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The Importance of Dissolved Free Oxygen During
Formation of Sandstone-Type Uranium Deposits

by

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by H. C. Granger and C. G. Warren

Abstract

One factor which distinguishes the genesis of roll-type uranium deposits from the Uravan Mineral Belt and other sandstone-type uranium deposits may be the presence and concentration of dissolved free oxygen in the ore-forming solutions. Although dissolved oxygen is a necessary prerequisite for the formation of roll-type deposits, it is proposed that a lack of dissolved oxygen is a prerequisite for the Uravan deposits.

Solutions that formed both types of deposits probably had a supergene origin and originated as meteoric water in approximate equilibrium with atmospheric oxygen. Roll-type deposits were formed where the Eh dropped abruptly following consumption of the oxygen by iron sulfide minerals and creation of kinetically active sulfur species that could reduce uranium. The solutions that formed the Uravan deposits, on the other hand, probably first equilibrated with sulfide-free ferrous-ferric detrital minerals and fossil organic matter in the host rock. That is, the uraniferous solutions lost their oxygen without lowering their Eh enough to precipitate uranium. Without oxygen, they then became incapable of oxidizing iron sulfide minerals. Subsequent localization and formation of ore bodies from these oxygen-depleted solutions, therefore, was not necessarily dependent on large reducing capacities.

Introduction

Supergene ore-forming solutions and other meteorically derived waters get their start in a virtually limitless reservoir of oxygen--the atmosphere. Equilibrium partitioning of oxygen between the vapor and fluid phases (Henry's Law) permits the water to contain a few parts per million dissolved free oxygen. If some of this dissolved oxygen is used by reactions with soils, rocks, or vegetation at the surface, it is constantly replenished. As meteoric water infiltrates deeper beneath the water table, however, it becomes more and more isolated from the atmosphere and, finally, additional oxygen is no longer available if it is depleted by reactions with the enclosing rocks. This small range of oxygen contents, from a few parts per million to essentially nil, makes remarkably significant differences in the behavior of supergene ore-forming solutions. Although speculative at best, it is our contention that solutions of similar origin can form deposits comparable to those at Yeelirrie, Australia, near the ground water table; can form roll-type deposits where they penetrate into pyrite-bearing rocks well below the ground water table, and can form deposits similar to those in the Uravan Mineral Belt, Colorado and Utah, where dissolved oxygen has been completely removed from the ore-bearing solutions. We are not suggesting that each of these types of deposits was formed from solutions whose only differences are in oxygen content, nor that a sequence of such deposits will be found at succeeding depths in any one place. We do suggest, however, that as a supergene uranium-bearing solution percolates downward, it may get more than one opportunity to have its uranium removed.

Because Yeelirrie-type deposits contain oxidized uranium minerals and occur near the ground water table, there is little question about the role played by oxygen in their formation. So, we will not discuss these deposits further but will concentrate on roll-type deposits and the primary Uravan Mineral Belt-type deposits.

Deposits in the Grants Mineral Belt, New Mexico, and in the Shinarump and Mossback Members, and other conglomeratic units at the base of the Chinle Formation in Colorado, Utah, and Arizona, may also have been formed from oxygen-depleted solutions. Among these several varieties of sandstone-type uranium deposits, the Uravan deposits were selected for comparison with roll-type deposits because each has such similar shapes and element distribution.

Background

In the late 1960's and early 1970's several papers pointed out the differences between Wyoming-Texas roll-type uranium deposits and other sandstone-type uranium deposits. By the late 1970's, however, some writers (Rackley, 1976; Gabelman, 1977, p. 63; DeVoto, 1978; Galloway, 1978) were implying that they were all genetically similar and appear to be different principally because of host rock differences and post ore alteration. In particular, these investigators point to the similarities in shape of the ore zones found in the Wyoming-Texas roll-type deposits and in the Uravan Mineral Belt deposits. They also emphasize the similarities in zonation of elements and minerals in deposits from the two areas.

We intend to show, in the parts that follow, that the differences in the above deposits may partly owe to differences in the oxygen content of the ore-forming solutions and resulting differences in the processes of localization. Roll-type deposits originated from solutions that contained dissolved oxygen; Uravan Minerals Belt deposits originated from solutions that

were relatively depleted in dissolved oxygen. The following descriptions of the Uravan and roll-type deposits are necessarily brief and are intended only to give the reader a cursory acquaintanceship with the genesis of these deposits. Greater detail can be gained from Garrels and Larsen (1959), Fischer (1968), Harshman (1972), Rackley (1976), Shawe, and others (1959), and Granger and Warren (1969).

