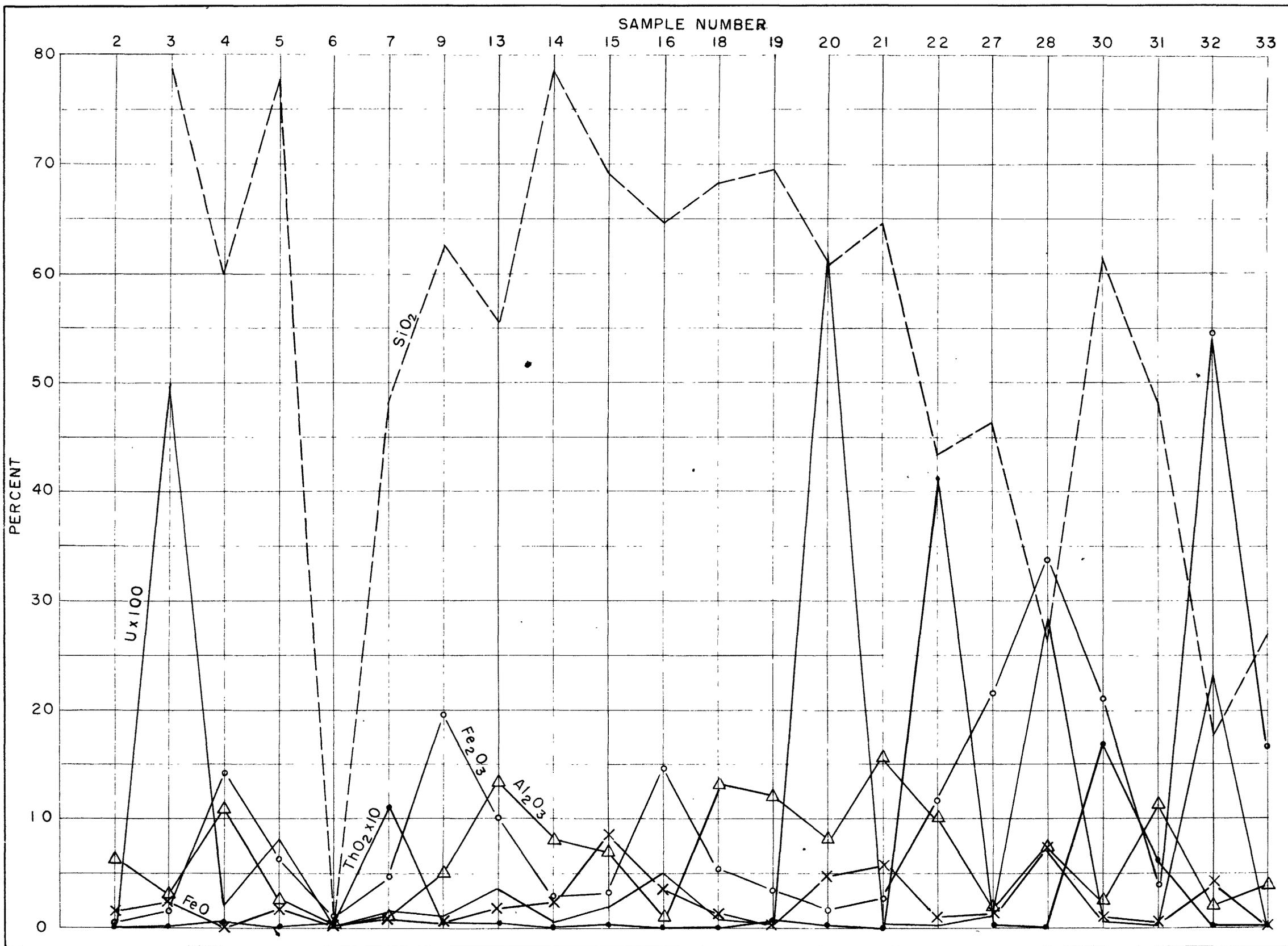
2/ Figures in parentheses are total number of samples analyzed.

Thorium, unlike uranium, shows a fairly consistent suite of associated elements in the few high thorium limonite samples on which analyses are now available. These elements are chromium, niobium, and the rare-earth elements cerium, lanthanum, neodymium, and samarium. Only about half the samples high in thorium are high in these elements, but all the samples high in these elements are also high in thorium.

