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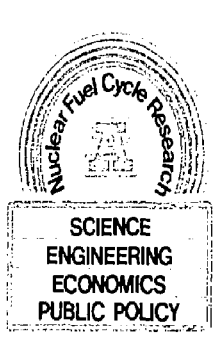

UNIVERSITY OF ARIZONA

Nuclear-Fuel-Cycle Research Program:

AVAILABILITY OF GEOTOXIC MATERIAL

SEPTEMBER 1982

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Subcontract 1879901
Lawrence Livermore National Laboratory
To Engineering Experiment Station
The University of Arizona

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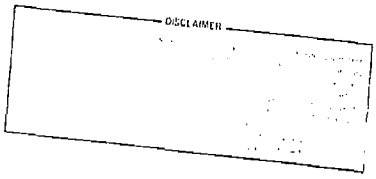

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ABSTRACT

This report represents an analog approach to the characterization of the environmental behavior of geotoxic waste materials as drawn from literature on the natural models:

a. Oklo natural fission reactors and uranium ore deposits relative to radioactive wastes, and

b. hydrothermal metal ore deposits relative to stable toxic wastes.

The geochemical literature proved to be the most significant source of information and direction of research. The geologic and hydrologic literature was found to be relatively less useful in this study. The natural analog data were examined in terms of mobility and immobility of selected radioactive or staple waste elements and are presented in matrix relationship with their prime geochemical variables.

A numerical system of ranking those relationships for purposes of hazard-indexing is proposed. This numerical system is based on the "availability" term developed by Smith et al. (1980), specifically in terms of their m-factors as discussed herein. Table summaries (matrices), text elucidation and additional technical excerpts in the appendix provide a tri-level look at the interaction between selected elements and their geochemical variables.

Geochemical parameters (especially oxidation/reduction potential) are apparently more potent mobilizers/immobilizers than geological or hydrological conditions in many, if not most, geologic environments for most radioactive waste elements. Heavy metal wastes, by analogy to hydrothermal ore systems and geothermal systems, are less clear in their behavior but similar geochemical patterns do apply.

Depth relationships between geochemical variables and waste element behavior show some surprises. It is significantly indicated that for waste isolation, deeper is not necessarily better geocnemically. Relatively shallow isolation in host rocks such as shale could offer maximum immobility. This paper provides a geochemical outline for examining analog models as well as a departure point for improved quantification of geological and geocnemical indexing of toxic waste hazards.

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EXECUTIVE SUMMARY

Geotoxicity study evaluates the behavior of toxic material emplaced in the earth's crust by either man or nature. It includes assessment of natural and man-made radioactive elements as well as certain stable metallic elements. The availability of geotoxic material is a major consideration in the Geotoxicity Hazard Index (GHI) which was developed by Smith et al. (1980). In their formulation, availability is dependent on a number of factors including the physical and chemical characteristics of the buried toxic material and its behavior in the geochemical environment. In the Geotoxicity Hazard Index, availability is characterized using the ratio of human intake to natural crustal abundance of the analog of the material under consideration. Since this value is indicative of the average availability of the analog material under normal conditions, it must be adjusted to accommodate the particular circumstances, natural or engineered, of the disposal situation under study. This is accomplished through the use of a modification factor, or m-factor, that defines the combination of parameters causing deviation of availability from the average value.

The purpose of this report is essentially three-fold. First, it describes an analog approach to the assessment of hazardous waste disposal. The analog approach attempts to provide real-world instances of hazardous materials interacting with the environment. Observations of these interactions are to be incorporated in the development of a set of modification factors.

Second, this report proposes a method to begin the definition of semi-quantitative m-factors for materials existing under various geochemical

conditions in the earth's crust. These factors are defined on the basis of the mobility of geotoxic materials in the geochemical environment and are intended for use in the GHI determination.

Third, this report attempts to answer the question "what is the advantage of deeper disposal of radioactive materials?" If depth is not a significant factor affecting geochemical behavior of waste elements, then relatively shallow isolation can provide sufficient immobility. Under these conditions increased depth is not necessarily justifiable from a public health standpoint.

Information for this assessment of availability is drawn from an extensive geochemical literature search. Natural models forming the basis for radioactive analogs are the Oklo fission reactors and uranium ore deposits; hydrothermal ore deposits of other metals provide analogs for stable toxic wastes.

An overview and salient insights derived follows:

1. The literature yields abundant geochemical information which could be used to describe the processes controlling the behavior and movement of some geotoxic materials in the environment, namely, their availability. From this information, a group of geochemical parameters are chosen to represent factors controlling waste component behavior. These include Eh, pH, mineralogy, presence of anions and cations, temperature and pressure.

2. Specific elements are selected to represent a waste package analog, particularly those deserving prime consideration as potentially mobile toxins. These include actinides, lanthanides, alkali metals, alkaline earths and others.

3. Results are presented in separate matrices for mobility and immobility conditions. The analog condition for immobility of wastes is the

deposition of materials as ores. For mobility, the analog situation is solution transport of ore materials to a concentrating point or dispersal.

4. Of the actinide elements selected for study, uranium has the greatest potential mobility. Conditions that minimize uranium mobility would imply minimized mobility of the other actinides.

5. The selected elements are discussed in terms of the effects of the geochemical parameters for both mobilizing and immobilizing conditions.

6. The effects of the various geochemical parameters (Eh, pH, etc.) are discussed for the most important group of elements, the actinides.

7. Sorption effects are significant, but certainly misunderstood, and perhaps over-rated as a subsurface barrier. They are discussed, but not dealt with as a matrix parameter, since sorption is affected by other geochemical parameters.

8. A table of proposed semi-quantitative *m*-factors, established on the basis of uranium mobility/immobility, is presented.

Major conclusions reached in this report are drawn from an analog approach to the geochemical behavior of a selected group of geotoxins. The geochemical literature proved to be the significant source of information rather than geologic or hydrologic data. The most important geochemical parameter for immobilization of most radioactive elements in most geologic environments appears to be the oxidation potential or Eh. A reducing environment would be generally desired for immobilization. Other immobilizing conditions are: moderate pH, low CO_2, low salt concentration, high porosity, and low permeability. Depth does not, in itself, appear to be an overriding consideration, since for some shales optimum immobilization via geochemical and thermodynamic considerations can be achieved at relatively

shallow depths. The m-factors could be generally defined on the basis of mobility as presented herein, but not numerically quantified for site-specific conditions. The study of hydrothermal ores indicates that toxic base metals behave similarly, but less predictably, to the radionuclides in their stability under reducing conditions.

Suggestions for further work include the following.

a) Much analog data appears to be available from diverse sources, and needs to be collected.

b) The m-factors need to be generalized to be easily applied to specific sites. They also need to be more fully quantified.

c) Existing drilling data, giving geochemical information at various depths, should be used to more fully answer the depth question.

d) Sedimentary basins should be examined to provide another analog data source.

e) Geothermal studies, which could provide extensive metal mobility data, should also be examined.

ACKNOWLEDGEMENTS

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I. PURPOSE AND REPORT ORGANIZATION

This project was funded by Lawrence Livermore National Laboratory (LLNL) as a continuance of and contribution to the Geotoxicity Hazard Index (GHI) developed at LLNL and described in Smith et al. (1980). That work took an "analog" approach to the assessment of hazardous waste disposal. The analog approach, drawn in part from arguments formulated by B. Cohen (e.g. Cohen and Jow, 1978) and others, attempts to circumvent the apparently infinite "what if..." component of theoretical or deterministic modeling of waste/environment interactions. It also substitutes observation of natural phenomena for the mass of laboratory research data and assumptions used in deterministic or predictive modeling.

This report extends the availability term of the GHI, specifically the m-factor as proposed by Smith et al. (1980):

$$m = A_i / A_{0i}$$

where A_i = actual availability of material i, in a specific burial setting

A_{0i} = average availability of analog material i.

The purpose of this report is essentially three-fold:

a) to provide real world input from geological and geochemical summaries of existing observations of natural geotoxic element behavior in pertinent geologic environments. (Geotoxic elements include natural and man-made radioactive elements and certain non-radioactive metallic elements buried in the earth's crust).

b) to begin the definition of semi-quantitative limits (m-factors) on natural geologic processes affecting possible waste isolation sites or natural deposits of buried toxic material and,

c) to attempt to answer the question "What is the advantage of deeper disposal of radioactive waste?"

This report is organized by sections. Section II, Approach, explains our arrival at a geochemical rather than a simple geologic or hydrologic approach to these tasks. Section II also sets our format and explains our choice of a matrix to guide the research work as illustrated in the total report.

Section II lists elements chosen to represent radioactive waste components. Selection of these representative elements considered:

1. those elements that are the most mobile and therefore the conservative proxy for their group;
2. those elements of significant half-life such as to be available to the biosphere over extended time periods; and
3. those elements for which some significant research is documented in the literature.

Section II lists and defines the geochemical parameters of significance in either radioactive waste or toxic metal behavior. These parameters are used then in conjunction with the selected waste elements above to form a matrix which sets the report format. Tables in Section II illustrate the final results of our work on radioactive elements as a capsule summary in matrix format, and another table represents an effort to quantify significant matrix relationships (quantification and semi-quantification of m-factors).

The report then elucidates the capsule matrix summaries in textual format. Information drawn from the Oklo natural fission reactors and from natural uranium deposits is discussed in Section III. Section IV then proceeds through the matrix headings by groups of selected elements, discussing their relationship to geochemical functions drawn from the literature.

Section V reverses the process by examining effects in terms of the geochemical variables (Eh, pH, mineralogy, anion effects, and temperature) on a very significant group of radioactive elements, the actinides.

Sorption effects emerge as a significantly misunderstood topic deserving separate treatment (Section VI), though it was not dealt with specifically as a matrix heading.

Section VII, Hydrothermal Ores, deals with the analog potential of such deposits and of hot water systems in the mobilization/immobilization potential of metals. No matrix format or m-factor quantification was attempted for hydrothermal environments, but avenues for further work are clear. Similarities and dissimilarities of metal behavior with the radwaste element geochemistry are noted.

Section VIII is a summary of geochemical benefits and problems of increased depth of radioactive and toxic waste burial, again in terms of mobility/immobility.

Conclusions and limits of all the proceeding work is presented by each individual author along with the potentially most rewarding analog-oriented work for the future. Note that two lists of references are included: A. Radioactive Waste Behavior, and B. Hydrothermal Ores.

Appendices A through M, present supplementary material included for technical verification of text and matrices, and for a more complete technical background.

II. APPROACH

A. Analog Application:

Geology is rich in analog traditions with its origin as a science of natural observation in the field. But like other natural scientists, geologists are now taught to mistrust natural observation until thoroughly tested and understood in theoretical terms. Today, natural systems are reported in the literature as an intricate combination of empirical and theoretical observations with continuous building of "models" (e.g., the *porphyry copper system; the plate tectonics systems; the geothermal systems*) that are undergoing constant revision as they slowly approach understandable "reality".

This report has approached geotoxic interactions more through the perceptions of geochemistry than of the interactions of waste materials with the broad geologic terrain. The following comments describe our evolved direction:

1. Our initial approach relating actual rock types to waste isolation provided little definitive material useful for our purposes.
2. Rock type differences, in a broad sense, appeared to be relatively unimportant except where gross geochemical differences exist (e.g. salt vs. granite vs. organic shale).
3. Physical differences between rock types are primarily of hydrologic (porosity, permeability) or of engineering concern.
4. We were surprised by our early results indicating that even profound hydrologic parameters, such as extreme permeability and high solution flow-rates, may be less important than geochemical parameters.

