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TRANSPORTATION AND PRECIPITATION OF URANIUM AND VANADIUM AT LOW TEMPERATURES, WITH SPECIAL REFERENCE TO SANDSTONE-TYPE URANIUM DEPOSITS¹

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ABSTRACT

Uranium and vanadium in sandstone-type deposits of the western United States apparently have been transported to their present environment from external sources by low-temperature aqueous solutions. In this paper an attempt is made to interpret the characteristics of aqueous solutions capable of transporting significant quantities of uranium and vanadium through continental sedimentary rocks, and the changes in these

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characteristics that might result in precipitation of uraninite and other ore minerals in concentrations of ore grade. On the basis of present knowledge, the transportation environment is shown to be that of weakly alkaline, moderately reducing ground water, with an average or larger than average concentration of dissolved carbonate species ($\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{--}$). Precipitation is induced by reduction, probably by carbonaceous material or hydrogen sulfide, or both. Uranium is transported mainly in the form of the highly stable uranyl dicarbonate and tr carbonate complexes. Precipitation results from reduction of hexavalent aqueous uranium species to form uraninite, reduction of tetravalent vanadium to form montroseite, and fixation of uranyl ions by combination with potassium ions and quinquivalent vanadium to form the mineral carnotite.

INTRODUCTION

STUDIES over the past several years have shown that the complex mineralogy of the sandstone-type uranium ores is the result of the oxidation of an originally simple mineral suite (18, 37). Apparently, the minerals of this primary suite were precipitated simultaneously from aqueous solution long after deposition of the enclosing sediments (27, 30, 34, 35). In any given deposit the primary minerals are few, the common ones being uraninite, UO_{2-x} , coffinite, $\text{UO}_2(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$, montroseite, $\text{VO}(\text{OH})$, vanadium silicates, pyrite, chalcopyrite, bornite, chalcocite, calcite, quartz, and gypsum.

It is noteworthy that in these minerals the elements are in the lowest valence states characteristic of natural occurrences. Indeed, it has been demonstrated that the conditions under which the primary minerals can co-exist at equilibrium in an aqueous medium at low temperatures and pressures are near the most strongly reducing environments attainable (18). This relation has led to the postulation that the presence of ore is the result of precipitation largely induced by reduction processes; a view bolstered by the widespread occurrence of woody materials replaced by ore minerals, and by the important ore occurrences reasonably ascribed to the reducing effects of hydrogen sulfide (26).

Coleman (11), in a summary of criteria suitable for the estimation of the environment of precipitation of the ore minerals, arrived at a temperature of the order of 100°C , and a pressure of the order of a few hundred atmospheres. This temperature estimate has been substantiated by the recent work of Breger and Chandler (7), who investigated the temperature dependence of extraction of humic constituents from coalified wood in mineralized horizons. Thus deductions based on low temperature and pressure chemistry are relevant to the actual process of ore formation.

Whatever the source of uranium and vanadium, all workers are in agreement that in numerous instances these elements had to be carried long distances (a mile or more) through the pores of the host sediments before deposition occurred (18, 27, 36). These sediments are characteristically lenticular continental sandstones and mudstones. Quartz, mica, and feldspar are common minerals of these rocks and there is a variety of clay minerals, including chlorite, montmorillonite, mixed layer mica-montmorillonite, and kaolinite.

The problems of ore-element transportation and deposition can be stated in the following questions:

1. In what aqueous environments, within the range of natural conditions, can all the ore-elements be transported simultaneously at some reasonable concentration?
2. If such environments exist, are they compatible with conditions expected during transportation of waters through the pores of the host rocks?
3. What changes in environment, induced by local variations in the nature of the host rocks, can be expected to lead to precipitation of the ore mineral suite?

Our attempts to answer these questions must be looked upon as a preliminary study. In our present state of knowledge we can hope only to delineate sets of conditions that are favorable for the transportation and deposition of ore elements, and then to test these conditions against actual occurrences. We emphasize the degree of solubility of uranium and vanadium in the presence of other ions common in subsurface waters in order to elucidate possible modes of ore-element transport. This simplifies the treatment of stability relationships among the insoluble ore minerals, which are of widespread occurrence, by eliminating the need for consideration of soluble, locally distributed minerals. Our approach is to begin with a discussion of uranium solubility in pure water, and then to assess the effects of addition of other constituents.

U-O₂-H₂O SYSTEM

Relations among uranium, oxygen, and water have been summarized by Garrels (19) and by Deltombe, de Zoubov, and Pourbaix (13). The only solid phases expected to occur stably in the presence of water and variable concentrations of oxygen are uraninite, UO_{2+x}, and schoepite, UO₂(OH)₂·H₂O, which spontaneously dehydrates when exposed to the atmosphere (10). Natural uraninites apparently maintain the cubic UO₂ structure for x values up to 0.6 (8). U₃O₈, easily prepared in the laboratory, has not been found in nature (16) and is probably metastable. Thermochemical data are available only for stoichiometric UO₂. Figure 1 shows schematically the composition relations among UO₂, UO₂(OH)₂·H₂O, O₂, and H₂O, and shows that the composition of uraninite in the presence of hydrogen and water is UO₂, but that for conditions sufficiently oxidizing to permit the coexistence of UO₂(OH)₂·H₂O, its composition is UO_{2.6}.

Stability ranges of UO₂(OH)₂·H₂O and stoichiometric UO₂ are shown as functions of oxidation potential (Eh) and hydrogen-ion activity (pH) in Figure 2. However, a good deal more information than is shown in Figure 2 can be gleaned from Eh-pH diagrams that portray thermochemical consideration of the solubility of uraninite and schoepite. This involves the calculation of the activities of all the ions in the system, in equilibrium with whichever solid phase is stable under specified Eh and pH conditions. For the details of such calculations the reader is referred to the papers of Garrels (19) and Deltombe et al. (13). Deltombe et al. and Garrels considered only three

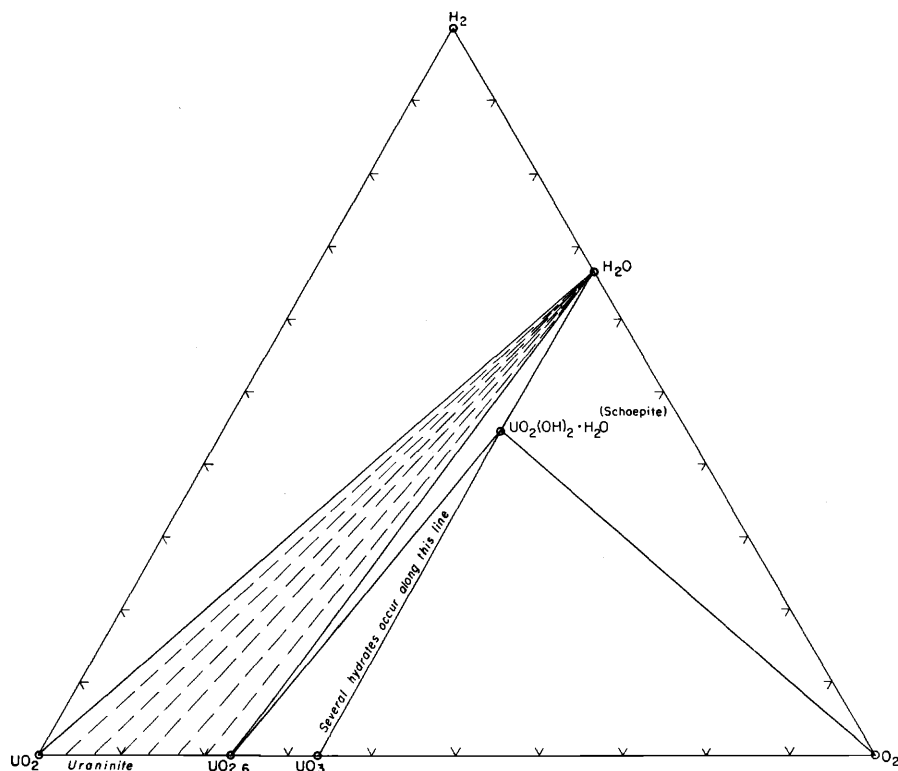


FIG. 1. Composition diagram showing probable relations among uraninite, schoepite, water, oxygen, and hydrogen at 25° C and 1 atmosphere total pressure. Percentages are molecular. Hydrates of composition lying between UO_3 and $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ are not considered.

ions, UO_2^{+2} , U^{+4} and $\text{U}(\text{OH})^{+3}$. Uranium is present in the hexavalent state in UO_2^{+2} and in the tetravalent state in U^{+4} and $\text{U}(\text{OH})^{+3}$. Figure 3 shows the relationship of these ions to schoepite and uraninite and to the additional hexavalent uranium species, H_2UO_4^- and $\text{UO}_2(\text{OH})^+$. Thermodynamic data for H_2UO_4^- and $\text{UO}_2(\text{OH})^+$ were derived from Gayer and Leider (24) and Bjerrum et al. (4) respectively.

It should be pointed out that for Figure 3 and for ensuing diagrams it is not, in general, possible to reach any selected Eh-pH value within the framework of the simple system under discussion. The addition of one or more components is necessary to reach selected Eh-pH values. The assumption is that the additional components will not disturb the diagrammed equilibrium relationships, and in simple, dilute systems such is usually the case. We return to a more critical discussion of this point in the section on correlation with natural ground waters.

In Figure 3 unbroken lines drawn between the stable solid phases and the fields of the ions indicate that total ionic activity of dissolved uranium

species in equilibrium with either solid phase is 10^{-6} . In other words, in the presence of uraninite or schoepite (whichever is stable), total ionic activity is fixed at 10^{-6} for the Eh and pH conditions shown by the solid lines. Along these lines the solid phase is no longer stable if total ionic activity is less than 10^{-6} ; all uranium is in solution. In the fields shown for the solid phases total ionic activity in equilibrium with that solid phase is less than 10^{-6} , while in the areas diagrammed for the ions total ionic activity must rise to a value greater than 10^{-6} before either uraninite or schoepite can be precipitated as a stable phase (Fig. 2 shows the stable solid phase). A dashed line representing a total ionic activity of 10^{-4} in equilibrium with the stable solid phase is included in Figure 3 to give the reader an idea of the activity gradient involved. A family of contours, parallel to the 10^{-6} and 10^{-4} contours, could be drawn to represent other values of total ionic activity in equilibrium with the solid phase. There are discrete Eh-pH conditions for which most of the uranium in solution is tied up in one ion; therefore, lines drawn between ions show conditions for which the activities of the two ions are identical.