Quantitative chemical analyses for  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  were made on twenty-two limonite samples   , and the results were plotted against concentrations of uranium and thorium. No consistent relationships were evident from the resulting graph (fig. 1). It was noted, however, that all the samples with an  $\text{FeO}$  content greater than 3 percent contained pyrite. The silica content of the samples ranges from 1.14 percent to 87.86 percent (in sample 2) and averages about 56 percent; the alumina content ranges from 0.22 percent to 15.47 percent and averages 6.7 percent; the ferric oxide content ranges from 0.55 percent to 54.66 percent and averages 11.7 percent; and the ferrous oxide content ranges from 0.00 percent to 8.18 percent and averages 2.24 percent.

Autoradiographs were made from polished sections of 10 samples containing large amounts of secondary iron and manganese oxides. Four samples were high in uranium, three were high in thorium, two were high in radium associated with barium sulfate, and one was low in all three elements with just enough uranium (0.01 percent) to expose the film slightly after 23 1/4 days. All of the samples high in uranium or high in thorium produced small local black dots on the film, which were usually traceable to discrete mineral particles in the polished section. The background fog produced by the iron oxide cement was slight, especially in the samples containing uranium. The two specimens whose radioactivity was largely due to the presence of radium showed much more background fog, and on megascopic examination appeared homogeneous, but these also produced local black spots and bands indicating an uneven distribution of radioactive material.

   / Samples analyzed by Harold Levine, Jesse Meadows and E. C. Mallory, Jr.



By T.G. Lovering

FIGURE 1.—GRAPH SHOWING RELATIVE AMOUNTS OF U, ThO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, AND Fe<sub>2</sub>O<sub>3</sub> IN LIMONITE SAMPLES.

Several powdered samples were tested on a portable differential thermal analysis machine to distinguish between goethite, lepidocrocite, siderite, and jarosite. The machine was first calibrated, using a series of metals and compounds with sharp melting or inversion points, to define a temperature correction curve for the machine. Known standard samples of goethite, lepidocrocite, siderite, and jarosite were then run on the machine to establish standard curves. Finally a number of unknown samples were tested on this machine and some were analyzed in the Washington laboratories of the U. S. Geological Survey 1/ on an improved model of the same machine. The results on duplicate samples agreed fairly well, although there was a tendency toward discrepancies in the low temperature range ( $20^{\circ}$  -  $250^{\circ}$ C). The resulting graphs were checked against mineral determinations made by X-ray studies, and also against the quantitative iron oxide assays. It appears that goethite, siderite, and jarosite each give characteristic endothermic peaks if the mineral makes up 10 percent or more of the sample tested. None of the samples analyzed contained sufficient lepidocrocite to give a diagnostic thermal break.

One sample was run on a thermal balance, but the resulting weight loss curve showed no strong inflections. Chemical and X-ray data indicate that this sample contains about 13 percent iron, nearly all of it in the form of jarosite. The weight loss curve showed two very slight, broad inflections, one at about  $400^{\circ}$ C, the other at about  $700^{\circ}$ C. These correlate approximately with the endothermic breaks given by jarosite.

X-ray powder diffraction studies 2/ have been made on twenty-two samples high in iron whose equivalent-uranium, uranium, and thorium content are known. Five of these samples contained more than 0.05 percent uranium and all of these contained goethite as a major constituent, two contained lepidocrocite, and one contained siderite and pyrite in addition; none contained hematite. Four samples were low in both uranium and thorium; one of these contained jarosite, and the other contained goethite and an unidentified manganese oxide mineral. These results suggest that uranium-bearing limonites are likely to be high in goethite and low in hematite, but considerably more data are needed to test this hypothesis adequately.

1/ P. D. Blackman, and C. J. Parker, analysts.

2/ A. J. Gude, 3rd, and W. F. Outerbridge, analysts.