5. The literature indicates that others have firmly arrived at these same conclusions. The best work, a combination of theoretical and empirical geochemistry tied to geologic field observation, appears to have been done by Brookins (1980, 1979, 1978, 1976) and Langmuir (1978, 1977).

6. In simple geologic terms, little can be said to answer the question "What are we buying with depth?". Beyond the simple hydrologic variable (decreasing porosity/permeability plus increasing distance to biosphere), temperature and pressure effects lead us into a family of potent geochemical mobilization/immobilization possibilities.

The geochemical approach coupled with the pursuit of depth-related parameters seemed to push us somewhat away from the analog approach and somewhat more into the theoretical than we had anticipated. This first-cut report is more complex, more scientifically illuminating, but less definitively reduced to the assessment format than we originally imagined.

B. m-Factor:

The m-factor as defined by Smith et al. (1980) includes both engineering, or engineered parameters as well as naturally imposed conditions of beneficial nature to waste isolation. For our purpose of focus, we separate the engineered parameters from the natural, and suggest that engineered parameters be considered separately in future hazard-indexing. This will help avoid confusion and temper the tendency to decrease the weight of natural barriers in a waste environment with assumed engineering solutions.

Smith et al. (1980) define $m = A_i/A_{0i}$, where A_i = the actual availability for material i, and A_{0i} = a reference availability. In this report, we begin the development of a semi-quantitative set of m-factors by considering m to be an estimate of the approximate influence of a given condition on the mobility/solubility of selected elements. A +m-factor implies an increase in mobility and a -m implies a decrease in mobility, with a zero m being the chosen standard corresponding to essentially immobile uranium species. Note that this notation is based on a logarithmic scaling in constrast to the original definition in Smith et al. (1980). Empirically, "immobility" may be assumed when molar concentrations of the species are at or below 10^{-11}. As a first approximation m is defined as $\log M/M_r$ where M = molar concentration of a species and M_r = the reference molar concentration (10^{-11}) taken from the immobile example $[UO_2]^{++}$ at neutral pH, 25°C. The quantity, therefore, has a great deal of variation either above (+m) or below (-m) the reference value (m=0). Where quantification is not possible, mobilities are expressed as "+m (great, small) etc." These first-cut symbols could be given as approximate values for purposes of semi-quantitative calculation.

C. Format:

We use a simple matrix to organize and summarize our work. Our selection of matrix-heading parameters forced us to focus on geochemical processes as the prime controllers of radioactive waste component behavior in the geosphere. Selection of headings also motivated selection of specific elements deserving prime consideration as mobile toxins. Table 1 lists the elements selected for this study from the complete listings of Table 2 and Table 3. The geochemical parameters used as matrix rows are defined in Table 4. (Note: In order to maintain continuity in the text, all Tables are presented at the end of Section II.)

The matrix format, using elements as column headings and selected geochemical parameters as horizontal rows, is illustrated in Table 5. Matrices were constructed for immobilizing and mobilizing conditions. Immobilizing conditions represent the important situation where the stabilization of wastes is analogous to the formation of ore deposits. For mobilizing conditions, the movement of buried wastes is analogous to the situation where solutions transport ore materials to a concentration point, or to dispersal. These matrices are presented in Tables 6 and 7.

We originally intended to do a matrix pair for each significant rock type (e.g., granite, shale, salt, tuff, basalt) considered for radioactive waste isolation. This intent lead us to the somewhat paradoxical realization that the simple geochemical parameters dominate (or at least define within themselves) the differences between rock types.

Similar matrices could be constructed for the hydrothermal ore (stable metal) model. But our treatment of that area of study is introductory, so matrices and the quantification steps, m-factor tables, were not attempted for the hydrothermal systems.

Essentially, our report format is governed by the matrix organization. For radioactive materials two natural models or groups of models are examined through existing literature, for matrix input:

1. Oklo Natural Fission Reactors
2. Uranium Ore Deposits
    a. Colorado Plateau-type
    b. Vein-type

These models are discussed briefly in the text with additional referenced material given in appendices. Pertinent data is summarized in the

mobilization and immobilization matrices (Table 6 and Table 7) and these matrix data are also discussed briefly in the body of the text as well as in referenced excerpts in the appendices.

Sorption requires text discussion in its own right, though it is dealt with throughout the matrix-based discussions. It was not chosen as a matrix heading, since sorption processes are controlled by the other geochemical parameters chosen as headings.

The matrices are working summaries of the radioactive element discussions. The m-factor Table 8 is a first attempt at summarizing semi-quantitative geochemical relationships.

TABLE I. Components of Radioactive Wastes; Elements Selected for this Study.

Actinides (Th, U, Np, Pu, Am, Cm)	The actinide elements, especially U through Am, have analogous geochemical behavior. Although, there are some minor distinctions between the geochemical behavior of the actinides (which will be characterized in the matrix), generally uranium has the greatest potential mobility. Conditions that minimize uranium mobility would imply minimized mobility of the other actinides.
Lanthanides	The lanthanide elements have analogous geochemical behavior as a group. Although some similarities do exist between the lanthanides and actinides, the aqueous chemistry of the lanthanides is different from that for the actinides, so the two groups are treated separately.
Alkali Metals (Cs)	This element has a high potential mobility. The geological toxic threat of ^{137}Cs (with a half-life of 30 years) is moderated by the short half life.
Alkaline Earths (Sr, Ba, Ra)	The activity of ^{90}Sr with a half-life of 28 years, is significantly reduced after 600 years. Radium-226 becomes a significant waste component as ^{230}Th decays. Radium-226 content of waste becomes significant after 50,000 years and increases for about 10^5 years.
Other Metals (Co, Ni, Sb, Ru, Fe)	All have relatively short half-lives. ^{63}Ni is the longest at 120 years.
Technetium	Technetium-99, with a half-life of 2.1×10^5 years has a relatively high potential mobility in its anionic form (TcO_4^-).
Iodine	Iodine-129, with a half-life of 1.7×10^7 years, has a high potential mobility and biological affinity. Its toxicity is moderated by its low specific activity.

TABLE 2. Significant Nuclides in Radioactive Waste Management (from NEA, 1977).

Nuclide	Half-life	Major mode of decay	Major generation mechanisms
Tritium	12.3 y	β	Fission and neutron capture
Carbon-14	5.7×10^3 y	β	Neutron capture
Argon-41	1.8 h	β[a]	Neutron capture
Iron-55	2.9 y	EC[b]	Neutron capture
Cobalt-58	72 d	β[a]	Neutron capture
Cobalt-60	5.3 y	β[a]	Neutron capture
Nickel-63	120 y	β	Neutron capture
Krypton-85	10.8 y	β[a]	Fission
Strontium-89	51 d	β	Fission
Strontium-90	28 y	β	Fission
Yttrium-91	59 d	β	Fission
Zirconium-93	1.5×10^6 y	β	Fission
Zirconium-95	64 d	β[a]	Fission and neutron capture
Niobium-95	35 d	β[a]	Fission and daughter of Zirconium-95
Technetium-99	2.1×10^5 y	β	Fission
Ruthenium-106	1 y	β	Fission
Iodine-129	1.7×10^7 y	β	Fission
Iodine-131	8 d	β[a]	Fission
Xenon-133	5.2 d	β[a]	Fission
Caesium-134	2.1 y	β[a]	Fission and neutron capture
Caesium-135	2×10^6 y	β	Fission
Caesium-137	30 y	β	Fission
Cerium-141	33 d	β[a]	Fission
Cerium-144	285 d	β[a]	Fission
Promethium-147	2.6 y	β	Fission
Samarium-151	93 y	β	Fission
Europium-154	16 y	β[a]	Fission and neutron capture
Lead-210	22 y	β	Daughter of Polonium-214
Radon-222	3.8 d	α	Daughter of Radium-226
Radium-226	1.6×10^3 y	α[a]	Daughter of Thorium-230
Thorium-229	7.3×10^3 y	α[a]	Daughter of Uranium-233
Thorium-230	8×10^4 y	α	Daughter of Uranium-234
Uranium-234	2.4×10^5 y	α	Daughter of Protactinium-234
Uranium-235	7.1×10^8	α[a]	Natural source, daughter of Plutonium-239
Uranium-238	4.5×10^9 y	α	Natural source
Neptunium-237	2.1×10^6 y	α	Neutron capture and daughter of Americium-241
Plutonium-238	87 y	α	Neutron capture and daughter of Curium-242
Plutonium-239	2.4×10^4 y	α	Neutron capture
Plutonium-240	6.6×10^3 y	α	Neutron capture
Plutonium-241	15 y	β	Neutron capture
Plutonium-242	3.87×10^5 y	α	Neutron capture
Americium-241	433 y	α	Neutron capture and daughter of Plutonium-241
Americium-243	7.37×10^3 y	α	Neutron capture
Curium-242	163 d	α	Neutron capture
Curium-244	18 y	α	Neutron capture

a) *With associated penetrating gamma radiation.*
b) EC = orbital electron capture.

TABLE 3. Initial Radionuclide Concentration of Input Solid Wastes (from Chipman et al., 1980).

Nuclide	Activity (Ci/kg)	Nuclide	Activity (Ci/kg)	Nuclide	Activity (Ci/kg)
^{79}Se	6.4E-05*	^{87}Rb	3.6E-09	^{90}Sr	1.3E+01
^{90}Y	1.3E+01	^{93}Zr	3.1E-04	^{93m}Nb	7.5E-05
^{99}Tc	2.1E-03	^{106}Ru	9.7E-01	^{106}Rh	9.7E-01
^{107}Pd	2.0E-06	^{126}Sn	3.2E-05	^{126m}Sb	3.2E-05
^{126}Sb	3.2E-05	^{134}Cs	3.3	^{135}Cs	7.5E-05
^{137}Cs	1.3E+01	^{137m}Ba	1.2E+01	^{144}Ce	8.2
^{144}Pr	8.2	^{144}Nd	0.0**	^{147}Pm	1.2E+01
^{147}Sm	0.0**	^{151}Sm	1.7E-01	^{154}Eu	1.8E-01
^{226}Ra	0.0**	^{230}Th	0.0**	^{233}Pa	0.0**
^{233}U	1.2E-12	^{234}U	4.3E-10	^{235}U	1.8E-09
^{236}U	1.0E-08	^{237}U	4.8E-12	^{238}U	1.0E-14
^{237}Np	4.8E-08	^{239}Np	0.0**	^{238}Pu	7.0E-02
^{239}Pu	7.0E-04	^{240}Pu	6.5E-04	^{241}Pu	1.6E-01
^{242}Pu	1.8E-06	^{241}Am	9.8E-04	^{243}Am	8.3E-06
^{242}Cm	6.5E-04	^{244}Cm	5.2E-04		
Total	8.5E+01				

* 6.4E-05 = 6.4×10^{-5} = 0.000064.