The foregoing discussion is based on the conventions of Eh-pH diagram-

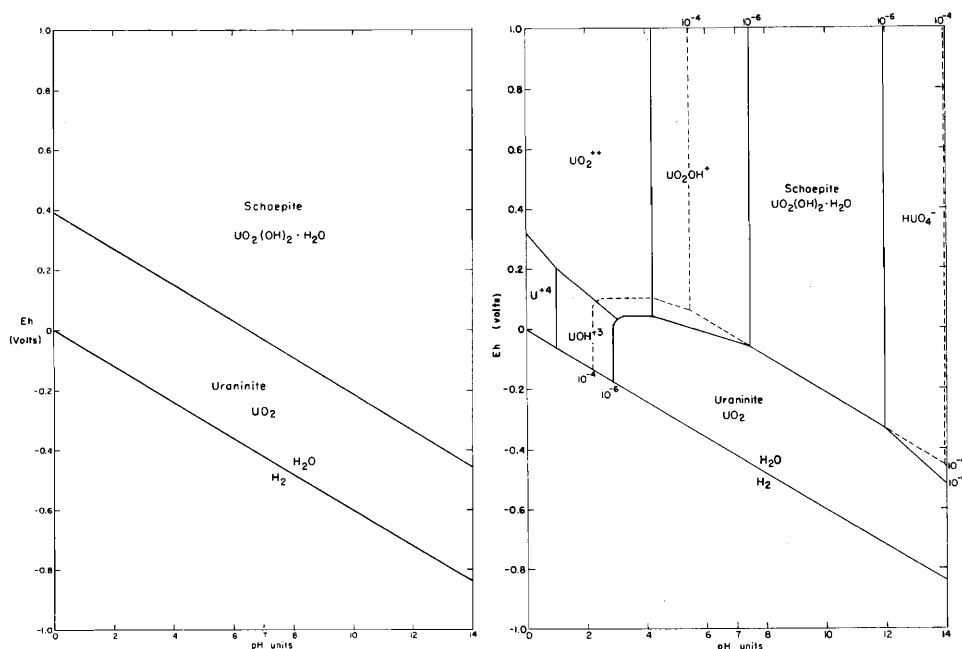


FIG. 2. (Left) Equilibrium diagram of the U-O₂-H₂O system at 25° C and 1 atm. Stability ranges of solid phases are plotted as a function of hydrogen-ion concentration and oxidation potential.

FIG. 3 (Right) Aqueous equilibrium diagram of the U-O₂-H₂O system at 25° C and 1 atm. Fields of solid phases and dissolved species are plotted as a function of hydrogen-ion concentration and oxidation potential. Boundaries of solid phases at total activity of uranium-bearing ions = 10^{-6} in unbroken lines, and at total activity = 10^{-4} in dashed lines.

ming developed by Pourbaix (31). It must be clearly recognized that the solubility areas, labeled with the ion that is their chief contributor, do not represent stoichiometric solubilities, but rather are areas in which the solubility is at least the value shown for thermodynamic equilibrium between solid phases and ionic activities. True solubility exceeds that calculated by a factor that depends on total concentration of all ions (ionic strength) and the degree of completeness of our knowledge of the ions which must be considered. In this system not all aqueous species have been considered, for a number of polyuranate complexes have been reported (4). Thermodynamic data or equilibrium constants reported for these species are in poor internal agreement. Nevertheless, it is clear that the polyuranate complexes are not sufficiently stable to alter significantly the relationships shown in Figure 3; their total effect is to increase slightly the solubility of schoepite over that portrayed in Figure 3.

Figure 3 shows that in the $\text{U-O}_2\text{-H}_2\text{O}$ system uranium is soluble only in acid or distinctly alkaline solutions and that the chief contributing ions in acid solution are the UO_2^{+2} and $\text{UO}_2(\text{OH})^+$ species, with small fields of the U^{+4} and $\text{U}(\text{OH})^{+3}$ ions also present. HUO_4^- is the main contributor to uranium solubility in alkaline solutions.

No species are shown below the water breakdown line, that is, for Eh-pH values at which the partial pressure of hydrogen exceeds one atmosphere. The assumption is that any reducing agent sufficiently powerful to reduce water and produce hydrogen at pressures of one atmosphere or greater (such as the U^{+3} ion) reacts with an excess of water to produce a more highly oxidized species.

The field shown in Figure 2 as " UO_2 " should be, as shown in Figure 1, a field of a solid changing in composition from UO_2 at the water-hydrogen boundary to $\text{UO}_{2.6}$ at the uraninite-schoepite boundary. In the absence of thermochemical data for UO_{2+x} we have assumed that only UO_2 is present. This places the uraninite-schoepite boundary at its lowest possible position on the Eh scale; the boundary between $\text{UO}_{2.6}$ and schoepite may be as much as a tenth of a volt higher, but parallel to the boundary shown. Our procedure gives uraninite its minimum stability, and somewhat overemphasizes the strength of the reducing agents necessary for its precipitation.

At any rate, we can conclude that nearly pure water is a poor transporting agent for uranium, except at pH values of about 5 or less. As will be seen later, such pH values are incompatible with the geologic occurrences of the ores.

$\text{U-O}_2\text{-H}_2\text{O-CO}_2$ SYSTEM

Essentially pure water is not to be expected in subsurface waters that are in intimate contact with rock minerals. Examination of analyses of ground waters reveals that dissolved CO_2 , in one form or another, is an important and ubiquitous constituent. The range of CO_2 content is large, but values of 100–300 ppm are common, whereas values of less than 10 and more than 10,000 ppm are uncommon.

Carbon dioxide markedly increases the solubility of the solid uranium

phases previously discussed. Bullwinkel (9) has studied its effects theoretically and experimentally, and concludes that the solid phases involved in the $\text{U-O}_2\text{-H}_2\text{O-CO}_2$ system are uraninite, schoepite, and rutherfordine, UO_2CO_3 . The dissolved species, in addition to those already considered, are $[\text{UO}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}]^{-2}$ and $[\text{UO}_2(\text{CO}_3)_3]^{-4}$. These complexes are hereafter referred to as UDC (uranyl dicarbonate complex) and UTC (uranyl tricarbonate complex) respectively. We have computed the free-energy of formation values of rutherfordine, UDC, and UTC using the data of Bullwinkel (9) and the recent ΔF°_f of schoepite given by Deltombe et al. (13). The equilibrium constant for the dissociation of UTC to UDC plus carbonate, reported by Blake and others (5), is in good agreement with that reported by Bullwinkel (9).

The $\text{U-O}_2\text{-H}_2\text{O-CO}_2$ system may be considered from two standpoints, either open to an externally controlled P_{CO_2} , or closed, with a fixed amount of CO_2 in the system. An Eh-pH plot with P_{CO_2} equal to the partial pressure of CO_2 in the atmosphere is useful for portraying surface weathering conditions. However, atmospheric CO_2 has limited access to percolating ground waters, so it is more realistic to consider such waters as constituting a closed system in which a fixed addition, or periodic additions, of CO_2 proportionate among various CO_2 -bearing species according to an Eh-pH characterized environment. In such a closed system P_{CO_2} is variable, a function of pH. The total of the activities of all CO_2 -bearing species is constant for any addition of CO_2 reaching equilibrium. This constant is referred to as ΣCO_2 .

Details of the calculations required in constructing the diagrams presented here are given in the Appendix.

Open System.—Relations among uranium-bearing solid and dissolved species as functions of Eh, pH, and a P_{CO_2} value of $10^{-3.4}$ atm. (the partial pressure of CO_2 in the atmosphere) are shown in Figure 4. The general Eh-pH- P_{CO_2} diagram is shown in Figure 5 (Fig. 4 is a cross-section of Fig. 5 at $P_{\text{CO}_2} = 10^{-3.4}$ atm.) As in Figure 3, unbroken contours between ions and solid phases represent a total activity of dissolved uranium species of 10^{-6} , while dashed contours represent a total activity of 10^{-4} . For clarity, 10^{-4} total ionic activity contours are omitted in Figure 5. In Figure 4 and thereafter, formulas designating fields for solid phases are underscored.

Comparing Figures 4 and 5 with Figure 3 shows the marked effect of CO_2 , even at low partial pressures. Whereas Figure 3 is composed largely of areas indicating fields of solid phases, Figures 4 and 5 are dominated by areas of dissolved species. Uranyl carbonate complexing causes a wide field of solubility to exist under oxidizing conditions at essentially all pH values. The field of schoepite, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, as an insoluble compound is almost entirely eliminated, and although rutherfordine, UO_2CO_3 , does appear as a new phase, it occupies a minor part of the diagrams. For a given temperature, the schoepite-rutherfordine transition depends only on activity of water and P_{CO_2} . Assuming that $a_{\text{H}_2\text{O}} = 1$, Garrels (20) has shown that the equilibrium P_{CO_2} between these two phases is very close to the partial pressure of CO_2 in the atmosphere.

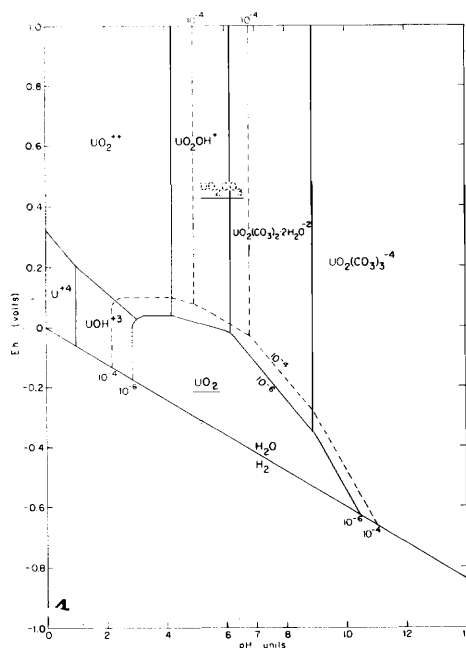


FIG. 4. Aqueous equilibrium diagram of the $\text{U-O}_2\text{-H}_2\text{O-CO}_2$ system at 25°C and 1 atm., and with P_{CO_2} constant at $10^{-3.4}$ atm. Boundaries of solid phases are drawn for total ionic activity of 10^{-6} (unbroken lines) and 10^{-4} (dashed lines). Formulas designating fields for solid phases are underlined.

Note that in Figure 4 a field for rutherfordine is only defined for a total activity of uranium bearing ions of 10^{-4} ; there is no field for this mineral when total ionic activity drops to 10^{-6} . Thus, in a weathering environment the concentration of uranium in solution must be around 10^{-5} moles/liter or greater before rutherfordine can be precipitated under the most favorable pH conditions (around pH 6.0).