Uravan Mineral Belt Deposits

The Uravan Mineral Belt deposits are enclosed by continental fluvial sandstones in the Salt Wash Member of the Jurassic Morrison Formation. This unit is overlain by the Brushy Basin Shale Member, which consists generally of montmorillonitic mudstones enclosing scattered, thin, discontinuous sand lenses.

Although it thins, locally, over some diapiric salt structures, the Brushy Basin evidently covered the Salt Wash throughout the Mineral Belt by the time the succeeding Cretaceous Dakota Sandstone was deposited. Towards the source, to the southwest, the Brushy Basin probably completely blanketed the Salt Wash for at least 150 km.

Ore deposits within the Salt Wash are dominantly tabular, peneconcordant layers but, in many places, these layers roll sharply across the strata. In cross section these rolls form crude S- or C-shapes. The axes of the rolls commonly follow depositional trends and their shapes and positions seem to be controlled partly by the permeability, attitude of mudstone lenses, scour surfaces, and crossbedding in the host rock.

Much of the Salt Wash is red and oxidized but the ore bodies are completely enclosed by pale-gray pyrite-bearing and coalified-fossil-wood-bearing zones. Distribution of ore layers and rolls within the bleached rock is seemingly about as random as the cut-and-fill and other fluvial features

which control them. There are no obvious visible or compositional differences between rock on opposite sides of unweathered ore layers and rolls. Both are bleached, variably pyritic, and commonly contain fragments of coalified fossil wood. There is no evidence that the rock on one side of the ore was once oxidized and has since been rereduced.

In some mines, the rocks on opposite sides of weathered ore bodies and thoroughly oxidized ore bodies show very subtle differences in appearance that have not been explained; from this, it does seem likely that rocks on opposite sides of ore have undergone slightly different geochemical histories. These visible contrasts have not been recognized,¹ however, in pristine, unoxidized ores.

Primary, unoxidized Uravan deposits contain uranium in the form of uraninite and coffinite; sparse molybdenum in the form of jordisite; and selenium in the form of ferroselite, clausthalite, and perhaps, native selenium. The most abundant ore element in most of the deposits, however, is vanadium and it commonly occurs as vanadium clays and micas that fill interstices and corrode and replace sand grains. Scattered within the vanadium alumino-silicate minerals, particularly within the richer deposits, are low valent vanadium oxide and oxyhydroxide minerals such as montroseite, paramontroseite, doloresite, duttonite, and others.

Trash zones containing fragments of coalified fossil wood commonly contain the richest uranium concentrations but lower grade ore tends to be a continuous layer even where little or no carbon trash occurs. Similarly, the

¹After this manuscript was written, D. J. Carpenter and M. B. Goldhaber, U.S. Geological Survey, showed us some unpublished data (1979) on uranium deposits in the Salt Wash Member in the Henry Mountains, Utah area, which indicate significant differences in permeability and the distribution of elements on opposite sides of unoxidized ore layers in that district.

pyrite-marcasite content of ore is commonly greater than that of adjacent barren sandstone but no consistent correlation between uranium and iron disulfides is evident. There is no good evidence that either sulfide or organic matter were dominant localizing controls throughout the ore layers.

Ore layers and rolls typically contain asymmetric distributions of uranium and vanadium. Although both elements are anomalously enriched across the dark, visible ore layer, the vanadium in some instances is richest to one side of the center of the layer and the uranium on the other (Shawe, 1966; Brooks and Campbell, 1976; also unpublished data). Selenium is generally concentrated in a narrow band along one side of the ore layer, particularly along the concave border of a roll. The distribution of jordisite has not been well described but it typically occurs, at least in part, as irregular patches as much as a few meters away from the uranium-vanadium ore layer. Data are so scanty that we do not know whether it can occur on both sides of an ore layer or only on one side. Neither do we know if it occurs on the side adjacent to the selenium layer or on the opposite side, although we suspect that jordisite must tend to occur on the side opposite the selenium layer.

These deposits probably formed early in the history of the host rocks (Miller and Kulp, 1963), when it is inferred that the rocks were saturated with essentially stagnant diagenetic-stage connate (?) waters. An unexplained change in the hydraulic system at that time permitted the penetration of an ore-forming solution whose movements tended to be localized in conduits controlled by the more permeable channel sand units of the enclosing reduced host rocks (Shawe, 1956). At the interfaces between the connate waters and the interpenetrating ore-forming solutions, ore bodies were formed by geochemical reactions which are not yet thoroughly understood. The choking of pore spaces by vanadium clays and micas lowered permeability in the ore zones,

which inhibited flow across the interface but permitted a certain amount of interchange by diffusion. Since the conduits for the ore solutions generally conformed to broad, horizontal-channel sand units, the resulting ore bodies also were typically fairly flat-lying, but were discordant or roll-shaped at local permeability barriers along the surfaces and near the lateral margins (See Shawe, 1956 and 1966; Granger, 1976).