** Initial input is 0.0, but they appear later as daughter products.

TABLE 4. Immobilization/Mobilization; Geochemical Parameters Used as Matrix Headings.

pH	The various controls on the pH in the near-surface environment include cation and anion concentration from interaction with minerals (especially those yielding carbonate ion, silica and sulfur), decaying organic matter and dissolved salts which can act as buffers. In deep environments pH is determined by the mineralogy of the rocks themselves.
Eh - (oxidation/ reduction potential)	Oxidation/reduction is the single most important factor affecting mobility, especially of the actinides. Major controls of Eh in the near-surface environment are carbon content, Fe^{+3}/Fe^{+2}, S^{-2}/SO_4^{-4} and P_{O2} (partial pressure of oxygen). The environmental Eh range is defined by P_{O2} (Eh = 1.22-0.059 pH) and P_{H2} (Eh = -0.059 pH). Carbonaceous matter may permit stronger local reducing reactions. There is also evidence to suggest that secondary mineral genesis (alteration) may be a factor in the reduction of uranium in sedimentary ore deposits.
Mineralogy	The mineralogy of a given rock type can significantly influence the behavior of waste components, especially adsorption characteristics, Eh and pH.
Presence of Anions	The presence and concentration of anions, like Cl^-, F^-, CO_3^{-2}, HPO_4^{-2} and SO_4^{-2} can influence the solubility and adsorption of waste materials grossly through the very important but poorly understood processes of complex formation.
Presence of Cations	The presence and concentration of cations such as Na^+, K^+, Ca^{+2}, Mg^{+2}, V^{+5}, can influence the adsorption of waste materials by competing for both ion exchange and complexing sites.
Temperature	Elevated temperatures, resulting from radioactive decay will influence both the mechanical and chemical properties of the rock and waste material. Waste heat will also set up pressure gradients and convection cells in the ground water around a repository. Heating effects on the mechanical properties of rock are currently being investigated at some of the pilot repository sites, i.e., Stripa, Hanford and the Nevada Test Site. The chemical effects are difficult to quantify. As a very general rule, a 10°C increase in temperature approximately doubles or triples the reaction rate. Solubilities will increase if dissolution is endothermic and decrease if dissolution is exothermic. Under the right chemical conditions, increased reaction rates, due to the elevated temperature may be favorable to waste immobilization. Interpretation of Eh-pH diagrams for elevated temperatures is problematic because most of the data for construction of these diagrams are based on surface environment (approximately 25°C-40°C) conditions.
Pressure	There is generally insignificant change in solubility of liquids and solids with pressure. The solubility of all gases is increased as the partial pressure of the gas is increased in proximity of a solution. Increases in the partial pressure of CO_2 may significantly affect actinide mobility and, of course, the partial pressure of O_2 greatly influences the oxidation potential.

TABLE 5. Matrix Summary Format.

GEOCHEMICAL PARAMETERS	SELECTED ELEMENTS						
	Actinides	Lanthanides	Alkali Metals	Alkali Earths	Other Metals	Technetium	Iodine
Immobilization Mechanisms			Cs	Sr, Ba, Ra	Ru, Co, Ni	TcO_4^-	I^-
pH							
Eh							
Mineralogy							
Cations							
Anions							
Temperature							
Pressure							
Mobilization Mechanisms							
pH							
Eh							
Mineralogy							
Cations							
Anions							
Temperature							
Pressure							

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TABLE 6. Mobilization of Selected Nuclides in Geochemical Environments.

Mobilization	Actinides	Lanthanides - Rare Earths	Alkali - Metals	Alkaline Earth
(radioactive)	Th, U, Np, Pu, Am		Cs	Sr, Ba, Ra
Eh	Uranium is a quite mobile trace element in oxidized environments, mainly due to its soluble carbonate complexes. Other actinides have analogous behavior but to a lesser degree. Oxidants are: oxygen, MnO_2 and possibly hematite under certain conditions (role of hematite debateable). Sorption is decreased by oxidizing conditions Self-induced oxidation/reduction reactions induced by radiolysis of water (producing O_2 and H_2O_2 by α-radiation of Pu, Am, and Np may increase mobility by oxidizing elements in a slightly reducing environment.		Some experimental evidence suggests that Cs sorption on tuff and shale is generally less from de-oxygenated. No such effect noted for granite.	Some experimental suggests that Sr sorption on tuff shale is generall from de-oxygenate but unchanged for granite. Radium concentrat apparently increa under uranium dep because of dissol Ra itself but rat to dissolution of hydroxides on whi Ra is adsorbed.
pH	Solubility of uranium increases for pH values below 6 due to complexing with halogens, sulfate and silica. Solubility increases for pH values above 8 because of carbonate complexing and possibly hydroxide formation. Sorption decreases at pH values <6 and >8, and desorption may result if solutions change from natural to acidic or alkaline conditions.		No Cs sorption from a simulated brine solution for pH values between 6.5 to 7.9 and no sorption from ground water for pH values of 7.5 to 8.2.	
Accessory Mineralogy	MnO_2 can convert fluids from reducing to oxidizing. Salts enhance solubility and decrease sorption capacity. Actinides have a strong tendency to form complexes. Complexes inhibit sorption and favor desorption.	Salts in solution inhibit lanthanide sorption on clay.	Sorption of Cs decreased from solutions of high dissolved salts. Crystalline iron and manganese oxides and hydroxides showed no sorption of Cs.	Sorption of Sr an decreased from so of high dissolved at pH values 6.5
Presence of Anions	The uranyl carbonate complexes are the single most important factor contributing to uranium mobility in oxidized environments. The mobilizing effects of carbonate complexes increase at pH values above 8 and for high partial pressures of CO_2. Very high CO_2 pressures also increase the solubility of the very insoluble uranous species. Carbonate complexes are significant under oxidizing conditions when pH values exceed 5 and temperature < 100°C. HPO_4^{-2} complexes are probably the second most important mobilizers of uranium under near-surface or oxidizing conditions. HPO_4^{-2} complexes are most significant for pH 6 to 8 if carbonate concentration is low. An HPO_4^{-2} concentration of 0.1 ppm at Eh=0.05v and pH=6 enhances both the solubility of uranous and uranyl species. SO_4^{-2} complexes are significant below pH=3 and may be important up to pH≤7 for sulfate concentration ≤100 ppm. Fluoride complexes with uranium are very important at pH ≤3 even at elevated temperatures. Silica complexes are significant at pH = 6 if CO_3^{-2} and HPO_4^{-2} are low. Hydroxide complexes may be significant at pH values > 8.			Radium concentrat increased ten to hundred times due complexing with C brine solutions. Mobilized under h pressure CO_3^{-2} as postulated from t carbonatite analo
Presence of Cations	Increasing cation concentration generally reduces sorption capacity. Dissolving waste cannisters are a potential source of cations.	Increased concentration of Na and Ca decreases sorption of rare earths on kaolinite and montmorillonite.	Both K^+ and Na^+ compete with Cs^+ for sorption sites, and therefore inhibit Cs sorption.	Na^+, Mg^{+2}, Ca^{+2}, tration decrease sorption by comp for sites. Little discrimin ^{85}Sr and ^{45}Ca in precipitation or exchange in soil
Temperature/ Pressure	Solubility of uranium generally increases with increasing temperature. Maximum solubility of about 75 ppm for UO_2 is at 260°C. Stability of uranyl carbonate complexes decreases with increasing temperature.		Temperature increase from 25° to 65°C reduced Cs sorption on bentonite.	

- Metals	Alkaline Earths	Other Metals	Technetium	Iodine
Cs	Sr, Ba, Ra	Ru, Co, Ni	TcO_4^-	I^-
imental evidence hat Cs sorption d shale is less from de-. No such ed for granite.	Some experimental evidence suggests that Sr and Ba sorption on tuff and shale is generally less from de-oxygenated water but unchanged for granite. Radium concentration apparently increases under uranium deposits not because of dissolution of Ra itself but rather due to dissolution of Fe-Mn hydroxides on which the Ra is adsorbed.			
·ction from a brine solution lues between and no sorption id water for pH 7.5 to 8.2.		Acidic pH values increase mobility.		
of Cs decreased ·ions of high salts. ne iron and oxides and s showed no of Cs.	Sorption of Sr and Ba decreased from solutions of high dissolved salts at pH values 6.5 to 7.9	Humic acid apparently inhibits Co^{2+} sorption.	Sorption on clays and rock materials very low in oxidizing solutions.	I^- can migrate in halides by diffusion.
	Radium concentration increased ten to several hundred times due to complexing with Cl^- in brine solutions. Mobilized under high CO_2 pressure $CO_3^{}$ as postulated from the carbonatite analog.	Nitrite ions strongly complex Co^{2+} and Ru^{2+} to form neutral and anionic complexes which are very mobile. Lead is relatively immobile in the presence of sulfate and sulfide. Ru forms numerous complexes with halides.	No sorption of TcO_4^- from brine solutions at pH = 6.5 to 8.2 Chemistry of Tc in complexes has been relatively little studied, but resembles rhenium.	No sorption of I^- from a brine solution at pH = 6.5 to 8.2
nd Na^+ compete for sorption id therefore Cs sorption.	Na^+, Mg^{+2}, Ca^{+2} concentration decrease Sr sorption by competing for sites. Little discrimination between ^{85}Sr and ^{45}Cs in either precipitation or cation exchange in soils.			
ure increase from 5°C reduced Cs on bentonite.				

TABLE 7. Immobilization of Selected Nuclides in Geochemical Environments.

	Actinides Th, U, Np, Pu, Am	Lanthanides - Rare Earths	Alkali - Metal Cs	Alkal Sr,
Eh	Solubility of reduced species increases greatly as CO_2 partial pressure increases. Very high solubility possible in carbonate rock terrains. The reduced species of the actinides are very insoluble. Reducing environment is the single most important variable influencing mobility of the actinides. Reduction is a principal mechanism postulated for uranium ore deposition. Reductants include: Carbon (humic acid, bitumens, petroleum, CH_4, graphite, carbonaceous matter), Fe^{2+} (biotite, pyrite, hornblende), sulfide (pyrite, H_2S). Complicated reactions involving carbonaceous matter and clays (as with Plateau-type deposits). Sorption is greatly enhanced in a reducing environment. Complexing can cause shifts in the oxidation potential and influence oxidation states.	The reduced species of the lanthanides are generally analogous to the actinides and are very insoluble. Reducing conditions would immobilize the lanthanides. Sorption is higher for Ce and Eu under deoxygenated conditions.		
pH	Minimized solubility of compounds and most complexes under both reducing and oxidizing conditions at pH values between 7 and 8. Maximized sorption capacity for pH values between 6 and 8.5.	Maximum sorption at neutral pH = 6-8.	Cs sorption on "smectite" clay is not effect by pH.	
Accessory Mineralogy	Clays and zeolites enhance sorption. Complex reactions of illite-montmorillonite and carbonaceous matter to form colorite may result in reduction of uranyl species. Iron and manganese oxyhydroxides may be effective adsorbers, however, under certain conditions they may enhance the oxidation of the uranous species. Organic matter, pyrite, biotite and hornblende enhance reduction and sorption. Organic matter plays the principal role as a reductant/adsorber in uranium deposition. Uranyl carbonate complexes can coexist with pyrite under conditions of high CO_2 pressure but are unstable in the presence of carbon. Redox characteristics of accessory minerals strongly influence the oxidation state for the actinides.	Gd is adsorbed onto chlorite. Lanthanides adsorbed on to crushed granite, bentonite and red clay. Preferential fixation of La and Ce into calcerous sediments due to similar ionic radii compared to Ca^{+2}. Ce^{+4} may be removed by coprecipitation with ferro-manganese nodules.	At low concentrations of Cs, sorption onto clay is high but decreases with increasing Cs concentration. Humic acid is a good Cs adsorber. Sorption of Cs on vermiculite is superior to montmorillonite but not as good as zeolites. Sorption and fixation depend on [Cs] and the charge density of the crystal layers. Sorption and fixation capacities for mixtures of clays, zeolites and oxide/hydroxides are greater than can be expected from their individual sorption capacities.	Sr f grea of z be e indi A mi Toli or p for Some clay Some Sr s Radi Sr c perh solu than
Presence of Anions	VO_4^{3-} favors precipitation of carnotite in an oxidizing environment with low CO_2 pressure (atmospheric). At atmospheric CO_2 pressure and a pH about 7, autunite may precipitate if $[HPO_4^{3-}]$ > 0.1 ppm and $[VO_4^{3-}]$ is less than 500x that of $[HPO_4^{3-}]$. Generally, anions favor mobilization rather than immobilization.	Lanthanides bond almost exclusively in ionic matter and have virtually no complexes or covalent compounds.		Max Sr^{2+} lim of Na_2 as to env
Presence of Cations				Max in pre sul. Rad Ca-
Temperature/ Pressure	The uranyl carbonate complexes appear to be unstable at elevated temperatures and of minor significance at 100°C. However, high CO_2 pressures may enhance their stability at higher temperatures. General conditions hypothesized for hydrothermal vein-type deposition is between 500°C and 150°C at ≤ 1 Kbar. The presence of organic matter and iron sulfides are sufficient to prevent oxidation of uranium at 200° to 300°C in shale. Temperature increases from 25-65°C resulted in sorption for clay, granite and ferrous minerals.	Study of a rare earth-enriched lamprophyre dike intruding an evaporite suggests that the lanthanides remained confined to the immediate area of the dike during and after high temperature emplacement.	Increased temperatures increased Cs retention on "smectite" clay. At 200°C and above, new crystalline phases appear in shale. Pollucite ($CsAlSi_2O_6$) appears as a dominant reaction product, since shales are alkali-poor and should act as scavengers for alkali elements to react with clays to form framework silicates, i.e., zeolites and/or feldspars.	