In acid, oxidizing solutions uranium is transported as UO_2^{+2} and $\text{UO}_2(\text{OH})^+$, in neutral solutions as UDC , and in alkaline solutions as UTC . Not only does addition of CO_2 tend to eliminate schoepite, it causes the field of uraninite to diminish. As P_{CO_2} increases in the system stronger and stronger reducing agents are required to remove uranium from solution as uraninite.

Closed System.—The complexing effect of CO_2 on uranium is also vigorous for those conditions where the total amount of CO_2 (ΣCO_2) in the system may be regarded as fixed. In Figure 6 ΣCO_2 is taken as 10^{-3} (that is, the sum of the activities of all ions that contain CO_2 , including UDC and UTC , is 10^{-3}). This corresponds to a modest 44 ppm CO_2 in solution. Uranium, as UDC and UTC , is soluble in a wide range of environments. The small field of rutherfordine (again defined only for total uranium ion activity of 10^{-4}) indicates the restricted conditions under which this mineral forms.

Schoepite is soluble under all but very alkaline conditions when uranium ion activity is 10^{-4} . It has no field of stability when aqueous uranium drops to 10^{-6} . The expansion of the UTC field, at the expense of the UDC field, under mildly reducing conditions is interesting. Recalling that the total amount of carbonate is fixed, it is obvious that the activity of carbonate and bicarbonate must increase as the uranyl carbonate complexes begin to break

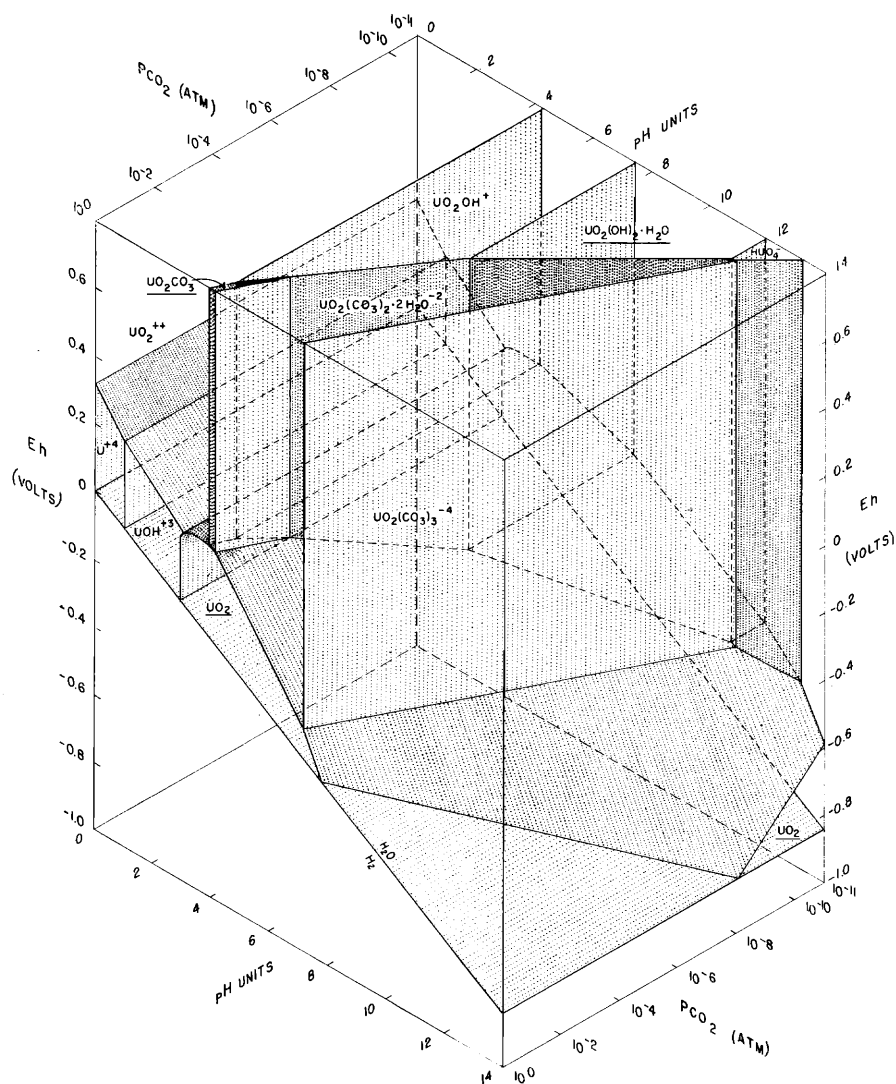
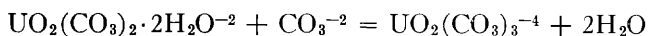


FIG. 5. Aqueous equilibrium diagram of the $\text{U}-\text{O}_2-\text{H}_2\text{O}-\text{CO}_2$ system at 25°C and 1 atm. PCO_2 is the third coordinate. Boundaries between solid phases and dissolved species are drawn for total ionic activity of 10^{-6} .

down under reducing conditions. The increased activity of CO_3^{2-} and HCO_3^- is reflected by an increase in the UTC/UDC ratio, as can be seen from the following reaction:



The uranyl carbonate complexes are stable enough to tie up considerable concentrations of uranium under slightly reducing conditions.

ΣCO_2 is raised to 10^{-2} in Figure 7, thus enlarging the dominant areas of UDC and UTC. Increasing ΣCO_2 extends the area of UTC relative to

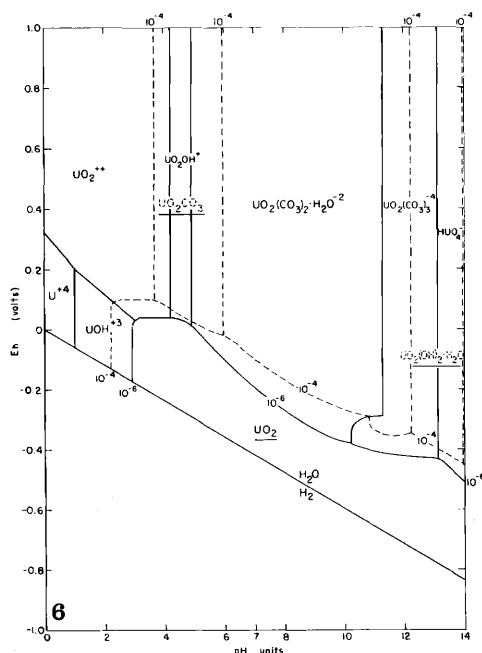


FIG. 6. Aqueous equilibrium diagram of the U-O₂-H₂O-CO₂ system at 25° C and 1 atm., and with $\Sigma\text{CO}_2 = 10^{-3}$. Boundaries of solid phases are drawn for total ionic activity of 10^{-6} (solid lines) and 10^{-4} (dashed lines).

UDC because UTC contains more carbonate. Conversely, the field of UTC disappears entirely when ΣCO_2 falls to $10^{-3.8}$. The upper boundary of the uraninite field in equilibrium with the uranyl carbonates is noticeably lower in Figure 7 than in Figure 6.

The trends discussed for Figure 7 are continued for Figure 8 where ΣCO_2 is 10^{-1} .

Equilibrium between carbonate species, water, and graphite is ignored in Figures 7 and 8 because it is generally irreversible. The effects of organic matter, hydrocarbons, and other reducing agents on the solubility of uranium is considered in a subsequent section. It is curious to note that in spite of

the increase in CO_2 , the field of rutherfordine remains the same size, although it does move to slightly more acidic conditions. The reason for this behavior is that the activity of UO_2^{+2} in equilibrium with rutherfordine decreases with increasing ΣCO_2 at exactly the same rate that the activity of UDC in equilibrium with rutherfordine increases. Actually, the field of rutherfordine increases very slightly at the expense of UO_2 .

All the relations discussed for the closed system are pictorially summed in Figure 9 with ΣCO_2 the third coordinate. All boundaries between solid

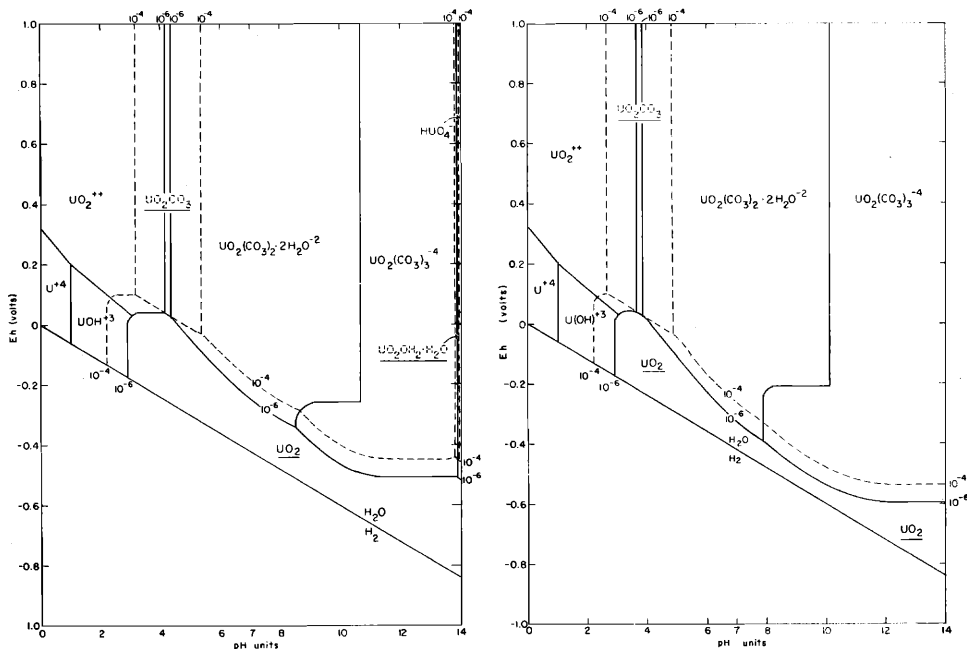


FIG. 7. (Left) Aqueous equilibrium diagram of the U-O₂-H₂O-CO₂ system at 25°C and 1 atm., and with $\Sigma\text{CO}_2 = 10^{-2}$.

FIG. 8. (Right) Aqueous equilibrium diagram of the U-O₂-H₂O-CO₂ system at 25° C and 1 atm., and with $\Sigma\text{CO}_2 = 10^{-1}$.

phases and ions in solution are shown for a total activity of uranium-bearing ions of 10^{-6} .