The elongation of ore bodies and the axes of rolls tend to be aligned along depositional directions in the host rocks. Preexisting minerals such as pyrite (Weeks, 1956, p.189; Weeks and others, 1959, p. 70; Elston and Botinelly, 1959, p. 210), apparently were not destroyed where enveloped by either the ore forming or connate solutions. In conclusion, it seems evident that the geochemical reactions which resulted in deposition of ore did not directly depend on alteration of minerals of the host rock. Rather, it was a reaction between the components of two unlike solutions which was instrumental in forming the ores, and the positions of the ore bodies mark the surfaces of the conduits in which the ore solutions flowed.

Roll-type uranium deposits

Roll-type uranium deposits typically occur in continental fluvial sandstones of Tertiary age although deposits in older rocks are known. For the most part, these sandstones are overlain by fine-grained, clay-rich, tuffaceous sedimentary units; in some cases tuffaceous rocks are also the host rocks. Sites of host rock deposition range from intermontane basins to broad interior or coastal alluvial plains.

In most instances there is evidence that the edges of the host and closely associated rocks were truncated and beveled by erosion before succeeding formations were deposited. Age determinations, in at least some instances, suggest that this beveling was closely related, in time, to ore

formation. The ore bodies are generally found no more than 20 or 30 km downdip from these beveled edges of the units in which they occur.

The unaltered host rocks are typically feldspathic to arkosic sandstones containing a little disseminated authigenic pyrite. The pyrite is inferred to have resulted from the early anaerobic reaction between biogenic H_2S and iron minerals such as magnetite and hematite. In most sandstones containing organic matter such as fossil wood, the H_2S probably originated from the actions of sulfate-reducing bacteria. In organic-free sandstones the H_2S seems to have been introduced into the host sandstones as fault-leaked sour gas from underlying formations (Goldhaber and others, 1978).

All roll-type deposits are accompanied by a tongue of oxidized host rock. This tongue seems to originate at the beveled surface, noted above, and to project downdip as much as about 30 km. Although unweathered host sandstone surrounding the tongue invariably contains as much as a few percent pyrite, most of this pyrite has been destroyed within the tongue and replaced by disseminated red iron oxides, orange oxyhydroxides, or white to green smectites. The ore bodies and mineralized rock, where present, faithfully follow the surfaces of the oxidized tongues. They are typically thinnest and lowest grade along the upper and lower surfaces (limbs) of the tongues and tend to thicken and become richer along the discordant, or roll, surfaces at the margins of the tongues.

Ore deposits are erratically distributed along the leading and lateral edges of the tongues. In some instances remnant ore bodies are found completely enclosed in the oxidized tongues.

The outline (roll front) of the oxidized tongue in plan view commonly has an irregular, almost amoeboid, shape. Protrusions of the tongue may extend along permeable paleo-channels. Ore bodies may occur along relatively smooth

parts of the roll front or along the tips or lateral margins of the protrusions. The axes of the rolls can be oriented parallel to or at any angle to the sedimentary trends in the host rock.

Primary unoxidized roll-type deposits contain uranium in the form of uraninite and coffinite, and selenium in the form of ferroselite and elemental selenium. Vanadium is anomalously enriched within the uranium ore in some instances as the minerals paramontroseite and haggite. Molybdenum may be present as jordisite or it may be missing. Iron sulfides as pyrite and marcasite are almost universally more concentrated in the ore than in barren unoxidized rock. These minerals typically form overgrowths and occupy interstices and display minor, if any, evidence of replacement of original detrital grains. Permeability of the rocks commonly does not appear to be seriously impaired even in fairly high grade ore.

The deposits invariably display some evidence of mineral and elemental zoning. The redox interface on the concave side of rolls commonly marks a narrow band in which selenium is concentrated. Bordering this band is the ore zone containing anomalous amounts of uranium and iron sulfides and variable concentrations of vanadium. On the convex side of the ore zone, and generally separate from it by a few to several hundred meters, there may be a zone enriched in molybdenum and variable amounts of calcite.

It is inferred that these deposits started to form when downward percolating, oxygen-rich meteoric waters gained access through the beveled edges of the host rocks. In some instances these waters were probably enriched in uranium through such processes as leaching of tuffaceous sediments newly deposited on these beveled surfaces. The oxygen-rich waters started to react with the pyrite (and marcasite) in the host rock and formed what has been referred to as a geochemical cell (Rackley, and others, 1968).²

Oxidation of pyrite, by waters with a limited amount of dissolved oxygen results in soluble, metastable, partly oxidized sulfur species which are carried along in the ground water until they spontaneously undergo a disproportionation reaction. This means that they divide into equivalent amounts of more reduced species such as H_2S , and more oxidized species such as $SO_4^{=}$. The sulfate ($SO_4^{=}$) is kinetically inert to further redox reactions leaving the more reactive reduced species such as the metastable species and H_2S to control the Eh of the environment. Oxidized uranium being carried in the ground water is reduced and precipitated in this environment where the Eh is changing from oxidizing to strongly reducing. Elements such as selenium, vanadium, and molybdenum also precipitate at appropriate places in this geochemical gradient, which is determined largely by Eh. Ore bodies, therefore, formed where optimum conditions of oxygen supply, pyrite, and uranium content occurred, together with the favorable pH, perhaps controlled largely by calcite.