A sample from Fall River County, S. Dak., contained carnotite associated with specks or bands of goethite in a white bleached zone of a red hematitic sandstone. At Garo in Park County, Colo., cavities in a red sandstone contain crystals of tyuyamunite. Bands of red hematitic sandstone in white sandstone at the same deposit have outer rims of brown limonite (goethite?); these in turn are bordered by a yellow zone containing disseminated tyuyamunite. On the other hand, a sample of silicified red hematitic sandstone from near Joseph City, Navajo County, Ariz., contains 0.08 percent uranium, but uranium minerals are not visible in the specimen. It thus appears that there are exceptions to the generalization that uranium does not occur associated with red hematite.

Megascopic studies on radioactive iron-oxide samples have thus far yielded relatively little information. No radioactive limonite sample exhibiting a relict boxwork or sponge texture has yet been received. Most of the samples contain ferruginous minerals either as a cement between quartz grains or as a thin coating on fracture surfaces; the few exceptions consist of dense massive limonites that are so fine grained as to appear amorphous. The color of the limonite samples that contain more than 0.05 percent uranium varies from a light-yellow ochre through various shades of yellow brown, orange, and chocolate brown to a very dark brown; the following color symbols on the rock color chart distributed by the Geological Society of America, are characteristic of these rocks; 10YR-7/4, 10YR-6/6, 10YR-5/6, 5YR-3/4, and 5YR-2/2. The red browns and reds are notably lacking. Most of the high thorium limonites, on the other hand, have a distinctly reddish color.

Only a few thin sections cut from radioactive limonite samples have yet been examined petrographically. Distinct uranium minerals are visible under the microscope in nearly all the samples that contain more than 0.05 percent uranium. One section showed a highly radioactive sooty black mineral that resembles pitchblende in appearance, intimately intergrown with goethite; in another, a veinlet partly filled with uranophane cuts massive goethite. Also, in the thorium-rich samples, intense radioactivity is usually traceable to small grains of thorite, but a few of these samples produced noticeable background fog on auto-radiographs, suggesting that some thorium was present in the limonite, possibly in the form of microscopic thorite particles.

## DISCUSSION

A primary ore body consisting largely of pyrite, with subordinate pitchblende in a relatively non-reactive gangue, should be chemically unstable in the zone of oxidation. According to Bateman and Emmons the pyrite oxidizes and dissolves with the formation of ferrous sulfate and sulfuric acid; ferrous sulfate in turn oxidizes to ferric sulfate and ferric hydroxide; and finally the ferric sulfate breaks down to yield ferric hydroxide and more sulfuric acid (Bateman, 1942; Emmons, S. H., 1892; Emmons, W. H., 1917). The presence of  $H_2S$  in solution will inhibit the solution of the sulfides and precipitate sulfides from acid sulfate solutions (Foreman, 1929).

Decomposing organic matter in sedimentary rocks could furnish hydrogen sulfide, and even after decomposition, carbonaceous material in the presence of calcium carbonate can reduce iron-sulfate solutions with the precipitation of iron sulfide (Thiel, 1930). This mechanism might explain the association of sulfides with carbonaceous material in some deposits of the Colorado Plateau.

On the other hand, in an oxidizing environment near the surface, where  $H_2S$  and carbonaceous matter are absent, pyrite should break down to the ferrous sulfate and sulfuric acid. Oxidation of ferrous sulfate to ferric sulfate is not noticeably affected by  $H_2SO_4$  in concentrations less than 0.5 N.; the reaction is facilitated by high concentration of oxygen and  $FeSO_4$ , and by high temperature (McBaine, 1901). This oxidation would be further facilitated by gamma radiation from any uranium associated with the sulfide (Amphlett, 1952; Hardwick, 1952). Ferric oxide hydrate forms by the hydrolysis of ferric sulfate on neutralization of the acid solution or by simple dilution at a pH of about 3. It is precipitated as a gelatinous hydrosol, which after ageing and partial dehydration yields goethite ( $Fe_2O_3 \cdot H_2O$ ); lepidocrocite is formed by the oxidation of hydrous ferrous iron compounds (Rooksby, 1951). Goethite yields hematite by dehydration; lepidocrocite yields magnetic ferric oxide or maghemite (Guild, 1934; Peacock, 1942). In the  $Fe_2O_3-H_2O-SO_3$  system goethite is the stable form below  $130^\circ C.$ , hematite above that temperature (Tunell and Posnjak, 1931). This may help to explain why, in supergene deposits, uranium is commonly associated with goethite rather than hematite.