arths	Alkali - Metal Cs	Alkaline Earths Sr, Ba, Ra	Other Metals Ru, Co, Ni, Pb	Technetium TcO_4^-	Iodine I^-
of the rally inides ile. would anides.			Reducing conditions retard Ru mobility in brine solutions, possibly by formation of sulfide or hydroxide.	Tc^{+4} is sparingly soluble in reducing conditions. Sorption enhanced 100-300X in reducing conditions.	Reducing conditions greatly enhance I^- sorption.
or					
s.					
neutral	Cs sorption on "smectite" clay is not effect by pH.				
chlorite.	At low concentrations of Cs, sorption onto clay is high but decreases with increasing Cs concentration.	Sr fixation is much greater in mixtures of zeolites than can be expected from the individual members.	Humic acid promotes Ru^{+6} sorption.	TcO_4^- was adsorbed on shale under oxidizing conditions, probably on the organic matter.	Iron and Al-hydroxides, clay, Cu, Pb and Ag compounds adsorbed I^- from reduced ground water.
n of onite	Humic acid is a good Cs adsorber.	A mixture of clinoptilolite with mordenite or phillipsite is best for Sr sorption.	Ni is enriched in clays associated with uranium deposits.		
of Le sediments radii $^{+4}$ may be ation with es.	Sorption of Cs on vermiculite is superior to montmorillonite but not as good as zeolites. Sorption and fixation depend on [Cs] and the charge density of the crystal layers.	Some Sr retention by clays.			
	Sorption and fixation capacities for mixtures of clays, zeolites and oxide/hydroxides are greater than can be expected from their individual sorption capacities.	Some humic acid promotes Sr sorption.			
		Radium adsorbed more than Sr on granite and bentonite perhaps because the $RaSO_4$ solubility product is lower than for $SrSO_4$.			
st matter				Reduced CO_3 content may enhance TcO_4^- retardation.	
		Maximum concentrations of Sr^{+2} in ground water is limited by precipitation of the insoluble carbonate.			
		Na_2SO_4 has been proposed as as canister overpack material to limit Sr mobility in brine environments.			
		Maximum concentration of Ra in ground water limited by precipitation of the insoluble sulfate			I^- absorbed on galena and copper metal under reducing conditions
		Radium coprecipitates with Ca- and Mg-carbonates.			
n-enriched rudfng s that ined fiate ing and -e	Increased temperatures increased Cs retention on "smectite" clay.				
	At 200°C and above, new crystalline phases appear in shale. Pollucite ($CsAlSi_2O_6$) appears as a dominant reaction product, since shales are alkali - poor and should act as scavengers for alkali elements to react with clays to form framework silicates, i.e., zeolites and/or feldspars.				

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TABLE 8. m-Factors: Factors That Affect the Mobility of Uranium.

Each m-factor represents a comparison to a set of reference conditions, given at the beginning of each section.

Conditions	m	Reference
Given reducing conditions (Eh below 0.273v at 25°C; uranium is in the +4 oxidation state. Concentration of the uranous ion is generally below 0.01 ppb except at pH values below 3 and above 7. Langmuir (1978) concludes that the extreme insolubility of uraninite and coffinite at normal ground water pH values (4-8) makes uranium practically immobile in low Eh environments.		Langmuir (1978)
@ pH = 7, $[UO_2]$ = ~ 0.01 ppb or 10^{-11}M $[UO_2]$ @ 25°C	0	Langmuir (1978)
@ pH = 9, [U] = ~ 1 ppb or 10^{-9}M $[UO_2]$	+2	Langmuir (1978)
@ pH = 4, [U] = ~ 0.0001 ppb or 10^{13}M $[UO_2]$	-2	Langmuir (1978)
@ pH = 2, [U] = ~ 0.01 ppb or 10^{-11}M $[UO_2]$	0	Langmuir (1978)
100-fold increase in uraninite solubility at pH = 6 and PO_4 = 0.1 ppm (10^{-6}M) and Eh exceeds +0.05 v.	+2	Langmuir (1978)
1000-fold increase in uraninite solubility with a rise of P_{CO_2} from atmospheric ($10^{-3.5}$ atm) to a ground water value of 10^{-2} atm @ Eh = -0.05 v, $[UO_2]$ = 10^{-7}M.	+3 to +4	Langmuir (1978)
Uranous fluoride complexes are stable up to pH = 4 @ 25°C, at 2 ppm [F] and pH = 2. [U] = 1 ppm or 10^{-5}M $[UO_2]$.	+6	Langmuir (1978)
Solubility of uraninite increases about tenfold as temperature increases from 25°C to 100°C.	+1	Langmuir (1978)
Well crystallized uraninite is much less soluble than amorphous UO_2 (pitchblende).	-2 to -6	Langmuir (1978)

TABLE 8 - CONTINUED

Conditions	m	Reference
Solubility of uraninite increases with temperature with maximum solubility at 260°C in pure water.		Langmuir (1978)
@ 25°C, $[UO_2]$ = ∿ 0.01 ppb	0	
@ 100°C, $[UO_2]$ = ∿ 0.1 ppb	+1	
@ 260°C, $[UO_2]$ = ∿ 75 ppm	+5	
Background values for uranium in streams is around 0.1 ppb. In uraniferous areas, the uranium concentration in waters can range from 1 to 400 ppb. (m-factor is expressed relative to the concentration of uraninite in pure water @ 25°C (10^{-11}M) because that represents "immobile" conditions. Uranium is oxidized above 0.273 v.		Langmuir (1978)
[Carnotite] = 10^{-7}M @ pH = 7 and P_{CO_2} = 10^{-2} atm @ 25°C w/0.1 ppm vanadium (10^{-6}M vanadate)	+4	Langmuir (1978)
[Carnotite] = 10^{-9}M @ pH = 7 and P_{CO_2} = $10^{-3.5}$ atm	+2	Langmuir (1978)
[Tyuyamunite] = 10^{-6}M @ pH = 7 and P_{CO_2} = 10^{-2} atm	+5	Langmuir (1978)
[Tyuyamunite] = 10^{-8}M @ pH = 7 and P_{CO_2} = $10^{-3.5}$ atm	+3	Langmuir (1978)
Solubility of carnotite and tyuyamunite increases above pH = 8 because of formation of carbonate complexes.		
[Autunite] = 10^{-4}M @ pH = 7 and P_{CO_2} = 10^{-2} atm Σ PO_4 = 10^{-6}M (0.1 ppm); [Ca] = 80 ppm or $10^{-2.7}$M and [K] = 39 ppm or 10^{-3}M.	+7	Langmuir (1978)
[Autunite] = 10^{-6} to $^{-7}$M @ 2 pH = 7; P_{CO_2} = $10^{-3.5}$M. Ground waters from granitic terrain were more likely to have a $[PO_4]$ of 0.1 ppm or more as compared to sedimentary rocks.	+5 to +4	Langmuir (1978)
[uranyl hydroxide] in slightly alkaline and slightly acidic solutions is about 10^{-5}M.	+6	Krauskopf (1967)

TABLE 8 - CONTINUED

Conditions	m	Reference
[uranyl carbonate] complexes at pH = 7 with 0.01 M [carbonate] is 10^{-4}M @ 25°C or ten times more solubility than in a carbonate free solution.	+7	Krauskopf (1967)
Uranyl Carbonate Complexes:		
$[UO_2CO_2]$ = $10^{-3.5}$M @ pH = 6 and CO_2 = 1 atm	+7	Rich, et al. (1975)
$[UO_2CO_2]$ = $10^{-2.8}$M @ pH = 6.5 and CO_2 = 1 atm	+8	Rich, et al. (1975)
$[UO_2CO_2]$ = $10^{-2.3}$M @ pH = 3 and CO_2 = 1 atm @ 25-50°C	+9	Rich, et al. (1975)
$[UO_2CO_2]$ with $NaHCO_3$ exceeds 10,000 ppm at low temperatures	+9	Rich, et al. (1975)
At CO_2 pressure of 10^{-2} atm and 25°C the uranyl carbonate complexes are the major species in pure water down to a pH = 5.		Langmuir (1978)
Uranyl fluoride complexes up to pH = 6.7 @ 25°C.	+m	Rich, et al. (1975)
Uranyl sulfate complexes stable up to pH = 4 possibly significant up to pH = 7.	+m weak	Langmuir (1978)
Uranyl silica complexes @ pH = 6 accounts for up to 50% of the soluble uranium species with SiO_2 = 60 ppm or 10^{-3}M.	+m moderate	Langmuir (1978)
Uranyl chloride complexes: neutral solutions saturated with respect to $UO_3 \cdot H_2O$ or $UO_3 \cdot 2H_2O$ contains 10 ppm uranium which increases in alkaline and greatly increases in acidic solutions.	+6 to >> +6	Rich, et al. (1975)
Carbon, carbonaceous matter and/or methane.	-m very strong	Langmuir (1978)
Sulfide (pyrite, H_2S).	-m strong	Langmuir (1978)
Fe^{+2} (i.e., biotite, augite).	-m moderate to strong	Langmuir (1978)
Presence of the above reducing agents will generally decrease the solubility to below the detection limit.		
Reduction of U due to metamorphic reactions involving the oxidation of ferrous ion and resultant reduction of uranyl ion.	-m	McMillan (1978)
Reduction of uranium during clay mineral formation.	-m	Brookins (1980)

TABLE 8 - CONTINUED

Conditions		m	Reference
Sorption of 1 ppm uranium @ pH = 5 to 8		0	Langmuir (1978)
	@ pH = 4	+2 or more	Langmuir (1978)
	@ pH = 9 with CO_2	" "	Langmuir (1978)
	@ pH = 9 without CO_2	0	Langmuir (1978)
Presence of sulfate, halogens, or carbonate inhibits sorption.		+m	Langmuir (1978)
Humic acid concentrates uranium 10,000:1 @ pH = ~ 5.		-m strong	Dyck (1978)
Sorption agents:	carbon	-m strong	Brookins (1980)
	zeolites	-m strong	Szalay (1967)
	clay	-m *moderate*	Shiao, et al. (1979), Beall, *et al.* (1979)
	augite and biotite	-m moderate	Haire & Beall (1979)
	oxides	-m weak	Allard, et al. (1980)

III. NATURAL MODELS FOR RADIOACTIVE WASTE BEHAVIOR.

A. Oklo Natural Fission Reactors (General):

The existence of well-preserved natural fission reaction sites such as those at Oklo provide the best possible natural analog for the geologic behavior of a modern radioactive waste mix.