It is evident that controlled oxidation of a sulfide mineral such as pyrite or marcasite is essential to maintain the conditions necessary for uranium reduction and precipitation. Therefore, ore bodies can only form along the advancing edges of an oxidizing tongue. Ore bodies can be bypassed and even surrounded by the oxidized tongue in positions where they are unstable but where they may persist for a considerable length of time. Ore bodies can also be shunted against the margins of paleochannels where they may persist but can not grow because little or no pyrite is undergoing

²Rackley and others (1968) suggest that pyrite oxidation and H_2S formation are the products of bacterial action. We are treating these processes as though they are entirely non-biogenic, following Granger and Warren (1969). The oxygen consumption is essentially the same under either concept, however.

oxidation. In this position, it may appear that the axis of the roll is parallel to the direction of ground water movement much as with Uravan Mineral Belt deposits, but it must be remembered that a roll-type deposit is essentially dormant in this position, whereas a Uravan deposit develops in this position.

Discussion

Where unweathered deposits occur below the water table in the Uravan Mineral Belt, they are completely enclosed by reduced, pyrite-bearing rock. The deposits are not localized along boundaries between oxidized and reduced rock, as is the case with roll-type deposits. It is conceivable that the rock on one side of the deposit was once oxidized and has since been reduced but no evidence for such a process has yet been presented. If the ore-forming solutions contained any dissolved oxygen, it would surely have reacted with the pyrite, leaving evidence of its passing in the form of iron oxyhydroxides. The implication to be gained is that the ore-forming solutions contained no free oxygen. The ore was localized, not owing to a reaction between solution and host rock, but owing to some other mechanism. Shawe (1956), referring to the roll-shaped, layer-like ore bodies in deposits near the south end of the Uravan Mineral Belt, wrote that they "were formed by precipitation of minerals at an interface between solutions of different composition".

The rolls in Uravan deposits, therefore, formed along the lateral margins of conduits containing the ore forming solutions; and the process of ore localization seemingly do not involve extensive alteration or destruction of minerals already present in the host rocks. In these respects they contrast sharply with Wyoming-Texas roll-type deposits.

Roll-type uranium deposits are formed where reducing conditions are imposed by the metastable sulfur species that are derived from reactions between sulfide sulfur and limited amounts of dissolved free oxygen. Other soluble oxidants normally found in natural solutions are generally carried at such low concentrations that, even if they react with sulfide minerals, they can form only insignificant amounts of metastable sulfur species. The total of oxidized Fe, Mn, and even uranium and vanadium species in solution under typical conditions probably do not exceed 1 ppm. Therefore, a most important point is that significant amounts of these reactive reducing metastable sulfur species are formed from sulfide minerals only if free oxygen is present or, if oxygen can be acquired from some other source. Oxidation by simple electron exchange will not produce the metastable species which are vital to the genetic system. Roll-type ore can form only where sulfide minerals are being destroyed. As stated by Granger (1976) this "is the fundamental difference between these deposits and (Uravan Mineral Belt-type) deposits--the roll-type deposits depend on contemporaneous host rock alteration for their growth and development." Therefore, during the period of ore development deposits accumulated along the distal edges of tongues where solutions were free to flow through the permeable ore bodies. Wherever a roll-type deposit got shunted to the lateral edges of the oxidized tongue, where the solution was flowing parallel to the roll surface, oxidation of pyrite became virtually nonexistent and ore accumulation ceased. Dormant ore bodies might persist at these localities, however, because of their protected position.