In short, then, the most noteworthy effect of adding CO₂ to the U-O₂-H₂O system is to increase enormously the solubility of uranium.

V-O₂-H₂O SYSTEM

The vanadium-water system has been studied by Garrels (17), Deltombe, de Zoubov, and Pourbaix (12), and Evans and Garrels (14). The V-O₂-H₂O diagram computed by Evans and Garrels (14) is shown in Figure 10. As the solid phase-ionic activity contours represent a total ionic activity of

merization states of the ions, but these differences are of very little importance in this study.

U-V-K-O₂-H₂O-CO₂ SYSTEM

The addition of vanadium and potassium to the U-O₂-H₂O-CO₂ system can now be discussed. No new ionic complexes are introduced. Carnotite, K₂(UO₂)₂V₂O₈·1-3H₂O, is the only new and well-defined solid phase that is insoluble, although a number of soluble solid phases are known. Mention will be made below of the rather widespread, but poorly defined, mineral, rauvite. No measured value of ΔF°_f of carnotite is available, however, we were able to compute a value from experimental solubility determinations conducted by Marvin and Magin (Marvin, R. F., and Magin, G. B., written communication). Data resulting from these experiments are not sufficiently accurate to permit a rigorous free-energy calculation, nor is such a calculation essential for the purpose of this paper. Instead, the lowest possible free-energy value

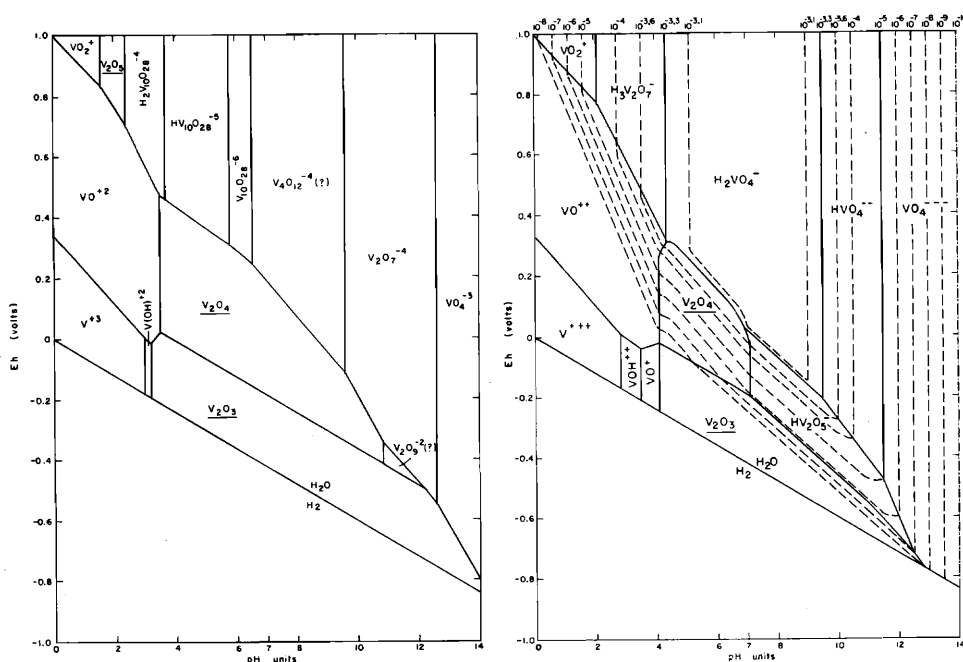
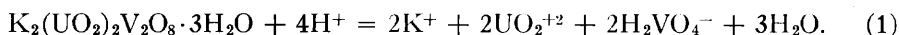


FIG. 10. (Left) Aqueous equilibrium diagram of the V-O₂-H₂O system at 25° C and 1 atm.; after Evans and Garrels (14). Boundaries between solid phases and dissolved species are drawn for total ionic activity of 10⁻². The formulas designating fields of solid phases are underlined.

FIG. 11. (Right) Aqueous equilibrium diagram of the V-O₂-H₂O system at 25° C and 1 atm. Ionic nomenclature is from Deltombe et al. (12). Boundaries between solid phases and ions in solution are drawn for total ionic activity of 10⁻³ (unbroken lines). Dashed lines represent ionic activity contours of the H₂VO₄⁻ ion.

was chosen consistent with Marvin and Magin's determinations. Thus, the field of carnotite shown in ensuing diagrams is the largest possible.

Briefly, calculations were made in the following manner. In pure water (devoid of CO_2) at a pH of 7.0 carnotite has a solubility of 3×10^{-7} moles/liter at 25° C. Assuming that ²:



The concentration of each of the ionic species is $2 \times 3 \times 10^{-7} = 10^{-6.22}$ moles/liter. As the solubility of carnotite in pure water is very low, concentration can be equated with activity. The activity gradient of UO_2^{+2} in equilibrium with schoepite is two orders of magnitude change per unit change in pH. At a pH of 7, and in the absence of CO_2 , the activity of UO_2^{+2} in equilibrium with schoepite is $10^{-8.4}$. At this pH, however, most of the soluble uranium is present as $\text{UO}_2(\text{OH})^+$. The activity of this ion in equilibrium with schoepite should be $10^{-5.55}$. Marvin and Magin's data, though, indicate that in pure water, carnotite slowly hydrolyzes to a colloidal hydrated uranium oxide, which suggests either schoepite is somewhat more stable, or $\text{UO}_2(\text{OH})^+$ less stable, than previously considered. The latter seems more probable.

The equilibrium constant for the reaction given by (1) is:

$$K_a = \frac{(\text{K}^+)^2(\text{UO}_2^{+2})^2 (\text{H}_2\text{VO}_4^-)^2}{(\text{H}^+)^4}. \quad (2)$$

Substituting ionic activities and assuming that if $a_{\text{UO}_2^{+2}}$ rises above $10^{-8.4}$ carnotite, rather than schoepite, will be stable (to give a minimum ΔF°_f carnotite):

$$K_a = 10^{-13.7}. \quad (3)$$

Since

$$\Delta F^\circ_{\text{reaction}} = RT \ln K_a = -1.364 \log K_a \quad (4)$$

$$\Delta F^\circ_{\text{reaction}} = 18.6 \text{ Kcal}. \quad (5)$$

The free-energies of all products and reactants are known except for carnotite.

$$\Delta F^\circ_{\text{reaction}} = \Delta F^\circ_{\text{products}} - \Delta F^\circ_{\text{reactants}} \quad (6)$$

$$\Delta F^\circ_f \text{ carnotite} = -1,294 (+0 \text{ to } +5) \text{ Kcal}. \quad (7)$$

A rough check on this value was provided from data given by Barton (3). Barton assumes $\text{V}_4\text{O}_{12}^{-4}$ is the vanadium ion causing precipitation of carnotite. Barton's experiments consisted, in part, of a determination of the time required to precipitate carnotite from a concentrated solution containing K_2SO_4 ,

² Calculations on this and the following pages concerning carnotite stability are made on the basis of the H_2VO_4^- ion of Deltombe et al. (12) rather than the $\text{V}_4\text{O}_{12}^{-4}$ ion of Evans and Garrels (14) because this choice enormously simplifies such calculations. While this procedure may be criticized for seeming to perpetuate a less probable interpretation of vanadium chemistry, careful comparison of the two interpretations shows that for neutral, alkaline or reducing conditions it makes no difference which interpretation is used in deriving carnotite stability. The scheme of Deltombe et al. (12) does give carnotite a slightly greater range of stability in acid environments than does that of Evans and Garrels (14).

$\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ and NaVO_3 , at various pH values. We obtained the approximate pH value of such a solution just saturated with carnotite by extrapolating precipitation time to infinity. Concentrations were modified by estimated activity coefficients. As the extrapolation was only an approximation, we derived a free-energy value for carnotite which lies in the range between -1288 and -1293 Kcal.

The question of carnotite stability relative to that of other solid phases in the system is resolved by a comparison of the activity of the common ion, either UO_2^{+2} or H_2VO_4^- , in equilibrium with each solid phase at a specified Eh and pH. The activity of the common ion is not only a function of Eh and pH, but also depends on the activities of the other two ions involved in the precipitation of carnotite. In this study carnotite stability is shown on the framework of the $\text{U}-\text{O}_2-\text{H}_2\text{O}-\Sigma\text{CO}_2$ system and potassium and vanadium are added to this system in such a way that $\text{K}^+ = 10^{-3}$ and total activity of all vanadium-bearing ions (ΣV) = 10^{-3} . In ground waters, an activity of 10^{-3} for K^+ is quite reasonable. The ΣV value given is high, but it may have been achieved locally during the time of ore deposition on the Colorado Plateau and has certainly been achieved in subsequent leaching and oxidation. ΣCO_2 is varied between 10^{-3} and 10^{-1} . Contours representing the activity of H_2VO_4^- in equilibrium with the various oxides of the $\text{V}-\text{O}_2-\text{H}_2\text{O}$ system are shown in Figure 11. These contours are drawn on the basis that the sum of the activities of all vanadium ions is 10^{-3} .

Assume, for purposes of illustration, a pH of 4.0, an Eh above $+0.38$ volts, and a ΣCO_2 value of 10^{-3} , so that either carnotite or rutherfordine, UO_2CO_3 , (Fig. 6) is the stable solid. The activity of $\text{K}^+ = 10^{-3}$ and the activity of $\text{H}_2\text{VO}_4^- = 10^{-3.4}$ (Fig. 11). From equations (2) and (3):

$$(\text{UO}_2^{+2})^2 = \frac{(10^{-13.7})(10^{-4})^4}{(10^{-3.0})^2(10^{-3.4})^2} \quad (8)$$

$$\text{UO}_2^{+2} = (10^{-16.9})^{\frac{1}{2}} = 10^{-8.45} \quad (9)$$

Comparing this activity of UO_2^{+2} with that of UO_2^{+2} in equilibrium with rutherfordine under the above conditions, from Figure 6 ($a_{\text{UO}_2^{+2}} = 10^{-4.7}$), indicates that carnotite is the stable phase. Based on similar calculations (see Appendix), Figure 12 was drawn for $\Sigma\text{CO}_2 = 10^{-3}$. Solid phases are numbered, with carnotite occupying the lion's share of the diagram. "Montroseite" (Fig. 12) represents synthetic, crystalline V_2O_5 , for which thermodynamic data are available. A free-energy value for true montroseite (VOOH or $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$) would enlarge the diagrammed field of "montroseite" slightly. Areas indicating a certain degree of solubility, shown stippled on Figures 12, 13, and 14, are based on total activities of 10^{-4} for uranium-bearing ions ($\Sigma\text{U} = 10^{-4}$), 10^{-3} for vanadium-bearing ions, and 10^{-3} for K^+ , indicating that 40 ppm of potassium, 51 ppm of vanadium, and 24 ppm of uranium are carried in solution. The weight percent ratio of vanadium to uranium in solution is 2/1, a value approximating the general ratio of these elements in many parts of the Colorado Plateau.