Oklo originated geologically as a uranium deposit in sedimentary rocks probably analogous to the much younger Colorado Plateau-type ore deposits, (Brookins, 1978) except that concentrations of fissionable uranium were high enough for natural criticality. It is likely that other natural fission reactors existed in pre- or near-post Oklo time of about 2 billion years before present. As earth history progressed beyond Oklo time, the probability of natural fission decreased to essential impossibility due to the decay of the fissile nuclide U-235.

About 10 tons of fission products and 4 tons of Pu were produced over the period of criticality of about 100,000 years by 9 identified reactors (Gancarz et al., 1980). Temperatures during reaction reached at least 600°C (probably 650-700°C) within the reaction zone and were at least 400°C several meters outside the reaction zone (Vidale, 1978).

Oklo is a hybrid analog consisting first of a near-surface "ore" deposit with approximate conditions 25°C, 1 atm., Eh = -0.05 to 0.45 and pH 7 to 8.5 (Brookins, 1978). Second, the critical phase would follow closely the deposition phase presumably under similar approximate geologic and geochemical conditions. If criticality continued for about 10^5 years there would be an interesting coincidence with a third phase, short to moderate term fission product behavior. The model value at this phase, though not identical to modern waste isolation, is perhaps enhanced by the continuing presence of

reaction heat which would approximate heat levels present in concentrated waste.

A fourth phase of the Oklo hybrid provides a look at long to very long time behavior (10^6 to 10^9 years) of the fission product mix, though during this phase as during later portions of the third phase, geologic and geochemical conditions may have varied considerably from the original apparently documentable conditions.

Conditions of actual waste isolation may also vary both in original (relative to Oklo) as well as in the post-historical geologic environments of moderate term. Therefore, the evidence for stability drawn from Oklo must diminish in statistical validity as the time factor relating it to waste increases. (Only one set of possible natural conditions prevailed at Oklo compared to many possible sets of conditions in actual isolation sites). However, long and very long times as generalized here can be eliminated from logical concern. Following the reasoning of Bredehoeft et al. (1978), times of more than 10^5 years could be dropped from predictive/engineering concern relative to waste isolation installations.

Other natural fission sites need to be found and studied to improve the model but it is apparent that the very long term stabilities illustrated in the study of Oklo are extremely important in verifying the conservatism of geologic modeling.

Also note that in the study of actual observed element distribution at Oklo, Eh-pH diagrams of theoretical behavior of geotoxic species do not always apply and certain theoretically expected relationships are not observed (Brookins, 1978; Duffy, 1978).

Studies of the Oklo deposit suggest: (1) Retention of the rare earths and actinides, probably in the host pitchblende; (2) Perhaps only local migration of the alkali and alkaline earths. These two statements essentially summarize the prime significance of the model developed by studies to date.

The use of the Oklo reactor as an analog to waste disposal sites assumes that the radioactive wastes are in reduced form and are for the most part incorporated into a stable mineral structure (i.e., uraninite in the Oklo case). Retention of the lanthanides and actinides at the Oklo site is primarily due to the stability of uraninite, in which they are contained.

Less than 10% of the fission products Rb and Sr were retained. Some migration of Tc and Ru was noted along with significant migration of Kr, Xe, Rb, Cs, Sr, Ba, Mo, and I. Heavy elements remained relatively fixed, conclude Walton and Cowan (1973).

Otherwise mobile or potentially mobile fission products must first escape from the uraninite (UO_2) grains by fission recoil (5-10%) and volume diffusion (very slow). "The principal geochemical requirements for a suitable storage site are those that ensure the survival of the UO_2 matrix, particularly that the Eh and pH are similar to the values of Oklo" (Cowan, 1978). So, the stability of uraninite relative to Eh and pH is important not only in the possible distribution of uranium and chemically (mineralogically) associated elements, but of physically retained elements as well.

During the long post-reaction time (approximately 2×10^9 billion years) of Oklo history much Pb has been lost to local migration following diffusion out of uraninite. Lead loss averaged about 50% over this time period. "Local migration" here means movement of 3 to 5 meters with redeposition below the reactor zone.

PuO_2 shows remarkable stability under Oklo conditions. $PuO_2(CO_3)_2^{-2}$ and $PuO_2(CO_3)OH^-$ fall within the stability field of water at high Eh (over wide pH range). So carbonate complexes may be important in high CO_2 environments. The ionic radii of Pu^{4+} and U^{4+} are nearly identical and an almost ideal solid solution exists between PuO_2 and UO_2 at high temperatures. Pu^{4+} remains unoxidized as some U^{4+} becomes oxidized to U^{6+} in pitchblende (Brookins, 1978).

Note that in the above discussions and in the literature words such as "significant movement" or "out of the reaction zone" may refer to actual distances of a few meters or a few tens of meters.

B. Uranium Ore Deposits - Introduction:

Study of the uranium ore deposits contributes to analog modeling of waste behavior in three genetic categories:

1. Pre-ore conditions contributing to mobilization of ore-associated elements.
2. Ore-localization and concentration conditions pointing to very specific immobilization.
3. Post-ore conditions that have allowed stability of the ore masses for times upwards of 10^9 years (10^6 year scale for Colorado Plateau-Type), or that may have remobilized or dispersed the ore concentrations.

Recall that "ore" is an economic term referring to high concentrations of valuable materials. This implies concentrations of uranium and associated elements in which the uranium exists as several hundredths of a percent to several percent of the present rock. Of all known radioactive ore bodies only Oklo has been proven to have fissioned, therefore study of uranium ore

deposits gives us information on the behavior of uranium and its decay products (not fission products) and any other elements concentrated along with the uranium in the ore-forming/retaining processes.

Associated elements very generally may include any of the heavy, or precious metals as in the multi-element ore locales known as porphyry-copper deposits. Porphyry-coppers may contain economically significant amounts of uranium. The uranium ore deposits proper have limited association with other elements such that only vanadium is routinely dealt with in genetic or economic studies of the deposits. As for decay products, experiments indicate that uranium is the "most mobile non-gaseous element in the uranium decay series within the surficial environment" (Dyck, 1978). This parallels our general assumption that uranium mobility exceeds that for most of its associates, whether decay or fission products, in the near-surface and the humanly obtainable sub-surface environments.

Figures 1 through 6 show the general geochemical conditions of uranium ore deposition and elucidate the use of Eh-pH diagrams.

1. Uranium Ore Deposit Types

Uranium ore deposition as dealt with herein is predominantly classifiable into two categories:

a. Hydrothermal ores (vein-types, "hardrock", replacement, etc.)

b. Colorado Plateau-type ores (sedimentary, "softrock", Grants-type, roll-type, etc.)

"Hydrothermal" implies hot-solution origin, generally associated with a local heat source (and possibly an ore-element source) such as a molten rock mass. Other less localized or intense heat sources are possible (Barnes, 1979), so

(Text continued on Pg. 31)

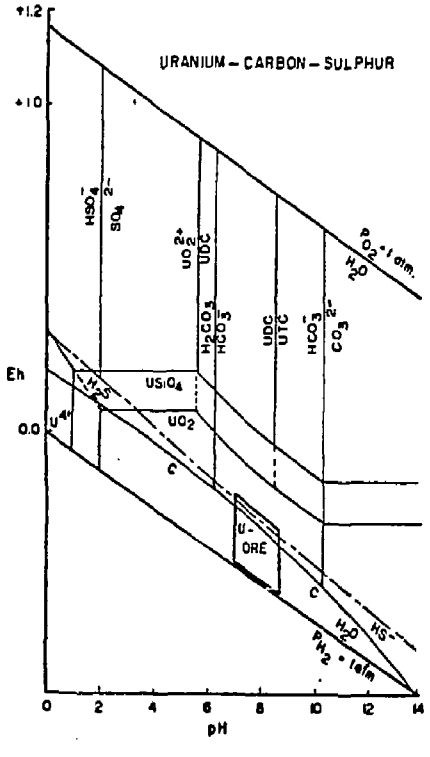

FIG. 1. Eh-pH diagram for part of this system U-S-Si-O-H-Fe. Assumed activities: U = 10^{-6}, Fe = 10^{-6}, S = 10^{-3}. (from I.A.E.A., 1978)

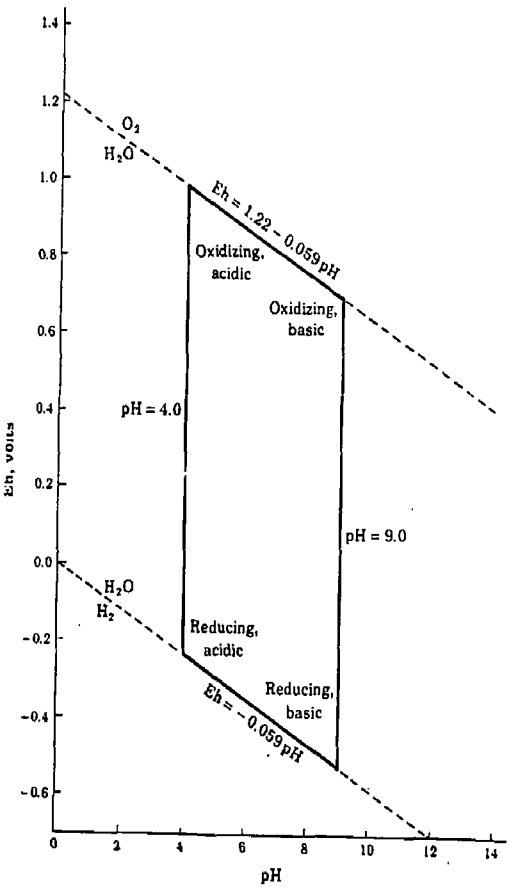

FIG. 2. Framework of Eh-pH diagrams. The parallelogram outlines the usual limits of Eh and pH found in near-surface environments. (from Krauskopf, 1967)

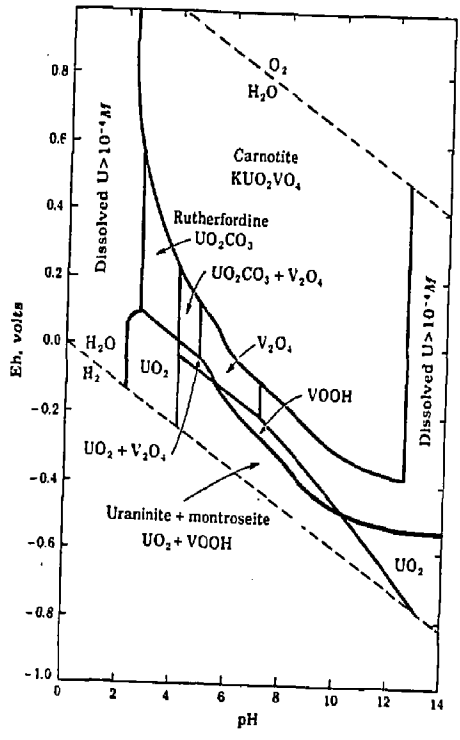

FIG. 3. Eh-pH diagram for uranium and vanadium compounds at 25°C and 1 atm total pressure. Total dissolved V = 10^{-3}M, carbonate = 10^{-1}M. (from Krauskopf, 1967)