If it is assumed that a supergene uranium-bearing solution got its start near the surface where abundant atmospheric oxygen was present, an obvious question is concerned with how oxygen might be removed from a uranium-bearing solution without reducing and precipitating the uranium. At intermediate pH

values, in systems whose dissolved oxygen concentration is fixed simply by the oxidation of, for example, magnetite to $\text{Fe}(\text{OH})_3$,³ equilibrium is reached at conditions represented by line A-B (fig. 1) and the oxygen content is depleted to about 10-29 ppm. The uranyl dicarbonate complex ion remains soluble under these conditions. On the other hand, in a system controlled by oxidation of iron disulfide to $\text{Fe}(\text{OH})_3$, the concentration of metastable sulfur species far exceeds the concentration of any soluble iron ions present. Redox reactions of the system are thus controlled, at least temporarily, by the metastable sulfur species in solution (fig. 2). Under these conditions uranium is reduced and becomes insoluble (Granger and Warren, 1969, and unpublished data). Although it may be a relatively sluggish process, uranium-bearing solutions can therefore be stripped of all dissolved oxygen in a sulfide-free system by reaction with ferrous-iron-bearing minerals such as amphiboles, pyroxenes, biotite, and magnetite. Under these conditions the uranium remains oxidized and in solution. However, in an iron disulfide-bearing system similar oxidation reactions result in uranium reduction and precipitation. Once oxygen is depleted, however, a uranium-bearing solution can flow through a pyrite-bearing rock without reacting with pyrite or precipitating uranium.

The reason for the contrast between roll-type ore solutions which were evidently relatively oxygen rich, and Uravan-type ore solutions which were probably oxygen depleted, may lie partly in the distance the ore solution must travel between the surface and the sites of ore deposition (fig. 3). A

³Uranyl ion cannot be reduced (under equilibrium conditions) as long as free oxygen is dissolved in the system. After oxygen is eliminated, however, thermodynamic calculations suggest that magnetite could be oxidized by uranyl ion if the product were Fe_2O_3 . Under the low temperature conditions generally present, ferric oxyhydroxides form more readily than Fe_2O_3 and uranyl ion reduction is improbable. We have assumed that the initial oxidized species is $\text{Fe}(\text{OH})_3$ following Hem and Cropper (1959) and Lindsay (1979).