Note that in Figure 12 the only solubility indicated is under quite acid conditions. ΣCO_2 is increased to 10^{-2} in Figure 13 where a further area of solubility is shown to occur for a mildly reducing, neutral to alkaline environment. Increased solubility under these conditions is due to the increased activity of the uranyl carbonate complexes in equilibrium with carnotite and uraninite. Vanadium in this environment is transported in the tetravalent state (Fig. 10). A hypothetical solution carrying the amounts of potassium, uranium, and vanadium given above would thus precipitate carnotite if subjected to oxidizing conditions. Uraninite and one of the tetravalent vanadium minerals, h  gite or doloresite, would form if the solution were acidified. Paramountroseite is presumably metastable and forms by oxidation of montroseite (14). Uraninite and montroseite would be precipitated if the solution had access to a distinctly reducing environment containing either carbonaceous material or H_2S .

A ΣCO_2 value of 10^{-2} is reasonable for natural ground waters. For example, a series of spring and well water samples taken across the southern part of the Powder River Basin in Wyoming (W. N. Sharp, written communication) show total alkali values, as HCO_3^- , varying from 175 to 320 ppm. These values approach the $\Sigma\text{CO}_2 = 10^{-2}$ value of 440 ppm. The pH of these waters is around 8.0, varying from 7.6 to 8.4. Should these waters be subjected to slightly reducing conditions, they would be capable of carrying considerable vanadium and uranium in solution.

The carnotite "curtain" continues to rise, and the UO_2 field to shrink in Figure 14, where $\Sigma\text{CO}_2 = 10^{-1}$. The ionic strength of solutions containing this much CO_2 precludes the equality of activity and molarity, hence the amounts of uranium, potassium and vanadium actually carried in solution are somewhat greater than given above.

DISCUSSION WITH REFERENCE TO THE ORES OF THE COLORADO PLATEAU

The portions of Figures 12, 13 and 14 which indicate the Eh-pH conditions necessary for aqueous transport of uranium and vanadium should be critically examined from two standpoints:

- 1) correlation with natural ground waters.
- 2) the environment of ore precipitation from such waters.

Correlation with Natural Ground Waters.—Considering the distance of migration of ore solutions on the Plateau, and the absence of intensive wall-rock alteration there, it is very unlikely that the ore solutions were sufficiently acid (pH 3 or less) to satisfy the acid requirements for aqueous solubility shown in Figures 12, 13, and 14.

Solutions characterized by those areas of Figures 13 and 14 which show solubility as a function of UDC and UTC have already been mentioned as having characteristics in common with some natural ground waters (neutral to alkaline, mildly reducing, moderately large amounts of CO_2). None of these characteristics is at variance with the commonly assumed aqueous environment of ore deposition on the Plateau. The effects of other ionic

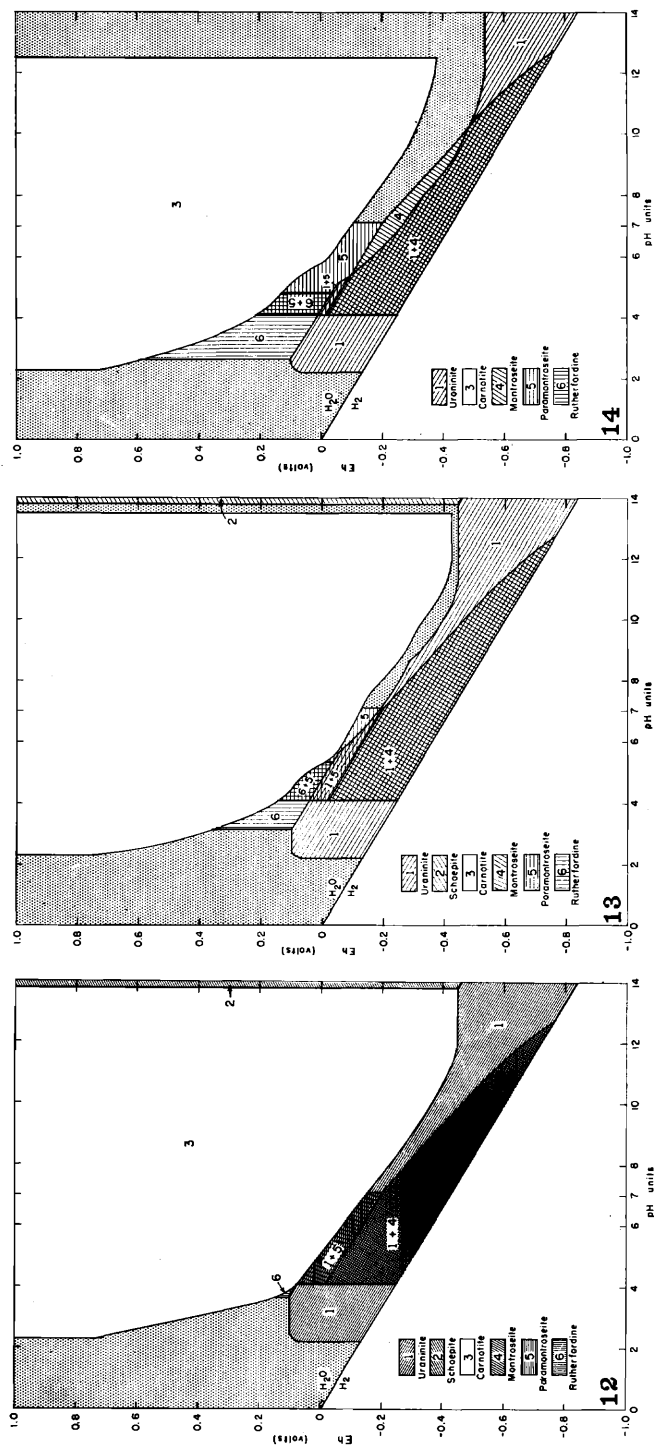


FIG. 12. Aqueous equilibrium diagram of the U-V-K-O₂-H₂O-CO₂ system at 25° C and 1 atm. Stability fields of solid phases are numbered and areas indicating soluble conditions are stippled. The boundary between solid phases and solution (see text) is fixed for $\Sigma U = 10^{-4}$, $\Sigma V = 10^{-3}$, $\Sigma K = 10^{-3}$, and $\Sigma CO_2 = 10^{-3}$.

FIG. 13. Aqueous equilibrium diagram of the U-V-K-O₂-H₂O-CO₂ system at 25° C and 1 atm. Other conditions as in Fig. 12 except that ΣCO_2 is fixed at 10^{-2} .

FIG. 14. Aqueous equilibrium diagram of the U-V-K-O₂-H₂O-CO₂ system at 25° C and 1 atm. Other conditions as in Fig. 12 except that ΣCO_2 is fixed at 10^{-1} .

species commonly found in subsurface waters and the associated problem of electrostatically balancing a large excess of HCO_3^- and CO_3^{--} ions remain to be discussed.

Significant additions of new ionic species into solutions of the U-V-K-O₂-H₂O-CO₂ system requires evaluation of three possible phenomena. First, such introduction may cause a reaction with existing ionic species to precipitate new insoluble solid phases (we are not concerned here with the soluble ones). Secondly, new ionic complexes, characteristic of definite Eh and pH conditions, may be formed, thus causing an increase in solubility. Lastly, even if the first two effects do not occur, any addition of new species increases the ionic strength of the solution. This effect is not shown on our diagrams, inasmuch as they are drawn for thermodynamic solubility (activities). Increasing the ionic strength causes solubility, in moles/liter, to exceed calculated thermodynamic solubility. Most subsurface waters are sufficiently dilute (concentration of major species less than 0.1 molal) so that true and calculated solubilities are approximately equal.

Specifically, subsurface waters containing notable uranium, vanadium, potassium and CO₂ will certainly also contain significant amounts of at least several of the following: sulfate, chloride, sodium, calcium and magnesium. No insoluble phases are formed as a result of addition of SO_4^{-2} and Cl^- , but these ions will form complexes with the uranyl and uranous ions. The uranyl sulfate complexes, $\text{UO}_2(\text{SO}_4)_2^{-2}$ and $\text{UO}_2(\text{SO}_4)_3^{-4}$, are stable only for pH values less than 3.5, while the uranous sulfate complexes, $\text{U}(\text{SO}_4)_3^{-2}$ and $\text{U}(\text{SO}_4)_4^{-4}$, form under even more acid conditions (29), hence the importance of such complexes in most natural waters is negligible. From the work of Ahrlund and his associates (1, 2) it is clear that uranyl and uranous chloride complexes have stability ranges very similar to their sulfate analogues.

The cations, Na^+ , Mg^{+2} , and Ca^{+2} , must be appealed to for electrostatic balance in natural solutions. Ca^{+2} can be quantitatively considered with the following limitations. For calcite:



From the thermochemical data of Latimer (28):

$$K_a = (\text{Ca}^{+2})(\text{CO}_3^{-2}) = 10^{-8.35} \quad (11)$$

If $\Sigma\text{CO}_2 = 10^{-2}$ or 10^{-1} , maximum $a_{\text{Ca}^{+2}}$ values in solution can be calculated with the aid of $a_{\text{CO}_3^{-2}}$ determined for the construction of Figures 7 and 8 (see Appendix). If $\Sigma\text{CO}_2 = 10^{-2}$, calcium ions can electrostatically balance all HCO_3^- and CO_3^{-2} ions in solution if the pH is no higher than about 7.5; if $\Sigma\text{CO}_2 = 10^{-1}$, the highest pH is only about 6.0. Similarly, dolomite or magnesite would control the amount of magnesium ions that could be carried in solution.

Although no solubility data are available for tyuyamunite, $\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$, we suppose that it is one or two orders of magnitude more soluble than carnotite. If such is the case, Ca^{+2} activities of 10^{-2} to 10^{-1} would suffice

to give a stability field for tyuyamunite similar to that of carnotite in Figures 12–14.