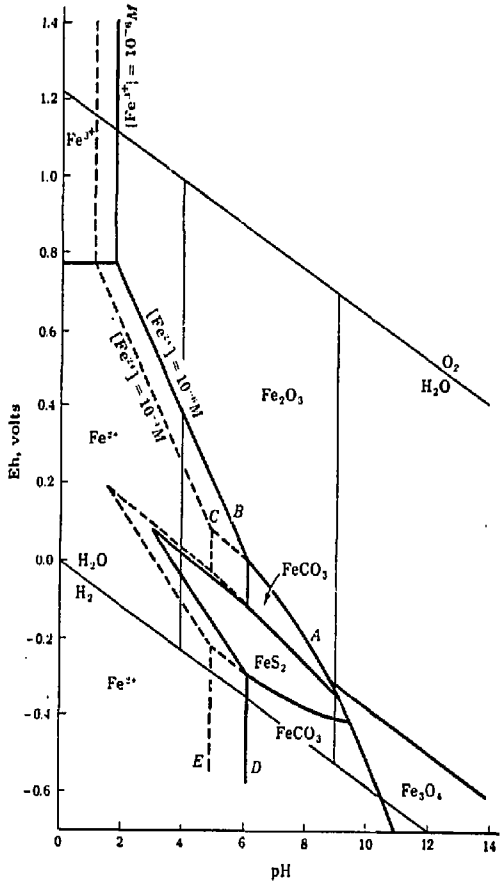

FIG. 4. Eh-pH diagrams showing stability fields of common iron minerals. Total activity of dissolved carbonate, 1M, of dissolved sulfur, 10^{-6}M. Solid field boundaries on left side of diagram are for total dissolved iron = 10^{-6}M, dashed lines for 10^{-4}M. (from Krauskopf, 1967)

Fe_2O_3 = Hematite; $FeCO_3$ = Sidarite; FeS_2 = Pyrite;

Fe_3O_4 = Magnetite.

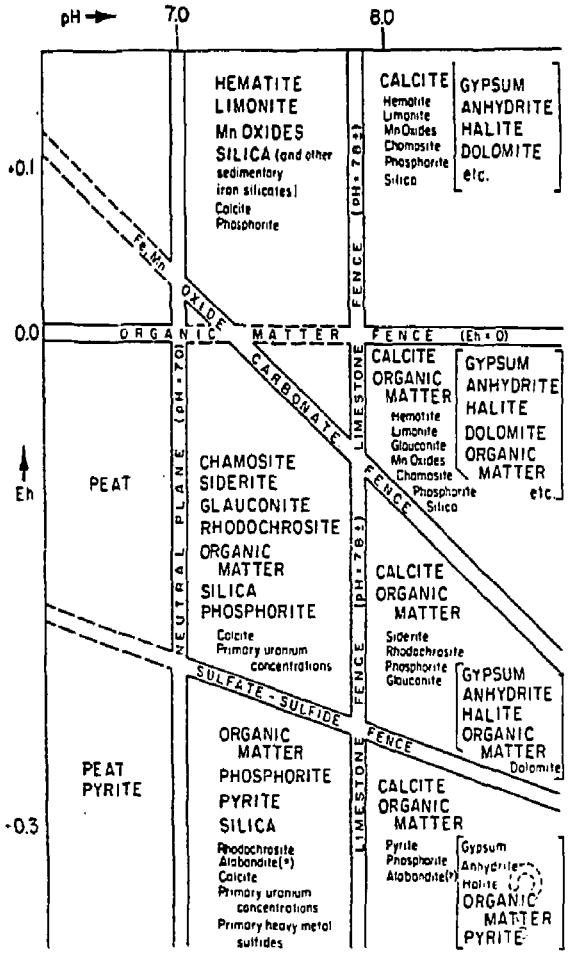

FIG. 5. Fence diagram showing Eh-pH fields in which chemical end-members of nonclastic sediments are formed under normal sea-water conditions. Associations in brackets are for hypersaline conditions (salinity >200‰) (in Park and McDiarmid, 1964).

Becquerelite, $UO_3.2H_2O$.
Ianthinite, $2UO_2.7H_2O$.
Rutherfordine, $UO_2.CO_3$.
Uranothallite, $2CaCO_3.U(CO_3)_2.10H_2O$.
Voglite, Hydrous U,Ca,Cu, carbonate.
Mackintoshite, U,Th,Ce, silicate.
Thorogummite, Silicate of U,Th,Ce.
Uranophane, $CaO.2UO_3.2SiO_2.7H_2O$.
Sklodowskite, $MgO.2UO_3.2SiO_2.7H_2O$.
Kasolite, $PbO.UO_3.SiO_2.H_2O$.
Soddyite, $5UO_3.2SiO_2.6H_2O$.
Delorenzite, Fe,U,Y, titanate.
Brannerite, $(UO,TiO,UO_2)TiO_3$.
Hatchettolite, U, tantalo-niobate.
Ishikawaite, U niobate.
Samirésite, U, *etc., niobate.*
Fergusonite, Y,Er,U, niobate.
Samarskite, Fe,Ca,U,Ce,Y, niobate.
Ampangabéite, U, etc., niobate.
Euxenite, Polycrase, Blomstrandine-Priorite } Y,Ce,U, niobate-titanates.
Betafite, U, niobate-titanate.
Pisekite, U,Ce, etc., niobate and titanate.
Mendelyeevite, Ca,U, niobate and titanate.
Plumboniobite, Y,U,Pb, niobate.
Torbernite, $Cu(UO_2)_2P_2O_8.8H_2O$.
Zeunerite, $Cu(UO_2)_2As_2O_8.8H_2O$.
Autunite, Bassetite } $Ca(UO_2)_2P_2O_8.8H_2O$.
Uranospinite, $Ca(UO_2)_2As_2O_8.8H_2O$.
Uranocircite, $Ba(UO_2)_2P_2O_8.8H_2O$.
Uranospathite, Hydrous uranyl phosphate.
Carnotite, $K_2O.2U_2O_3.V_2O_5.3H_2O$.
Tyuyamunite, $CaO.UO_3.V_2O_5.nH_2O$.
Rauvite, $CaO.2UO_3.6V_2O_5.20H_2O$.
Renardite, $PbO.4UO_3.P_2O_5.9H_2O$.
Dewindtite, $3PbO.5UO_3.2P_2O_5.12H_2O$.
Dumontite, $2PbO.3UO_3.P_2O_5.5H_2O$.
Parsonsite, $2PbO.UO_3.P_2O_5.H_2O$.
Phosphuranylite, $(UO_2)_3P_2O_8.6H_2O$.
Trögerite, $(UO_2)_3As_2O_8.12H_2O$.
Uvanite, $2UO_3.3V_2O_5.15H_2O$.
Ferghanite, $U_2(VO_4)_2.6H_2O$.
Walpurgite, $Bi_{10}(UO_2)_3(OH)_{24}(AsO_4)_4$.
Uraninite, Uranyl, etc., uranate.
Clarkeite, $(Na_2,Pb)O.3UO_3.3H_2O$.
Gummite, alteration of uraninite.
Thorianite, Th and U oxides.
Curite, $2PbO.5UO_3.4H_2O$.
Fourmarierite, Hydrous Pb uranate.
Uranospharite, $Bi_2O_3.2UO_3.3H_2O$.
Johannite, Hydrous Cu,U sulphate.
Uranopilite, $CaO.5UO_3.2SO_3.25H_2O$.
Zippeite, Hydrous U sulphate.

FIG. 6. Uranium Minerals (from Dana, 1966).

great variation in genetic conditions and final form are also possible, but "hydrothermal" possibilities range to the deeper, hotter, more chemically active end of the depositional spectrum which may be stretched to include "metamorphic" ores.

Colorado Plateau-types imply a more limited range of conditions, generally as in the near-surface environment. Circulating ground water and a broad source of uranium and its ore associates are the generalized genetic agents. Elevated temperatures are often postulated, as is a hydrothermal source for ore-elements, so that a hydrothermal categorization may be at least occasionally proper here also. A family distinction is desirable, and particularly for our purposes, the Colorado Plateau-type, which dominates U.S. uranium production and information in American scientific literature, more closely resembles some proposed waste environments. The hydrothermal model is covenient relative to possible high local heat and reactive brines likely to occur from presently favored disposal methods and environments.

2. Summary of Uranium Deposit Chemistry

This section summarizes the prime points affecting uranium mobility and immobility in all three genetic categories noted above.

Conclusions of this summary, and of Tables 6 and 7, may be previewed and abbreviated as follows. In the sense of minimizing the mobility of uranium:

a. Maintain a moderately reducing environment (as expected in most groundwaters in most rock types). This appears to be the overriding variable in uranium immobility.

b. Keep the pH range between 6 to 8 (normal surface and near-surface environments).

c. Minimize CO_2 pressure which minimizes dissolved carbonate as readily attainable in arid and semi-arid environments.

d. Minimize halide concentration in associated waters. (Note the implication here relative to salt disposal).

Natural or man-made buffer zones of iron, manganese, titanium, and especially carbonaceous matter would maximize sorption and buffer potentially serious changes in Eh. Though sorption processes may be valuable as delay or concentration limiting factors relative to migrating toxins, these processes are highly variable, poorly understood and apparently by-passed in many natural mobile systems.

3. Uranium Deposition and Mobility; Reducing Environment

a. The extreme insolubility of uraninite and coffinite at normal ground water pH's (4-8) makes uranium practically immobile in low Eh environments regardless of other moderate geologic and hydraulic variables (Langmuir, 1978).

b. Uraninite solubility increases at elevated CO_2 pressures (in high alkalinity waters) due to dissociation of $CaCO_3$. At high pH, $CO_3^=$ is the predominant dissociation species so uranyl carbonate complexes form.

c. Uranous fluorides are important (stable and soluble complexes) at typical fluoride concentrations in reducing ground waters below pH = 4. They greatly enhance uranium solubility at low pH values. (Note: chloride complexes may have a similar but less profound effect.)

Overall, uranium is immobile in reducing environments unless relatively unusual conditions prevail as noted above. A change from reducing to

oxidizing conditions (near-surface to surface environments) may instigate drastic increases in uranium mobility, although uranium still may not be extremely mobile even in the surface environment unless certain conditions prevail.