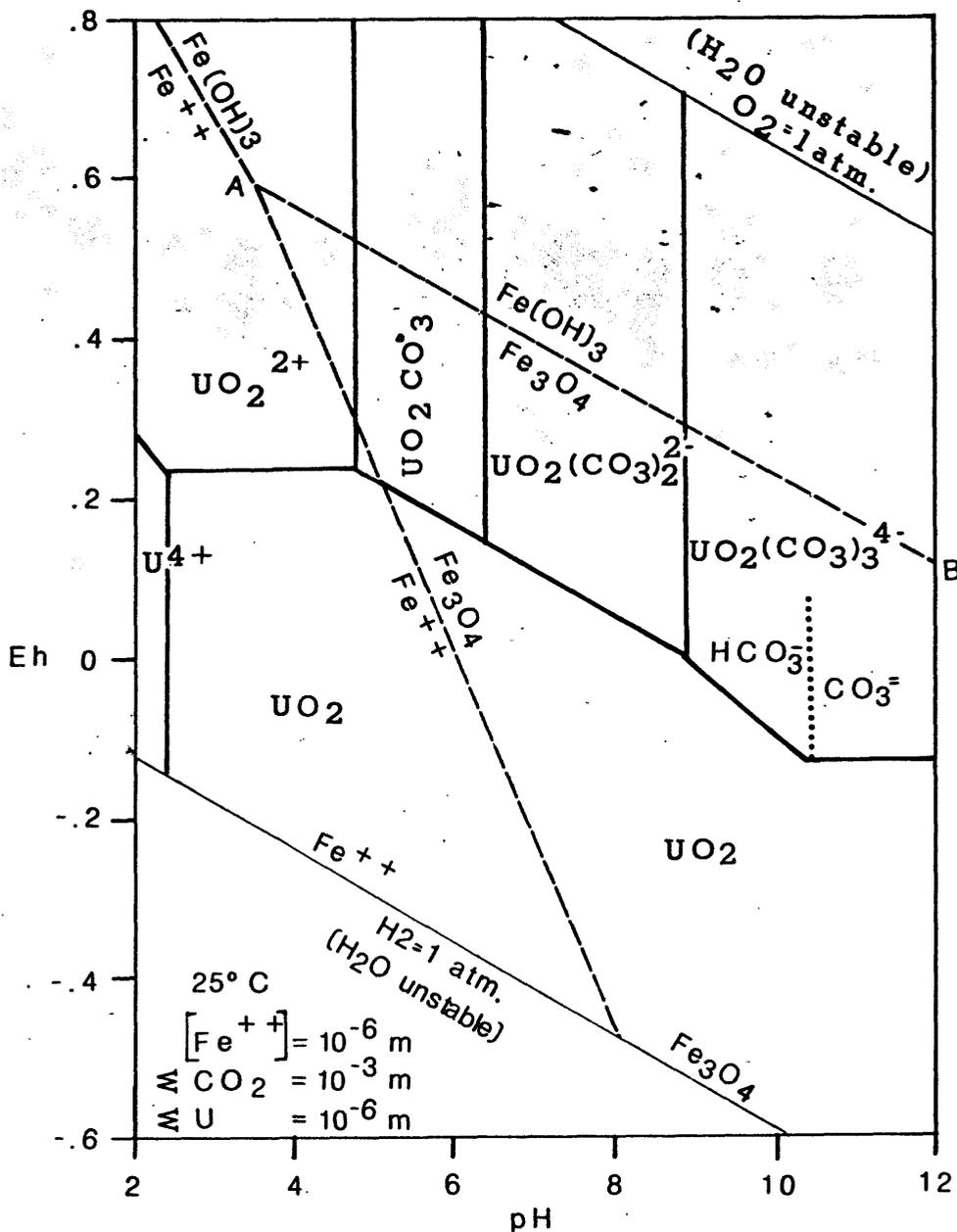


Figure 1.-Combined Fe-O-H₂O (dashed) and U-O-CO₃-H₂O (solid line) Eh-pH stability diagrams.

A solution containing dissolved O₂ and uranyl di- or tri-carbonate ions will not precipitate uranium simply by reaction with magnetite (or most other detrital mafic minerals). Once all oxygen is depleted by reaction with excess magnetite, the Eh is controlled by the iron phases and, at equilibrium, will tend to lie on or near line A-B. This is well within the fields for reasonable concentrations of soluble uranyl species.