Rauvite, $x\text{UO}_3 \cdot y\text{V}_2\text{O}_5 \cdot z\text{H}_2\text{O}$, is fairly widespread on the Colorado Plateau. Apparently y is somewhat greater than x (14). Two analyses reported by Frondel (16) show about 2.7 percent CaO each, but it is not known whether calcium is an essential constituent of rauvite. Low pH and moderately large concentrations of pentavalent vanadium should theoretically favor the formation of rauvite rather than carnotite or tyuyamunite. Indeed, Barton (3) has found that rauvite, rather than carnotite, is precipitated from acid solutions of pH 1.5–2.0 and 0.01 molar in uranium and vanadium. The association of rauvite with navahoite, $\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, at Monument Valley (38) suggests that where aqueous pentavalent vanadium is sufficiently concentrated in an acid environment for the formation of navahoite, then rauvite is stable relative to carnotite or tyuyamunite. As the formation of rauvite appears to be restricted to acid, oxidizing environments it is unnecessary to consider further the stability of this mineral within the framework of a mildly reducing, neutral-alkaline ground water.

Na^+ is the most likely choice to balance a large excess of anions. The addition of Na^+ to the systems discussed above produces no insoluble minerals, hence Na^+ can balance the solutions electrostatically over the entire Eh-pH range of interest.

The net effect of the addition of those ionic species common in natural ground waters to the neutral-alkaline solutions of the type indicated in Figures 13 and 14 is that the boundaries between solid phases and solution remain valid as drawn (no significant complexing with SO_4^{2-} or Cl^- for these pH conditions) and that sufficient quantities of the cations, Ca^{+2} , Mg^{+2} , and especially Na^+ , can be carried in solution to electrostatically balance all the anions present. Accordingly, part of the area of solubility shown in Figure 13 is particularly compatible with subsurface waters because of its pH values and reasonable CO_2 content (440 ppm). The narrow Eh range of the solubilities shown definitely suggests that ore deposition is characterized by certain redox potentials and indicates the desirability of evaluating activity gradients for this area of solubility. This evaluation is shown in Figure 15 where the increment of decreasing total ionic activity is an order of magnitude and $\Sigma\text{CO}_2 = 10^{-2}$. Shaded lines in Figure 15 thus represent solid phase-solution contours for a total activity of uranium-bearing ions equal to 10^{-5} , and total activities of 10^{-4} for K^+ and vanadium-bearing ions. Five ppm vanadium, 4 ppm potassium and 2.4 ppm uranium can be carried in solution under conditions indicated by the shaded lines. The conditions for solubility indicated on Figure 13 are shown here with dashed lines. For an Eh-pH characterized environment varying from the shaded to the dashed lines, vanadium solubility may increase from 5 to 50 ppm, potassium from 4 to 40 ppm, and uranium from 2.4 to 24 ppm.

Environment of Ore Deposition.—In Figure 15 ionic activity contours for ions in equilibrium with carnotite are more widely spaced than contours for ions in equilibrium with uraninite and montroseite, indicating that the

stability of carnotite is much more sensitive to decreasing amounts of uranium and vanadium in solution than is the stability of uraninite or montroseite. Indeed, if the activity of potassium, uranium and vanadium ions should each drop to $10^{-6.3}$ carnotite would completely disappear from Figures 13 and 15, whereas uraninite has a sizeable field of stability under such conditions (Fig. 7). Such values, reasonable for uranium and vanadium, are distinctly low for potassium, but even if K^+ is raised to 10^{-3} , the field of carnotite stability is very small.

Consider a potential ore solution migrating slowly through pore spaces in the host rock under thousands of feet of sediments. Such a solution would almost certainly be devoid of significant oxygen. Redox potential would be

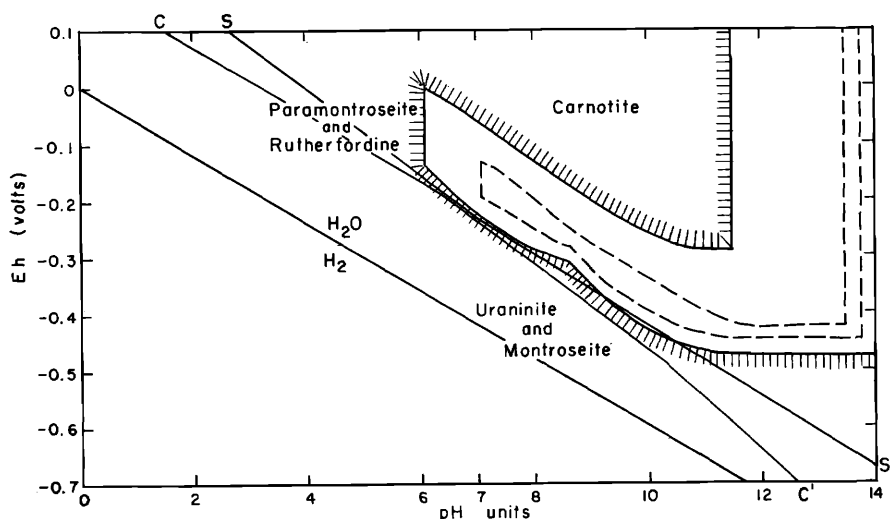


FIG. 15. Aqueous equilibrium diagram of the U-V-K-O₂-H₂O-CO₂ system at 25° C and 1 atm., and with ΣCO_2 fixed at 10^{-2} . Boundaries between solid phases and solution are fixed for $\Sigma\text{U} = 10^{-5}$, $\Sigma\text{V} = 10^{-4}$, and $\Sigma\text{K} = 10^{-4}$ (shaded lines), whereas dashed lines represent solid phase-solution boundaries for $\Sigma\text{V} = 10^{-3}$, $\Sigma\text{K} = 10^{-3}$ and $\Sigma\text{U} = 10^{-4}$.

poorly buffered. Since carnotite is stable over a wide range of Eh and pH conditions its formation would be most critically controlled by the amounts of uranium, vanadium and CO₂ in solution.

Migration through pockets of carbonaceous material or areas of entrapped H₂S would, of course, make the solution Eh more reducing. Two likely redox potentials are shown in Figure 15 by lines c-c' and s-s'. Line c-c' represents a calculated equilibrium potential between graphite and aqueous carbonate species which is analogous to an equilibrium potential between carbonaceous material and carbonate species. Line c-c' was calculated for $\Sigma\text{CO}_2 = 10^{-2}$, but the change in potential is only 15 mv. when ΣCO_2 is altered by a factor of 10. Line s-s' shows the redox potential of equal con-

centrations of SO_4^{-2} and sulfide ions as calculated by Garrels and Naeser (22). Migrating solutions at 25° C containing SO_4^{-2} and encountering gaseous H_2S would reach a potential very close to this line independently of the amount of sulfur species in each phase because of the very steep activity gradient involved for each aqueous sulfur species away from line s-s'.

Between pH 6 and pH 10 both potentials are very close to the bottom of the area designating solubility in Figure 15. At 25° C and 1 atmosphere pressure the reducing environment indicated by these potentials is sufficient to precipitate uraninite and montroseite if solution concentration is about 0.5 ppm or higher for uranium and 2 ppm or higher for vanadium. Natural uraninite precipitated in such an environment, however, is probably closer to $\text{UO}_{2.6}$ than to UO_2 , indicating that the saturation concentration of uranium is somewhat less than 0.5 ppm because $\text{UO}_{2.6}$ is more stable and therefore less soluble than UO_2 . An environment of rising temperature should not significantly reduce the effectiveness of H_2S and woody material as precipitation agents for uraninite and montroseite from natural solutions. Rafalsky (32) heated uranyl sulfate solutions with aluminum sulfide in closed silica ampules and found that at 150° C the concentration of soluble uranium in the presence of uraninite is 1.6 ppm. At 125° C Miller (29) noted about 1.2 ppm uranium in solution after precipitation of uraninite by H_2S . It thus seems likely that the Plateau uraninite was deposited from solutions that contained a minimum of about 0.5 ppm uranium.

It is noteworthy that the uranyl carbonate complexes become increasingly unstable above 120° C. Rafalsky's data (32) indicate that uranium solubility in carbonate solutions diminishes by a factor of about 100x between 100 and 200° C and that the decrease in solubility is slight between 100 and 120° C but becomes much greater above 120° C. A similar temperature range (120–215° C) was used in Miller's experiments (29) and the resulting decrease in uranium solubility was found to be one order of magnitude. Neither author offers any data for uranium solubility in carbonate solutions between 25 and 100° C, but Rafalsky's work between 100 and 120° C suggests that solubility is either fairly constant in the 25–100° C interval or may even rise to a maximum somewhat under 100° C. Increased H_2S pressure (up to 9,000 lbs/sq inch) also decreases uranium solubility, according to Miller (29), but its total effect is small.

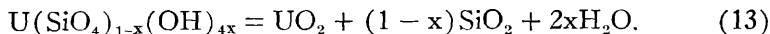
The foregoing considerations lead to a consistent pattern of aqueous transport and deposition of ore elements on the Colorado Plateau. The ubiquitous spatial and temporal relationship of uranium and vanadium ore minerals points to a common origin and transportation medium for these elements. Although this common origin cannot be pinpointed, it seems likely that in late Cretaceous or early Tertiary time, perhaps even earlier, a heavy load of overlying sediments forced uranium- and vanadium-bearing solutions out of sediments rich in volcanic ash, such as the Chinle Formation of Late Triassic age and the Brushy Basin Member of the Morrison Formation of Late Jurassic age (36). These solutions, comparable to the type discussed in the previous two sections of this study, migrated through pore spaces and

permeable channels in the Shinarump Member of the Chinle Formation or the Salt Wash Member of the Morrison Formation, where they undoubtedly encountered reducing environments with concomitant ore precipitation (see Jensen (26), p. 611–615, for a more complete discussion of this point). These environments may have been pockets of carbonaceous material and/or H_2S , or even H_2 which may have been locally produced by the reaction of H_2S with Fe_2O_3 . Gaseous hydrogen will precipitate uraninite and montroseite from very dilute solutions.

By the end of Cretaceous time the thickness of the stratigraphic column atop the Salt Wash Member in the Uravan district was nearly the same as that above the Shinarump Member in northeastern Arizona, a thickness of about 6,000 feet (L. C. Craig, oral communication). Normal geothermal gradients across this thickness during the time of ore-solution migration would mean temperatures around 75°C . This is well below the temperature (120°C) at which the uranyl carbonate complexes begin to break down. Of course, a deeper depth of burial, or higher geothermal gradients, might have produced temperatures in excess of 120°C in the vicinity of the migrating solutions, in which case uraninite should precipitate as a result of decomposition of UDC and UTC. Because this control of ore formation, unlike those given earlier, is selective towards uranium, there is no reason for uraninite so formed to be found in association with trivalent vanadium minerals, sulfides or carbonaceous material. Lack of such ore on the Plateau supports the hypothesis that temperatures in the environment of ore deposition were not above 100 to 120°C .