Secondary limonite minerals may be derived from ferruginous carbonates as well as from pyrite. In this paper emphasis has been placed on limonite of sulfide derivation because of the close association between pyrite and uranium oxides both in the vein deposits of the Colorado Front Range and in the sandstone deposits of the Colorado Plateau. Siderite is present, however, in many thorian limonites and recent studies of carnotite deposits in South Dakota indicate that uranium may have been precipitated with iron-manganese carbonates. Limonite formed from these carbonate deposits should be radioactive (L. R. Eage, oral communication).

Pitchblende is also unstable in an oxidizing acid environment. This mineral is commonly assigned the formula  $UO_2$ ; actually it does not have a fixed composition but consists of a mixture of  $UO_2$ ,  $UO_3$  and daughter products such as Ra and Pb in varying proportions. The  $UO_3$  forms hydrates, which are fairly stable under ordinary atmospheric conditions but which are readily soluble in acid sulfate waters.  $UO_2$ , on the other hand, does not readily form a hydrate, nor is it susceptible to attack by dilute  $H_2SO_4$  (Katz and Rabinowitch, 1951). This results in differential leaching of  $UO_3$  and residual enrichment of  $UO_2$ , Pb, and Ra, where pitchblende is subject to attack by sulfuric acid solutions (Phair and Levine, 1953). The  $UO_3$  hydrates go into solution to yield  $[UO_2]^{++}$  (uranyl ion), and in acid sulfate solutions this may form complexes such as  $[UO_2(SO_4)_2]^{2-}$  or  $[UO_2(SO_4)_3]^{4-}$ . Uranium is precipitated from acid solutions when they are neutralized; the pH at which this takes place is a function of the original concentration of  $[UO_2]^{++}$ . A decrease in  $[UO_2]^{++}$  concentration from 1 percent to 0.1 percent raises the precipitation pH from 4.5 to 6.0. At high dilution uranium can remain in solution as the solution goes from acid to alkaline (Kraus and Nelson, 1948). In alkaline solutions it is present as the uranate  $[UO_4]^{=}$  or diuranate  $[U_2O_7]^{=}$ . The uranyl ion  $[UO_2]^{++}$  is strongly adsorbed on hydroxide soils of Fe, Si, or Al (Rankama and Sahama, 1950), and ferric oxide hydrate will remove uranium from solution down to a concentration of one or two parts per million (Rodden, 1951).

Because the ionic radius of uranium is about 1.05 (Katz and Rabinowitch, 1951) and that of Fe is about 0.67, it is unlikely that uranium would substitute for Fe in minerals formed from a uranium-bearing ferric hydroxide hydrosol.

Thus it is suggested that uranium originally present as pitchblende would be adsorbed by colloidal ferric oxide hydrate; and, subsequently, when the ferric oxide hydrate crystallizes, the uranium is expelled to form any of a variety of secondary uranium minerals depending on the environment. In the absence of some such adsorbing or precipitating agent dilute uranium-bearing solutions could move for long distances, as a change from acid to neutral or alkaline conditions alone might not cause precipitation.

Thorium minerals are more stable in the zone of oxidation than uranium minerals and tend to form mechanical concentrations (Fersman, 1952). However,  $\text{ThO}_2$  (thorianite) that has not previously been heated above  $600^\circ\text{C}$  is slightly soluble in dilute  $\text{H}_2\text{SO}_4$ .  $\text{Th}^{+4}$  is removed from solution by  $\text{Fe}_2\text{O}_3$  hydrate. It co-precipitates as thorium hydroxide, which slowly goes over to the more stable thorium oxide hydrate (Rodden, 1951).

The end product of the alteration and leaching of sulfide ore bodies-- the limonitic gossan--has been carefully studied by Emmons, S. H. (1892) and Emmons, W. H. (1917), Locke (1926), Blanchard and Boswell (1927, 1928), Bateman (1942), and others. They all emphasize the importance of the following three factors in interpreting the leached outcrop: (1) the composition (chemical reactivity) of the gangue or country rock, (2) the mineral assemblage and texture, and (3) the chemical processes involved in the leaching of the outcrop (Blanchard and Boswell, 1928).