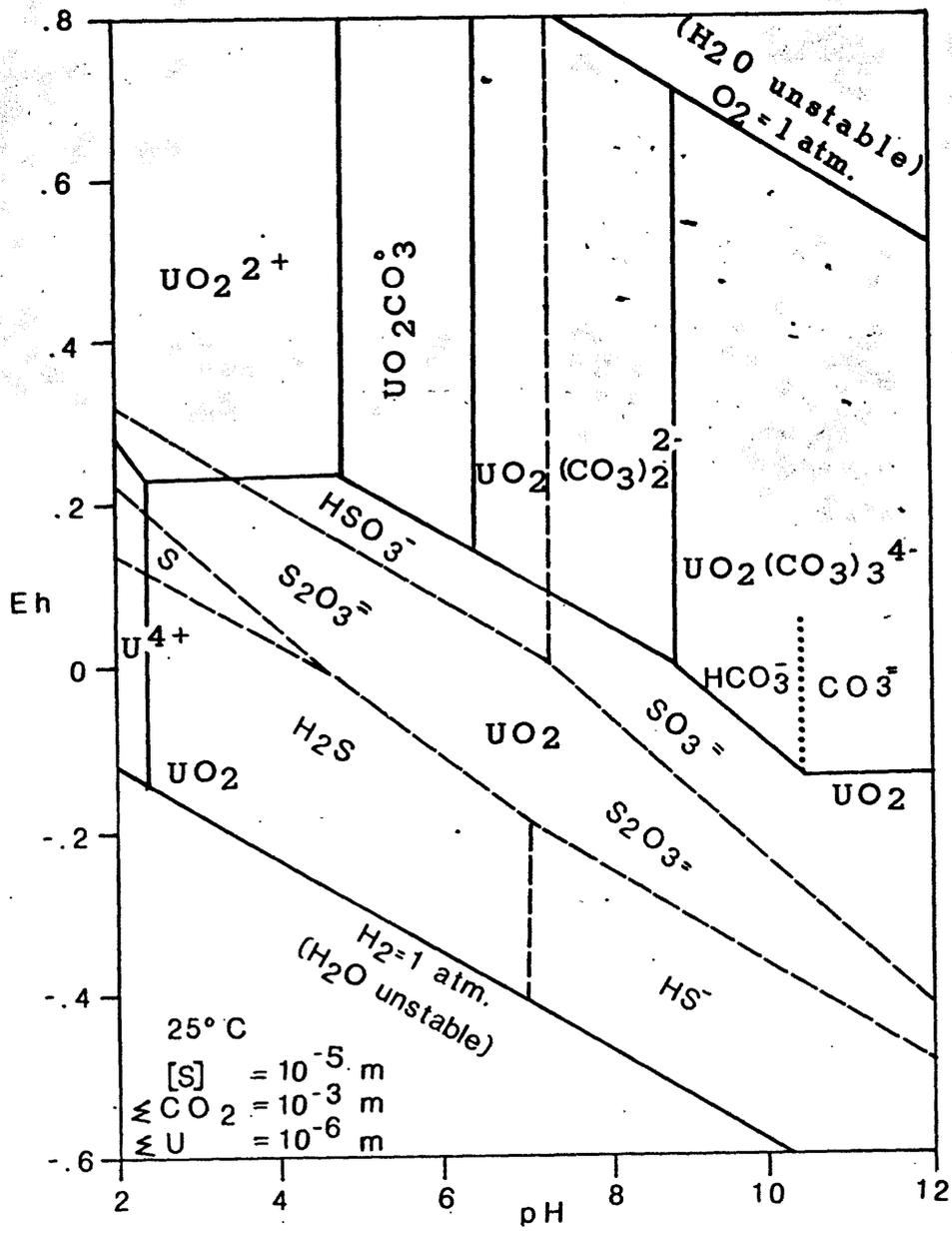
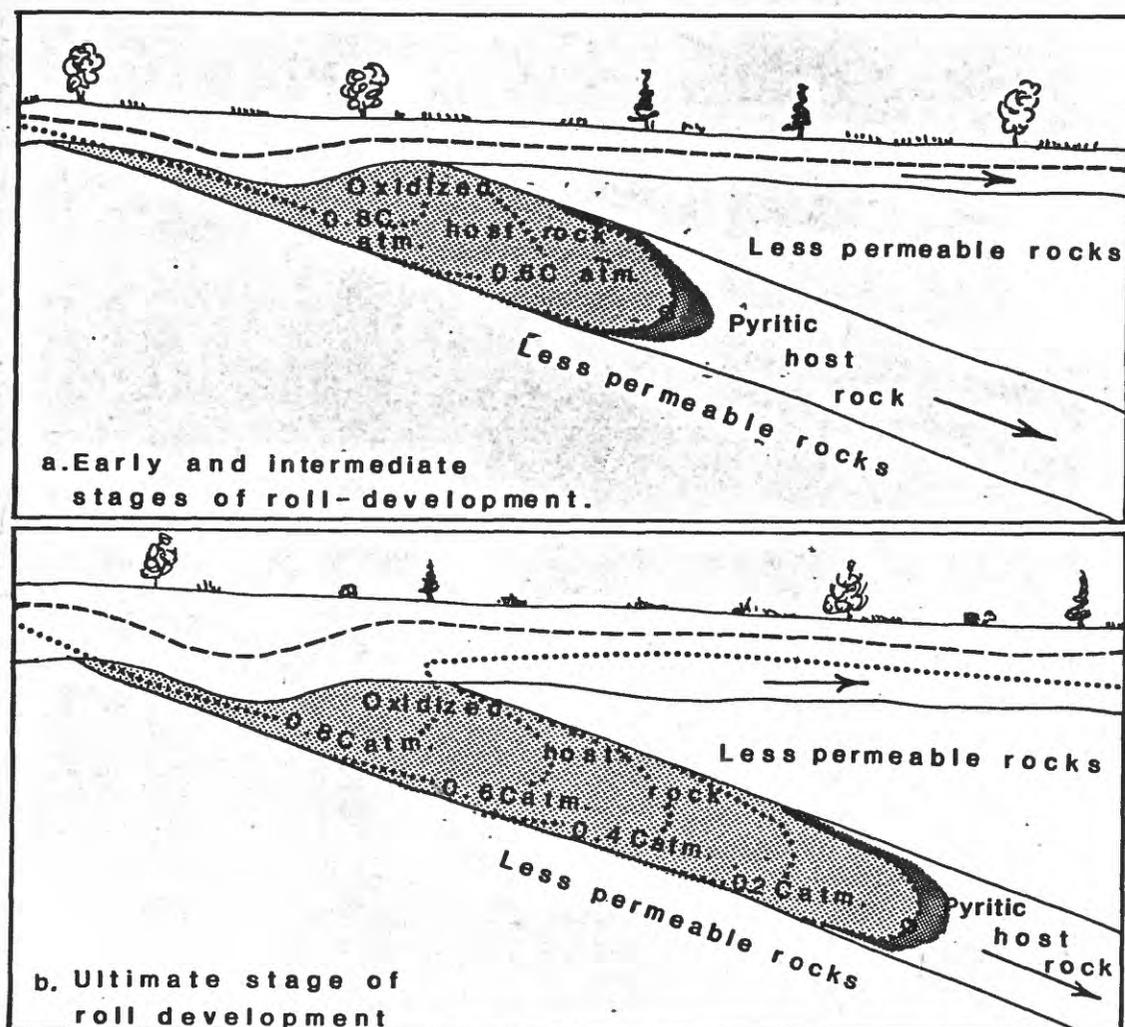


Figure 2.-Combined S-O-H₂O (dashed) and U-O-CO₃-H₂O (solid line) Eh-pH stability diagram. Oxidized sulfur species shown are the immediate, metastable products of limited or controlled oxidation of pyrite.

A solution containing dissolved O₂ and uranyl di- or tri-carbonate ions can precipitate uranium by reactions with pyrite. Once all oxygen is depleted by reaction with excess pyrite, the Eh is controlled by the metastable sulfur phases and will tend to lie within or near the S₂O₃²⁻ field. This is well within the field of stability of uraninite (UO₂).