Formation of Coffinite and Vanadium Silicates.—Ore deposition has many ramifications that are not discussed here, such as comparison of precipitation conditions for locally abundant copper, molybdenum and selenium minerals of the Plateau with those precipitation conditions given here for uranium and vanadium minerals. Such a comparison would make an excellent future study (many of the pertinent thermochemical data are known for 25°C). Some remarks about the stability of coffinite, $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$, and the vanadium silicates are appropriate because of their widespread occurrence as primary minerals on the Plateau. No thermochemical data are available for these minerals.

Coffinite and uraninite are the only known minerals from the Colorado Plateau in which the dominant uranium is in the +4 oxidation state, and their intimate association indicates mutual low solubility under reducing conditions (21). The uraninite-coffinite equilibrium may be written:



At a given temperature and total pressure, equilibrium between the solid phases is a function of the activity of water and aqueous silica. In high-temperature hydrothermal veins and in pegmatites reaction (13) goes to the right. The environment of ore deposition on the Plateau must have been such that reaction (13) went either way, depending on small $a_{\text{H}_2\text{O}}$ and a_{SiO_2} fluctuations. Descriptions of corroded quartz grains in impregnated sand-

stone and nearby secondary quartz overgrowths (33, 39) indicate a liquid phase that hovered around quartz saturation values.

As coffinite is rapidly altered under oxidizing conditions (21), it seems probable that in the presence of excess quartz coffinite occupies much the same position as uraninite in the Eh-pH diagrams previously shown.

The vanadium silicates of the Plateau ore deposits are the vanadium mica (roscoelite, $K(Al,V)_2(Al,Si_3)O_{10}(OH,F)_2$), and vanadium-bearing clays (chlorites and mixed layer montmorillonite-micas and montmorillonite-chlorites). Several workers (15, 23, 39), emphasizing the pronounced chemical and mineralogical similarity between mineralized and nearby barren clays, have concluded that most of vanadium clays originated by replacement of octahedrally coordinated aluminum by vanadium in preexisting clay minerals. Roscoelite and some of the vanadium clays probably precipitated directly from solution (15).

The presence of montroseite at those localities on the Plateau where roscoelite is abundant (6) suggests that, at low temperatures and moderate concentrations of K^+ , Al and +3 vanadium, roscoelite has a field of stability similar to montroseite on Figures 12–15. Apparently, a decreasing V/U ratio is accompanied by a relative decrease of roscoelite and increase of montroseite in primary vanadium ore (39). Abundant clay minerals in both types of ore (high roscoelite or high montroseite) indicate that soluble K, Al, and Si do not change noticeably as the V/U ratio fluctuates and that the formation of roscoelite is probably more sensitive to decreasing concentrations of +3 vanadium than is montroseite.

Most of the vanadium in the mineralized clays is tetravalent, even in oxidized ore (15, 23). This observation has led to the suggestion (Garrels et al., (23)) that the vanadium was transported in the tetravalent state in the ore solutions. Reasoning based on available thermochemical data (Figs. 13–15) supports the notion that vanadium was tetravalent during transport. However, if this reasoning is correct, an equally fundamental question remains; namely, why should only those clay minerals in ore deposits contain +4 vanadium? Barren clay minerals a few inches from mineralized clays contain only one tenth as much vanadium as the mineralized clays (15). This selective substitution of octahedral Al by +4 vanadium is especially puzzling as the ore solutions probably migrated considerable distances (27, 36). We conclude this paper by speculating a bit on this question.

First, +3 vanadium may replace octahedrally coordinated aluminum more readily than does +4 vanadium. If this is true then most of the vanadium was originally emplaced in the clay minerals in the trivalent state. The Eh values of the sulfide-sulfate and carbon-carbonate redox potentials which we believe control primary mineralization (lines s-s' and c-c' of Fig. 15) require most, but not all, of the aqueous vanadium at these potentials to be trivalent. The association of vanadium clay minerals with montroseite, as in the Uravan district (33, 39) and with roscoelite and montroseite, as at Placerville and Rifle (6), also implies trivalent aqueous vanadium at the site of clay mineralization. The intimate association of roscoelite with the vanadium clays is

particularly suggestive of original +3 vanadium in the clays, for Hathaway (25) has shown that completely transitional mixed layering occurs between pure roscoelite and randomly interstratified roscoelite-montmorillonite clays.

From her study of the present oxidation states of vanadium in selected, mixed-layer roscoelite-montmorillonite clays in partially oxidized ore, Foster (15) concludes that the vanadium was originally emplaced in the +4 state. Foster (15) argues that assuming that all vanadium was originally trivalent leads to abnormally large negative charges for the sum of the tetrahedral and octahedral layers of the clay minerals. Foster assumes, though, that none of the vanadium is lost in the theoretical oxidation of vanadium in these clays to the +4 state. The increase in stability of aqueous ionic species bearing +4 vanadium compared to those containing +3 vanadium (cf. Fig. 2 in Evans and Garrels (14)) suggests that oxidation of vanadium from the +3 to +4 state in clays would be accompanied by a modest loss of vanadium to solution. If the clays described by Foster were to lose only ten percent of their vanadium during theoretical oxidation the total negative charge of the tetrahedral and octahedral layers would be reasonable for mixed layer roscoelite-montmorillonites (about -0.90).

Clearly, analyses are needed of the oxidation state of vanadium in vanadium clays closely associated with unoxidized assemblages.

A second hypothesis, put forward by Roach and Thompson (33) to explain the presence of vanadium clay in otherwise unmineralized sandstone at the Peanut Mine, states that these clays originated from tetravalent vanadium made available during oxidation of primary vanadium minerals.

A third, but less plausible, method for selectively replacing Al^{+3} by V^{+4} within the clay minerals of the ore deposit appeals to relatively impermeable boundaries, such as festoon surfaces, to detain migrating ore solutions for a sufficient length of time for replacement to occur. Replacement by tetravalent vanadium presumably occurred away from local "hot spots" of carbonaceous material. The released aluminum might eventually react with aqueous potassium, silica, and trivalent vanadium (available nearer carbonaceous material) to form roscoelite.

SUMMARY

1. Eh-pH diagrams at 25°C were constructed with the aid of published thermodynamic data for the $\text{U}-\text{O}_2-\text{H}_2\text{O}$ and $\text{U}-\text{O}_2-\text{H}_2\text{O}-\text{CO}_2$ systems. Uraninite, UO_{2+x} , and schoepite, $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, are the only solid phases expected to be stable in the presence of water and variable concentrations of oxygen in the system $\text{U}-\text{O}_2-\text{H}_2\text{O}$. The addition of CO_2 to this system causes formation of stable uranyl carbonate complexes and a significant increase in the solubility of uraninite and schoepite.

2. Following a rough calculation of the free-energy of carnotite, Eh-pH diagrams of the $\text{U}-\text{V}-\text{K}-\text{O}_2-\text{H}_2\text{O}-\text{CO}_2$ system were drawn for various values of total carbonate (ΣCO_2). These diagrams show stability fields for carnotite and other uranium and vanadium solid phases, and indicate the conditions

necessary for vanadium and uranium solubility. One set of conditions was found to indicate solubility in a mildly reducing, neutral to alkaline environment containing fairly abundant CO_2 , and thus is comparable with some natural ground waters.

3. Analysis of solubility controls indicates that increasing CO_2 increases solubility. Oxidizing conditions cause carnotite to precipitate from solution while more reducing conditions cause montroseite and uraninite to form.

4. The possible effects of other ionic species commonly found in natural ground waters were investigated within the Eh-pH framework of aqueous transport in the U-V-K-O₂-H₂O-CO₂ system. No significant changes in such transport were found. Sodium and, to a lesser degree, calcium and magnesium can balance electrostatically the concentrations of HCO_3^- , CO_3^{2-} , and other anions in solution. Activity gradients showing varying transportation conditions were presented.

5. In the presence of excess quartz the field of coffinite stability is probably very similar to that of uraninite. With favorable conditions (moderate concentration of its constituent elements) the field of formation of roscelite should approximate that of montroseite.

6. Carnotite stability is very sensitive to changes in ionic activity rather than changes in Eh and pH (except for distinctly reducing conditions); its precipitation is critically controlled by the amounts of uranium, vanadium and CO_2 in solution. The reducing environment provided by ore-solution migration into carbonaceous and/or H_2S rich areas was shown to be sufficient to precipitate uraninite and montroseite from dilute solutions at 25° C. Temperatures above 120° C might be sufficient to precipitate uraninite from the postulated ore-bearing solutions because of the breakdown of the uranyl carbonate complexes. Sulfides, carbonaceous material and trivalent vanadium minerals would not be expected to occur with uraninite formed in this way. The lack of such ore is interpreted as supporting evidence for a depositional temperature of 120° C or less.

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APPENDIX

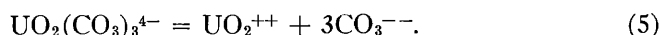
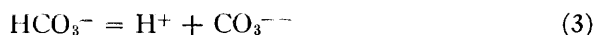
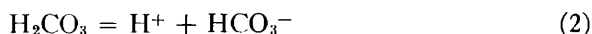
This Appendix was prepared for those readers who desire the details of construction of the Eh-pH diagrams here presented. An introduction to the methods of Eh-pH diagramming, based on the use of free-energy data to calculate equilibrium constants, is given by Pourbaix (31). All free-energy values used in our calculations have been taken from Latimer (28) except as noted below. The values for uraninite and schoepite are from Deltombe et al. (13), while those for rutherfordine and the uranyl carbonate complexes are from Bullwinkel's data (9) corrected for the recent ΔF°_f of schoepite given by Deltombe et al. A value for HUO_4^- was calculated from the published equilibrium constants of Gayer and Leider (24). Bjerrum et al. (4) tabulate six fairly consistent constants for the dissociation of $\text{UO}_2(\text{OH})^+$ at 25° C. We averaged these and so obtained a ΔF°_f of $\text{UO}_2(\text{OH})^+$ at 25° C. The value for carnotite was derived in the text. Free-energy values for the vanadium oxides are taken from Evans and Garrels (14), while that of H_2VO_4^- is from Deltombe et al. (12). All free-energy values pertinent to the construction of the diagrams presented in this paper are listed in Table 1.