4. Uranium Deposition and Mobility; Oxidizing Environment

   a. Uranium transport generally occurs in oxidizing surface and ground waters as uranyl species, most often as UO_2^{2+} or uranyl fluoride-, chloride-, phosphate-, carbonate- or sulfate-complexes. Highly oxidizing fluids, in a CO_2 environment, are those most likely to favor uranium transport over large distances.

   b. At intermediate Eh's, oxidation and leaching of uraninite and coffinite are greatly enhanced (by several orders of magnitude) when phosphate and/or carbonate are present to form their highly stable uranyl complexes. Uranyl minerals are most stable in pH range 5 to 8.5 (Langmuir, 1978).

   c. In unusually acidic near-surface environments (temperature under 100°C and pH values from 0 to 3) uranium sulfate and fluoride complexes are important soluble species. At common ground water concentrations of sulfate (100 ppm), uranium sulfates may be a significant mobile species up to pH = 7.

   d. Hot brines, which are of an acidic oxidized nature, are considered carrier solutions for uranium mineralization.

   e. Soil bacteria and microflora have been noted to increase uranium solubility, probably due to biosynthesis of complexing and chelating compounds. In general, the role of organisms in transport and

precipitation or uranium is poorly understood. The role may be more important in fixation of uranium rather than transport.

f. Under conditions of low carbonate concentration, phosphate complexes are important soluble species. With the pH range of ground waters in the Wind Rivers Formation, Wyoming (pH = 6.6 to 8.3) both uranyl phosphate and carbonate complexes are abundant.

g. In the absence of vanadium and at atmospheric CO_2 pressure the most common oxidized uranyl minerals are the autunites (Fig. 6) indicating a major role of phosphate (Langmuir, 1978).

h. With uranium in an oxidized environment at low to moderate pH values, carnotite is most likely to form. *Tyuyamunite* is several times more soluble than carnotite but like carnotite it has a very low minimum solubility near 1 ppb [U] at about pH = 7 (Langmuir, 1978). In other words, vanadium decreases the mobility of uranium even in moderately alkaline oxidizing environments.

i. If vanadium and phosphate concentrations are low, but silica is high the mineral uranophane will form and demobilize uranium. This is not a typical ground water condition, however (Langmuir, 1978).

j. Generally, even the soluble uranyl minerals are least soluble at pH's within the range 5 to 8.5. Above pH = 8.5, uranyl carbonate complexes form; below pH = 5, UO_2^{2+} and other soluble cations form.

k. The pH range (5 to 8.5) of minimum solubility of the uranyl minerals is also the pH range of maximal sorption on most important natural colloidal materials. In the context of an oxidizing environment, sorption (not solubility) controls total uranium in water up to mineral saturation, therefore sorption can be important at low uranium concentration.

l. Sorption experiments for clays, phosphates, and iron and titanium hydroxides in the pH range of 5 to 8.5 and in the absence of strong uranyl sulfate, fluoride and carbonate complexes which inhibit sorption, suggest that clays are relatively unimportant sorbers.

m. Titanium and iron oxyhydroxides are the most important sorption media. There is good evidence that uranyl sorption is an important preconcentrating step leading to the formation of both uranyl and uranous minerals even though sorption effects over-all are unpredictable and not functional in open (highly mobile) solution systems.

n. Reductants such as, humic acids, pyrite, hydrogen sulfide, carbon, solids, liquids or gases, and petroleum can cause uranium precipitation across very abrupt spatial changes from oxidizing to reducing environment. Especially clay rich traps, with abundant organic matter, establish the redox fronts along which near-surface uranium is deposited. These deposits may be destroyed or moved by continued flows of oxidizing waters, "although presently recognized redox front(s) may have been essentially stationary since early Tertiary" (Brookins, 1980).

o. Uranyl dicarbonate may coexist with pyrite under certain conditions but no uranyl species are thermodynamically stable in the presence of carbonaceous matter (Kimberly, 1978).

IV. SELECTED ELEMENT GEOCHEMISTRY, MATRIX PARAMETERS

This section discusses the relationship, as drawn from the literature, between groups of selected elements and the geochemical functions presented in the matrices.

A. Actinide Geochemistry:

The general geochemical conditions that minimize uranium mobility would also minimize the mobility of other actinides. These conditions are characterized by:

1. reducing environments (Fe^{+2} in biotite and/or pyrite, also organic matter);
2. pH in the range of 6.5 to 8.5;
3. small to moderate bicarbonate/carbonate ion concentration; and
4. low dissolved salt content.

Figures 7 through 16 illustrate the type of data that form the basis of m-factor assignments relative to behavior of actinides in solution environments.

Self-oxidation/reduction cycles due to α-radiation induced radiolysis in an aqueous environment could enhance mobility of the actinides, especially Am and Pu.

Actinides form an extensive series of complexes with halogens and, oxo-anions, such as NO_3^-, SO_4^{2-}, Ox^{2-}, CO_3^{2-} and PO_4^{2-}. The general tendency to complex formation is influenced by ionic size and charge such that:

$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$ and,

$CO_3^{2-} > Ox^{2-} > SO_4^{2-}$ (Cotton and Wilkinson, 1967).

(Text continued on Pg. 45)

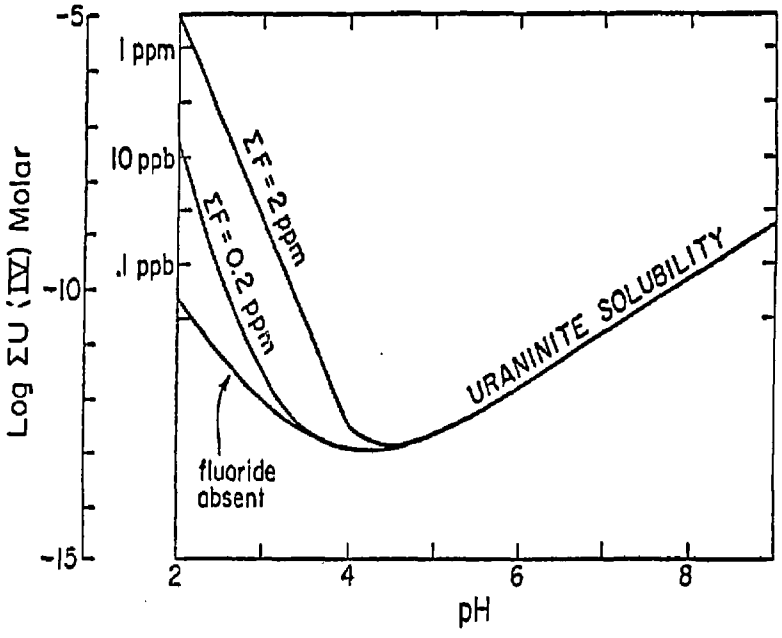

FIG. 7. The effect of uranous-fluoride complexing on the solubility of uraninite $UO_2(c)$, versus pH at 25°C. (from Langmuir, 1978).

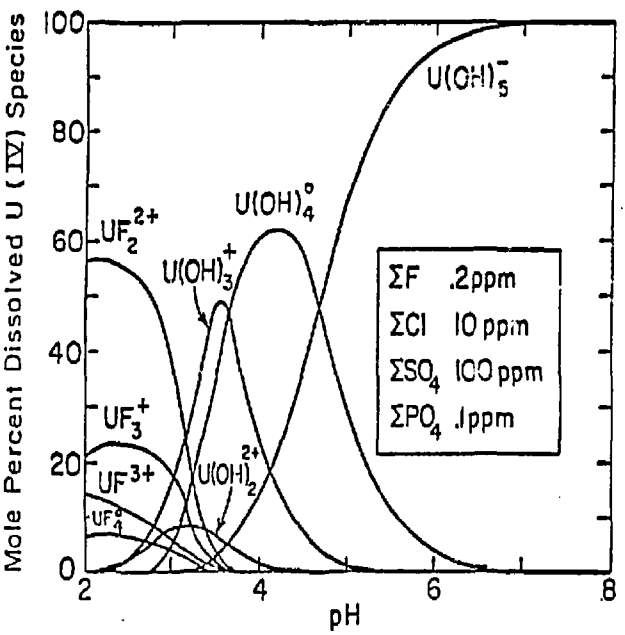

FIG. 8. Distribution of uranous complexes versus pH for some typical ligand concentration in ground water at 25°C (from Langmuir, 1978).

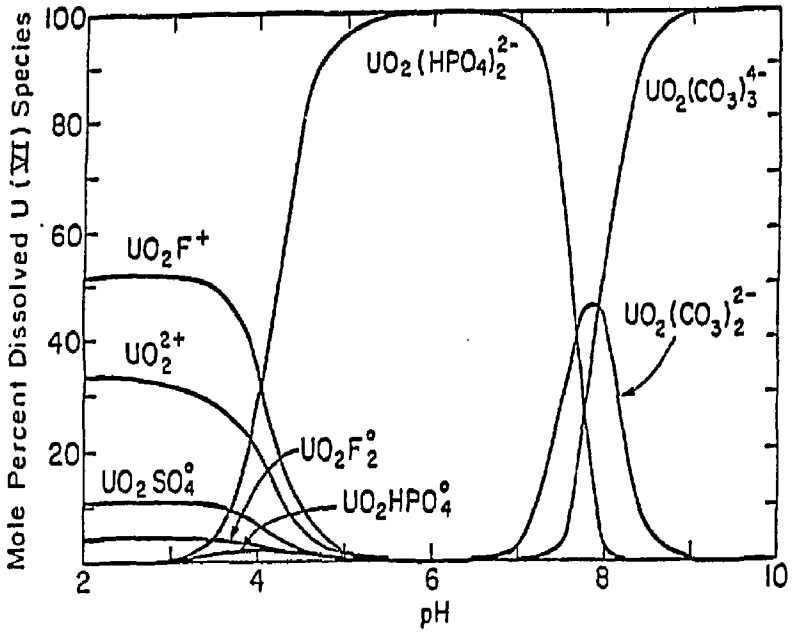

FIG. 9. Distribution of uranyl complexes versus pH for some typical ligand concentrations in ground waters of the Wind River Formation at 25°C. P_{CO_2} = $10^{-2.5}$ atm, ΣF = 0.3 ppm, ΣCl = 10 ppm, ΣSO_4 = 100 ppm, ΣPO_4 = 0.1 ppm, ΣSiO_2 = 30 ppm (from Langmuir, 1978).

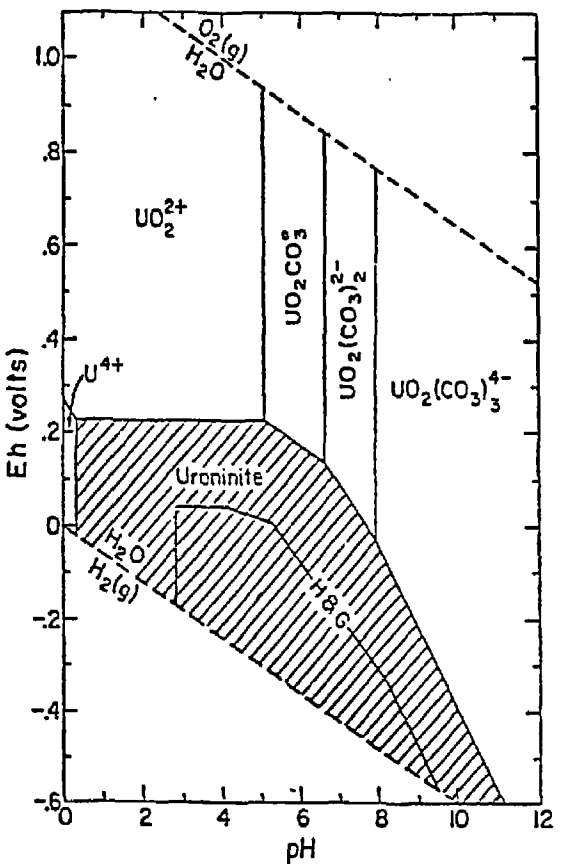

FIG. 10. Eh-pH diagram in the U-O_2-CO_2-H_2O system at 25°C for $P_{CO_2} = 10^{-2}$ atm. Uraninite, $UO_2(c)$, solution boundaries are drawn at 10^{-6} M (0.24 ppm) dissolved uranium species. "H & G" denotes the boundary of the uraninite stability field according to Hostetler and Garrels (1962) (in Langmuir, 1978).