EXPLANATION

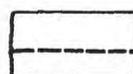
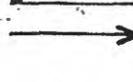
-  Unconsolidated alluvial fill and static water table
-  Host rock and roll-type uranium deposits.
-  Direction of ground water movement
- 0.6C atm.
- Contour of dissolved oxygen concentration in ground water (That is, 0.6 of the concentration in equilibrium with atmospheric oxygen)

Figure 3.-Diagrammatic cross sections to illustrate stages of groundwater maturation.

This is a highly diagrammatic, vertically exaggerated, caricature to illustrate how oxygen-bearing ground water reacts relatively abruptly with pyrite but much more slowly with most detrital ferrous iron-bearing minerals. Ultimately, as in (b), equilibrium with the detrital minerals will diminish the oxygen content to such an extent that further reaction with pyrite is not possible and the roll ceases to advance. (Actually the rate of advance becomes controlled by reaction with the detrital minerals rather than with pyrite and the roll probably becomes "smeared out" and indistinct.) If no pyrite is present, the concentration contours will be similar to (b) but no roll-type deposit will be formed. Oxidized iron minerals, however, might stain the rocks where oxygen is present. Under the conditions of (b), even after the solutions are depleted of oxygen they will continue to carry their load of soluble oxidized uranium until a favorable depositional environment is encountered.

solution traveling short distances (empirically these seem to be less than about 30 km) through a permeable oxidized tongue may retain much of its oxygen till it can react with pyrite and fossil organic matter near the distal edge of the tongue. On-the-other-hand, an oxygenated solution traveling 100 km or so through rocks containing hornblende, biotite, and magnetite may lose so much of its oxygen that it is virtually unable to oxidize significant amounts of pyrite or organic matter. Under these conditions, too low a concentration of the metastable sulfur species will be created to reduce uranyl ion and the dissolved uranium will simply pass through, virtually unaffected. It can be seen that the permeability, ground water recharge, and ferrous iron content at the host rock can markedly affect the distance through which the solutions must percolate before they reach equilibrium with the detrital ferrous-iron-bearing minerals. These distances are a function of the time that the oxygenated ground water is in contact with reactive rock and will vary greatly from aquifer to aquifer.

Uranium must be oxidized to the U^{+6} state to be mobile under most low temperature natural conditions. Therefore, it can be seen that in both roll-type and Uravan Mineral Belt types of deposits the mineralizing solutions must have been oxidizing relative to uranium and, because uraninite (UO_2) is generally present in the ore, the uranium must have been localized by reduction. This indicates that conditions within the accumulating ores were reducing with respect to uranyl ion, and an Eh gradient must have existed in and adjacent to the ore body. Associated minerals whose stabilities are sensitive to Eh would be localized at specific intervals within this gradient. It is, therefore, not surprising that element and mineral zoning are found to be similar in roll-type and Uravan-type deposits. Selenium minerals, for example, are found on the side of both deposits with highest Eh during ore genesis.

Conclusions

We think that this distinction between the ore-forming solutions that produced roll-type and primary Uravan-type uranium deposits helps to clarify several observations.

1. It explains the apparent lack of redox differences in the iron minerals on opposite sides of the ore layers in Uravan deposits, whereas pyrite is oxidized on one side of roll-type deposits.

2. Roll-type deposits seem to occur at limited distances--ordinarily less than 30 km--downdip from the truncated edges of the host rock whereas the Uravan deposits may occur 100 km or more from comparable truncated edges (that is, edges exposed at about the time of ore deposition).

3. Rather than almost invariably being enriched as are roll-type deposits, the ore stage pyrite content of primary Uravan-type deposits is erratic and shows no consistent, direct correlation with uranium content.

4. The zoning pattern of both minerals and elements across ore layers and rolls in both roll-type and Uravan-type deposits is generally similar.

Some types of organic matter can adsorb chelate, or exchange the uranyl ion directly (Szalay, 1964; Leventhal, 1979) or they may reduce it under localized nonequilibrium conditions even in the presence of dissolved oxygen (Kochenov and others, 1977). For systems not dominated by organic reactions, however, the fundamental, albeit obvious, conclusions of this study are that a uraniferous solution that is saturated with dissolved oxygen will not drop its load of uranium by reduction under equilibrium conditions until the oxygen is consumed by some means. Likewise, a uraniferous solution containing no free dissolved oxygen will not form a redox interface or roll-type deposit, in pyrite sandstone, by reactions with the pyrite. The amount of reductant required to precipitate uranium from these oxygen-free solutions is much less

than from oxygen-bearing solutions. Localization of Uravan-type deposits, therefore, probably consumed very little reductant compared to the large amounts of pyrite consumed during deposition of a roll-type deposit.

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