TABLE 1
FREE-ENERGY VALUES FROM THE ELEMENTS, AT 25° C AND 1
ATMOSPHERE TOTAL PRESSURE

Aqueous species	ΔF°_f (Kcal)	Solid phases	ΔF°_f (Kcal)
H_2O	- 56.69	UO_2	- 246.6
H^+	0.0	$\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$	- 398.8
OH^-	- 37.6	UO_2CO_3	- 385.0
$\text{H}_2\text{CO}_3^\circ$	-149.00	V_2O_3	- 271.0
HCO_3^-	-140.31	V_2O_4	- 381.0
CO_3^{--}	-126.22	V_2O_5	- 344.0
K^+	- 67.46	$\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$	-1,294.0
H_2VO_4^-	-248.8		
UO_2^{++}	-236.4		
U^{+4}	-138.4		
$\text{U}(\text{OH})^{+3}$	-193.5		
$\text{UO}_2(\text{OH})^+$	-287.4		
HUO_4^-	-317.6		
$\text{UO}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}^{--}$	-630.0		
$\text{UO}_2(\text{CO}_3)_3^{--4}$	-648.0		

U-O₂-H₂O-PCO₂ DIAGRAMS

The following equations are pertinent:



The thermodynamic equilibrium constants for reactions (1)–(5) are as follows:

$$\frac{H_2CO_3}{P_{CO_2}} = 10^{-1.47} \quad (6)$$

$$\frac{(HCO_3^-)(H^+)}{H_2CO_3} = 10^{-6.38} \quad (7)$$

$$\frac{(CO_3^{--})(H^+)}{HCO_3^-} = 10^{-10.31} \quad (8)$$

$$\frac{(UO_2^{++})(CO_3^{--})^2}{UO_2(CO_3)_2 \cdot 2H_2O^{--}} = 10^{-20.4} \quad (9)$$

$$\frac{(UO_2^{++})(CO_3^{--})^3}{UO_2(CO_3)_3^{4-}} = 10^{-24.2} \quad (10)$$

For a fixed P_{CO_2} , H_2CO_3 is calculated from (6). For a given pH value CO_3^{--} can be calculated from equations (7) and (8). Next, all ions containing uranium are considered to be in equilibrium with schoepite.



or,

$$K_a = \frac{UO_2^{++}}{(H^+)^2} \quad (12)$$

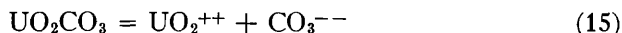
Hence, UO_2^{++} can be calculated from stipulated pH values by (12). Lastly, activities for the uranyl carbonate complexes can be derived from equations (9) and (10) with the aid of CO_3^{--} and UO_2^{++} values calculated above.

If P_{CO_2} is high enough, rutherfordine (UO_2CO_3) is the stable hexavalent uranium solid phase rather than schoepite.



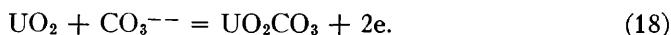
$$K_a = \frac{1}{P_{CO_2}} \quad (14)$$

When P_{CO_2} is $10^{-3.8}$ the two solid phases rutherfordine and schoepite are in equilibrium. For P_{CO_2} values higher than this, UO_2^{++} must be determined from CO_3^{--} values (above) as follows:



$$(UO_2^{++})(CO_3^{--}) = 10^{-16.4} \quad (16)$$

For reducing conditions uraninite becomes the stable solid phase.



Employing the Nernst equation for equations (17) and (18):

$$Eh = E^\circ + \frac{0.06}{2} \log (H^+)^2 \quad (19)$$

$$Eh = E^\circ + \frac{0.06}{2} \log \frac{1}{(CO_3^{--})}. \quad (20)$$

E° for each reaction is evaluated from free-energy data. Depending on the P_{CO_2} value under consideration, either (19) or (20) is chosen. If P_{CO_2} is less than $10^{-3.8}$ the Eh-pH boundary between uraninite and schoepite is found by substituting pH values in (19). For P_{CO_2} greater than $10^{-3.8}$ the rutherfordine-uraninite boundary is established by substituting the CO_3^{--} values derived from equations (7) and (8) in equation (20). In each case the solid-solid boundary has a linear slope of 60 mv/pH unit. In the UO_2 field then:



$$Eh = E^\circ + \frac{0.06}{2} \log (UO_2^{++}). \quad (22)$$

UO_2^{++} is calculated from (22) for arbitrary Eh values (UO_2^{++} is not pH dependent in the UO_2 field as expressed in (21)). UCD and UTC activities are then calculated as before; these ion activities are now both Eh and pH dependent.

U-O₂-H₂O-Σ CO₂ DIAGRAMS

Equation (1) is no longer applicable since P_{CO_2} is variable. Equations (2)–(5) and, hence, (7)–(10) are used, but note that now, after selecting arbitrary pH values, CO_3^{--} cannot be solved from equations (7) and (8) because there are three unknowns. Since Σ CO₂ is fixed, the following expression is used.

$$\Sigma CO_2 = H_2CO_3 + HCO_3^- + CO_3^{--} + 2UO_2(CO_3)_2 \cdot 2H_2O^{--} + 3UO_2(CO_3)_3^{4-}. \quad (23)$$

Rewrite equations (7)–(10) so that ionic activity sought is a function of UO_2^{++} and CO_3^{--} :

$$HCO_3^- = \frac{(CO_3^{--})(H^+)}{10^{-10.31}} \quad (24)$$

$$H_2CO_3 = \frac{(HCO_3^-)(H^+)}{10^{-6.38}} = \frac{(CO_3^{--})(H^+)^2}{10^{-16.69}} \quad (25)$$

$$UO_2(CO_3)_2 \cdot 2H_2O^{--} = \frac{(UO_2^{++})(CO_3^{--})^2}{10^{-20.4}} \quad (26)$$

$$UO_2(CO_3)_3^{4-} = \frac{(UO_2^{++})(CO_3^{--})^3}{10^{-24.2}}. \quad (27)$$

If $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ is the stable solid phase, UO_2^{++} is fixed for arbitrary pH values. Equations (24)–(27) are substituted in equation (23) which is solved for CO_3^{--} using the desired ΣCO_2 value. Equation (23) is best solved by approximation as it is a third-order equation. Remaining ion activities are then determined using (24)–(27).

Equation (16) is used to determine the $\text{UO}_2\text{CO}_3 - \text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ boundary.

$$\text{UO}_2^{++} = \frac{10^{-16.4}}{\text{CO}_3^{--}} \quad (16)$$

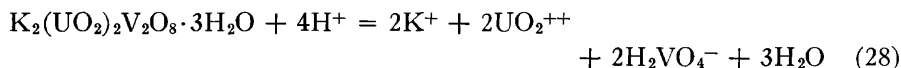
Substitute this expression for UO_2^{++} in equations (26) and (27). As above, substitute (24)–(27) in equation (23) and solve for CO_3^{--} . Finally, use this CO_3^{--} value to determine UO_2^{++} in equilibrium with rutherfordine from (16). If this value for UO_2^{++} is less than UO_2^{++} in equilibrium with schoepite for a given pH then UO_2CO_3 is the stable solid. The boundary between the two phases (UO_2^{++} values in equilibrium with each are identical) is dependent on both ΣCO_2 and pH, but not on Eh.

The rutherfordine-uraninite and uraninite-schoepite bounding equations have been given ((17)–(20)). The uraninite-schoepite boundary is not dependent on CO_2 . Use the CO_3^{--} values obtained from (23) and (16) for establishing the uraninite-rutherfordine boundary.

Ionic activities in equilibrium with UO_2 are cumbersome to determine when ΣCO_2 is fixed. UO_2^{++} values for (26) and (27) are derived from (22) for arbitrary Eh values. Substituting (26) and (27) in (23) indicates that CO_3^{--} is both pH and Eh dependent. Activities for each ion must be calculated on a point-by-point basis in the field of stability of uraninite.

U–V–K–O₂–H₂O–CO₂ DIAGRAMS

Carnotite stability must be considered in relation to both uranium and vanadium solid phases.

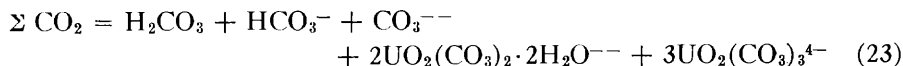


$$\frac{(\text{K}^+)^2(\text{UO}_2^{++})^2(\text{H}_2\text{VO}_4^-)^2}{(\text{H}^+)^4} = 10^{-13.7} \quad (29)$$

For any Eh–pH value, the activity of H_2VO_4^- is taken from Figure 11 (see text). $\text{K}^+ = 10^{-3}$, and UO_2^{++} values are taken from the results of calculations for the U–O₂–H₂O– ΣCO_2 diagrams. When these values, for the particular Eh and pH in question, are inserted in the left-hand side of equation (29), carnotite is the stable solid if the value of the left-hand side of the equation exceeds $10^{-13.7}$. Carnotite is not stable relative to the other uranium and vanadium solids if the left-hand side of (29) is less than $10^{-13.7}$. Equation (29) is thus used as a criterion for determining at specified Eh and pH conditions, whether carnotite is or is not stable relative to the combination of the stable uranium oxide (or carbonate) plus the stable vanadium

oxide plus potassium hydroxide. The solid-solid boundaries for Figures 12-14 are drawn for those Eh-pH conditions where the left-hand side of (29) is equal to $10^{-13.7}$.

Keeping ΣCO_2 constant, equations (23)-(27) remain applicable:



$$\text{HCO}_3^- = \frac{(\text{CO}_3^{--})(\text{H}^+)}{10^{-10.31}} \quad (24)$$

$$\text{H}_2\text{CO}_3 = \frac{(\text{CO}_3^{--})(\text{H}^+)^2}{10^{-16.69}} \quad (25)$$

$$\text{UO}_2(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}^{--} = \frac{(\text{UO}_2^{++})(\text{CO}_3^{--})^2}{10^{-20.4}} \quad (26)$$

$$\text{UO}_2(\text{CO}_3)_3^{4-} = \frac{(\text{UO}_2^{++})(\text{CO}_3^{--})^3}{10^{-24.2}} \quad (27)$$

Rearranging equation (29):

$$\text{UO}_2^{++} = \left[\frac{(10^{-13.7})(\text{H}^+)^4}{(\text{K}^+)^2(\text{H}_2\text{VO}_4^-)^2} \right]^{\frac{1}{2}} \quad (30)$$

UO_2^{++} values from equation (30) are substituted in (26) and (27), and ion activities in equilibrium with carnotite are determined in the manner described above.

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