The wall rock or gangue surrounding sulfide ore bodies may be either non-reactive (quartz or barite), moderately reactive (feldspar) or highly reactive (calcite). In regions of moderate rainfall in a non-reactive environment many sulfides, on weathering, break down to soluble sulfates; these are carried away in the ground water leaving only voids. In an arid climate in a non-reactive environment a substantial part of the iron is precipitated as hydrous oxides coating fractures, even at some distance from the source. In a moderately reactive environment the acid sulfate waters resulting from the oxidation of sulfide bodies are

slowly neutralized, resulting in the development of gossans with textures characteristic of the sulfides from which they were derived. In a highly reactive environment the acid waters are neutralized almost immediately, resulting in the formation of a hard, dense, siliceous limonite replacing the former sulfide (Locke, 1926).

The mineral assemblage and texture determine the nature of the leached outcrop. In finely disseminated sulfide deposits, the sulfide particles are commonly too small to produce a relict sponge or boxworks; the outcrop of a massive sulfide deposit, on the other hand, frequently develop these textures. No sponge or boxworks textures were developed in any of the radioactive limonite samples examined by the author, hence the original mineral assemblage is not known. The chemical processes involved in the leaching of a pyrite-bearing outcrop have been previously discussed.

"Limonite" gossans consist largely of goethite, hematite, silica, sulfates of iron and lead, and rarely lepidocrocite (Boswell and Blanchard, 1927). The presence of jarosite in a gossan indicates the oxidation of pyrite above the water table in an arid climate (Boswell and Blanchard, 1927); abundant kaolinite clay or red limonitic jasper on a leached outcrop are also characteristic of the weathering and oxidation of pyrite. In leached cappings resulting from the oxidation of copper-iron sulfides a high ratio of copper to iron is indicated by: 1) a high proportion of indigenous to transported iron, 2) a high proportion of hematite relative to goethite or jarosite (Locke, 1926). The color of a gossan may be diagnostic of the parent sulfide (Bateman, 1942). The color of a limonite depends on the composition, the degree of hydration and the size of the grains. Brick red indigenous limonite is usually derived from pyrite, maroon or seal brown indigenous limonite suggests the former presence of chalcocite with pyrite, and orange to ochre yellow indigenous limonite may represent a mixed sulfide ore containing galena (Bateman, 1942, p. 251-254; Blanchard and Boswell, 1928). The color of transported limonites is a less reliable criterion of the primary minerals from which they were derived than that of indigenous limonites.

Only a few samples containing indigenous limonite associated with pyrite and pitchblende have thus far been collected by the author. In all of these the color is dark brown (5 YR 2/2 - 5 YR 3/4). The color of transported radioactive limonite varies widely.

#### SUMMARY

Uranium minerals in an oxidizing sulfide body dissolve in the acid sulfate waters produced. Uranium is probably carried in these waters either as the uranyl ion or as a uranyl sulfate complex. As these acid waters become neutralized, either by reaction with wall rocks or by dilution, the ferric ion hydrolyzes to form colloidal ferric hydrate. This  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  sol, together with any colloidal silica present, coagulates and precipitates; the uranyl ions are adsorbed on the surface of the colloidal particles and removed from solution. As the ferric hydrate ages and dries, it crystallizes to form the mineral goethite. As uranium has a much larger atomic diameter than iron, it cannot substitute for the latter in the space lattice of goethite or hematite. It is, therefore, excluded from the crystal structure and forms distinct secondary uranium minerals scattered through the iron oxide minerals. Various other elements such as arsenic and molybdenum, that have ionic radii closer to that of iron, may substitute to some extent for iron in the lattice of goethite.

Uranium or uranium minerals are rarely associated with hematite, but a few radioactive hematite gossans are known. The ratio of hematite gossans to goethite gossans is very small, and the scarcity of radioactive hematite may largely reflect this relation.

Thorium is most frequently found in such minerals as thorite and monazite, which do not readily decompose in the zone of oxidation. Most of the high thorium limonite samples that have been studied contain grains of thorite in an iron oxide matrix. This is to be expected because thorium, like uranium, has a much larger atomic diameter than iron. Thorium, however, differs from uranium in that it does not form a soluble thoranyl ion in acid solutions. On the basis of this preliminary study, it appears probable that, unless the ore has a primary zoning, the tenor of thorium in oxidized gossans should closely approximate the grade of primary ore at depth, allowing for the porosity of the gossan. No such generalization for uranium deposits can be made.

## LITERATURE CITED

- Amphlett, C. B., 1952, The radiation chemistry of ferrous-ferric systems, part I, reactions in air equilibrated solutions: *Discussions, Faraday Soc.*, no. 12, p. 144-155.
- Bateman, A. M., 1942, *Economic mineral deposits*, John Wiley and Sons, New York, p. 245, 250, 251-254, 256-257.
- Blanchard, Roland, and Boswell, P. F., 1928, Status of leached outcrops investigation: *Eng. and Min. Jour.*, v. 125, p. 280-285, 373-377.
- Boswell, P. F., and Blanchard, Roland, 1927, Oxidation products derived from sphalerite and galena: *Econ. Geology*, v. 22, no. 5, p. 420-453.
- Emmons, S. H., 1892, The chemistry of gossan: *Eng. and Min. Jour.*, v. 54, p. 582-583.
- Emmons, W. H., 1917, The enrichment of ore deposits: *U. S. Geol. Survey Bull.* 625, p. 106-107.
- Fersman, A. E., 1952, *Geochemical and mineralogical methods of prospecting*: *U. S. Geol. Survey Circ.* 127. (translated from Russian by Lydia Hartsock and A. P. Pierce.)
- Foreman, Frederick, 1929, Hydrothermal experiments on solubility, hydrolysis, and oxidation of iron and copper sulphites: *Econ. Geology*, v. 24, no. 8, p. 811-837.
- Guild, F. N., 1934, Microscopic relations of magnetite, hematite, pyrite and chalcopyrite: *Econ. Geology*, v. 29, p. 107-120.
- Hardwick, T. J., 1952, The oxidation of ferrous sulfate solutions by X-rays--the absolute yield: *Can. Jour. Chem.*, v. 30, p. 17-22.
- Katz, J. J., and Rabinowitch, Eugene, 1951, The chemistry of uranium, part I, the element, its binary and related compounds: *McGraw Hill Book Co.*, New York, p. 244-330.
- Kraus, K. A., and Nelson, F., 1948, The hydrolytic behavior of uranium and the transuranic elements, part I, the +5 and +6 oxidation states: *U. S. Atomic Energy Comm. Rept.* MDDC-1705.
- Locke, Augustus, 1926, *Leached outcrops as guides to copper ore*: *Williams and Wilkins Co.*, Baltimore.
- McBaine, J., 1901, Oxidation of ferrous solutions by free oxygen: *Jour. Phys. Chem.*, v. 5, p. 623-628.
- Peacock, M. A., 1942, On goethite and lepidocrocite: *Trans. Roy. Soc. Canada*, ser. 3, v. 36, p. 107-118.
- Phair, George and Levine, Harry, 1953, Notes on the differential leaching of uranium, radium, and lead from pitchblende in  $H_2SO_4$  solutions: *Econ. Geology*, v. 48, no. 5, p. 358-369.

- Rankama, Kalervo, and Sahama, T. G., 1950, *Geochemistry*: University of Chicago Press, p. 632-639.
- Rodden, C. J., 1951, *Analytical chemistry of the Manhattan Project*: McGraw Hill Book Co., National Nuclear Energy Series, Manhattan Project, Tech. Ser., Div. VIII, v. 1, p. 4, 8-9, 166.
- Rooksby, H. P., 1951, Oxides and hydroxides of aluminum and iron; in Brindley, G. W., *X-ray identification and crystal structures of clay minerals*: London, The Mineralog. Soc. Clay Minerals Group, p. 244-265.
- Thiel, G. A., 1930, Experiments bearing on the biochemical reduction of sulphate waters: *Econ. Geology* v. 25, p. 242-250.
- Tunell, George, and Posnjak, Eugen, 1931, The stability relations of goethite and hematite: *Econ. Geology*, v. 26, p. 337-343.