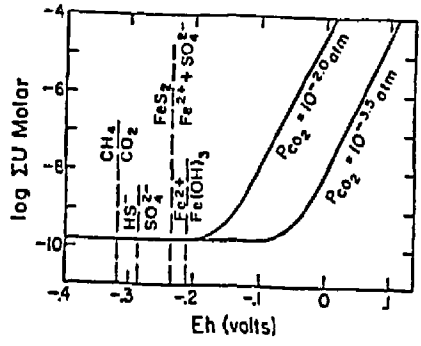

FIG. 11. The solubility of uraninite, $UO_2(c)$ at pH = 8 and 25°C as a function of Eh and P_{CO_2}. Also shown are the Eh values for some important redox reactions computed assuming:

$CH_4 = CO_2$, $SO_4^{2-} = HS^-$, $Fe^{2+} = 10^{-4}M$, and

$SO_4^{2-} = 10^{-3}M$ (From Langmuir, 1978).

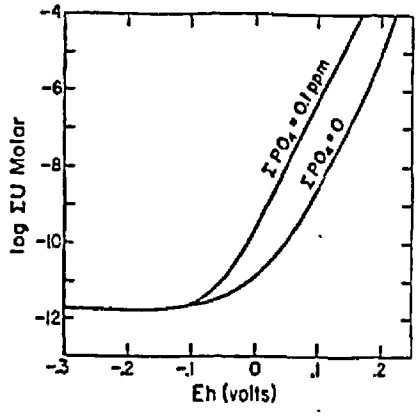

FIG. 12. The solubility of uraninite, $UO_2(c)$, at pH = 6 and 25°C as a function of Eh for $P_{CO_2} = 10^{2.0}$ atm, with PO_4 absent, and for $\Sigma PO_4 = 10^{-6}M$, (0.1 ppm) (From Langmuir, 1978).

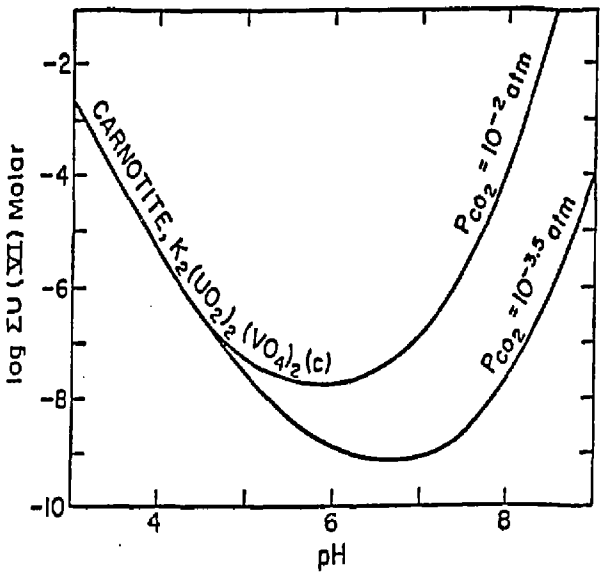

FIG. 13. Solubility of carnotite at 25°C as a function of pH and P_{CO_2} for $K = 10^{-3}$ M (39 ppm) and $\Sigma V = 10^{-6}$ M (0.1 ppm as VO_4) (from Langmuir, 1978).

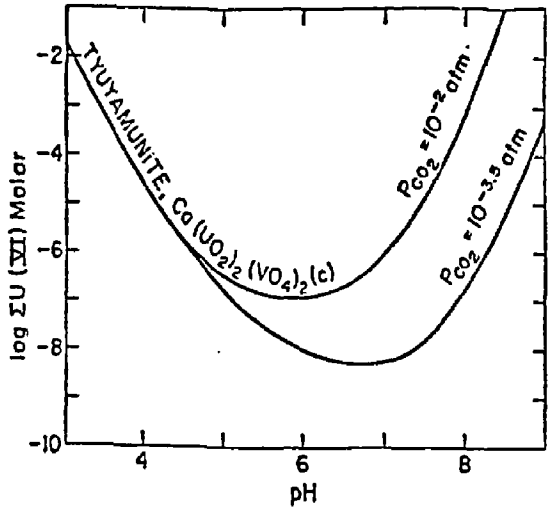

FIG. 14. Solubility of tyuyamunite at 25°C as a function of pH and P_{CO_2} for $Ca = 10^{-2.7}$ M (80 ppm), and $\Sigma V = 10^{-6}$M (0.1 ppm as VO_4). (From Langmuir, 1978).

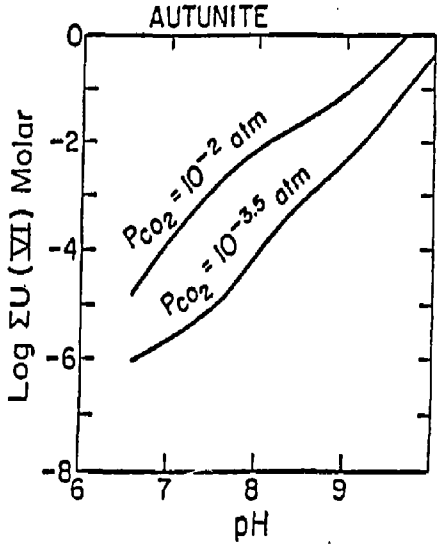

FIG. 15. Solubility of autunite at 25°C as a function of pH and P_{CO_2} for Ca = $10^{-2.7}$M (80 ppm), and ΣPO_4 = 10^{-6}M (0.1 ppm).

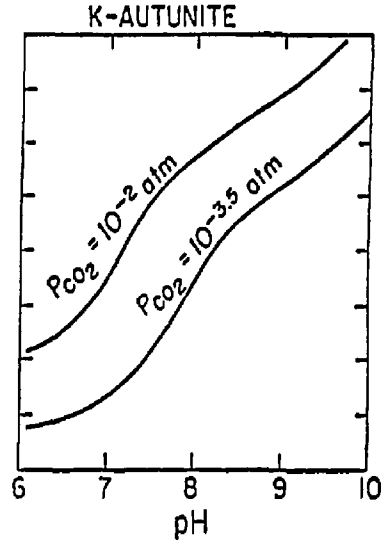

FIG. 16. Solubility of potassium autunite at 25°C as a function of pH and P_{CO_2} for K = 10^{-3}M (39 ppm) and ΣPO_4 = 10^{-6}M (0.1 ppm).

(Both figures from Langmuir, 1978).

Stabilities of the oxidation states are:

$UO_2^{2+} > NpO_2^{+} > PuO_2^{2+} > AmO_2^{2+}$; $Am^{3+} > Pu^{3+} >> Np^{3+}$.

Complex formation can shift the oxidation potential and influence the relative stabilities of oxidation states for actinides. The stability of the higher oxidation state falls from uranium through americium.

"Under anoxic conditions to be expected in a deep underground repository in igneous rock, the actinides would be expected to exist predominately in the tri- and tetra-valent state. The aqueous chemistry in these valence states at environmental pH levels is largely dominated by hydrolysis reactions. In oxic systems like surface waters, the penta-and hexa-valent states would predominate (for U, Np and possibly Pu). For these higher valence states the aqueous chemistry would be entirely different at environmental pH levels, with a much lower degree of hydrolysis and higher overall mobility," (Beall et al., 1980).

Therefore, mobility is not only a function of the behavior of stable states but also a function of the rates of conversion from other oxidation states.

Given the relative stabilities of the oxidation states and very similar chemical properties, geochemical environments which immobilize uranium would be expected to also immobilize Np, Pu, and Am.

The tendency of actinides to hydrolyze is: Am > Pu > Np > U and $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$ (Cotton and Wilkinson, 1967).

The maximum concentration of tetravalent elements in solution is limited by the precipitation of hydroxides, which like for uranium, might be transfixed into dioxides (Allard, 1979).

Neptunium exists as NpO_2^+ in an aerated solution (Allard, 1979). The formation of sulfate complexes of Np^{4+} and NpO_2^{2+} is also noted (Cotton and Wilkinson, 1967). This illustrates influence of complex forming anions on tne oxidation state of Np and other oxides.

The aqueous chemistry of Pu (like U, Np and Am) is complicated by the fact that all four oxidation states can coexist in appreciable concentration in a solution. Aqueous solutions of Pu and Am^{+4} and Am^{+6} undergo rapid self-reduction due to their α-radiation (Cotton and Wilkinson, 1967).

The oxidation state of Pu in aqueous solutions is affected by radiolysis of the water: "Water radiolysis will be a major factor in determining the oxidation state of Pu solutions in the near vicinity of the radiation field of a waste repository. It can be postulated that even small quantities of Pu carried away from the repository by some leaching and transport process and subsequently adsorbed on some mineral in a rock will be subjected to the oxidation effects of radiolysis from its own alpha activity." The net result of a series of reactions initiated by radiolysis of the water is that Pu may undergo a cycle of oxidation and reduction. The period of the cycle will depend on Pu concentration, radiation field intensity, pH, temperature and formation of complexes; Pu^{+3} + α-radiation + H_2O + Pu^{4+} + Pu^{6+} (Fried et al., 1980). (AmO_2^+ is reduced [4%/hour] by products from its own α-radiation).

Two random examples from real world tests:

1. The mobility of Pu in natural soils was determined to be 0.2 to 2 cm/year (Jakubick, 1979).
2. Concentration factors of Pu in aquatic plants and animals can be quite high, for example, 2 x 10^4 ppm in North Atlantic sargassum; 10^3 ppm in edible bivales; but less than 19 ppm in edible fish tested (NEA, 1977).

Also note the following excerpt from Ogard et al. (1980):

"It has been suggested for the management of nuclear waste that the reducing conditions that frequently occur in deep geologic burial would result in very slow leaching of spent-fuel elements in contact with water. We have conducted leaching experiments both in the oxidizing condition of air-saturated water and in reducing conditions produced by bubbling hydrogen or hydrogen-argon gas mixtures through the water. A reducing solution produced in this manner proved not to be very reducing as evidenced by the high concentration of uranium found in the leachant. The concentration of uranium in the reducing water was only a factor of 10 less than in the air-saturated water whereas estimates of up to a factor of 10^{10} less were thought possible. These results do, however, provide other information of value to the management of nuclear waste.

We have compared the concentration of uranium, fission products and other radionuclides found in the leachant to their concentration in the spent-fuel element and have concluded three things: 1) The radionuclides cerium, plutonium, americium, and europium reach a maximum concentration in the leachant and precipitate as further dissolution of the UO_2 matrix takes place. 2) The precipitate appears to have a negative temperature coefficient of solubility. 3) Congruent dissolution of the UO_2 matrix is the primary mechanism for release of the radionuclides into the leachant under oxidizing and slightly reducing conditions."

The solubility limits in water of the rare-earths and actinides investigated in this system are listed in Table 9.

TABLE 9. Observed Solubility Limits at pH4, Deionized water (From Ogard et al., 1980)

Element	Moles/Liter 25°C	70°C	Condition
Eu	≥3 E-8	2 E-9	O & R
Ce	≥3 E-7	1 E-8	O & R
Am	≥5 E-8	2 E-9	O & R
Pu	≥3 E-7	1 E-8	O & R
U	>5 E-5	>3 E-4	O
		~2 E-6	R

O = air-saturated water, R = reducing conditions

3 E-8 = 3×10^{-8} moles/liter

B. Comparison of Actinide and Lanthanide Chemistry:

The actinide elements, especially U through Am, have analogous geochemical behavior. Also the lantnanide elements, have analogous geochemical behavior within their group. The actinides do not necessarily behave like the lanthanides. Although some similarities do exist, the aqueous chemistries of the groups are significantly different.

"Major characteristics of the distribution of rare elements (rare metals and rare earths) in sedimentary rocks can be related to ionic size, charge and bond character. Substitution of rare-metals ions for major ions in crystal structures is of minor importance and adsorption of rare-metal ions on the surface of particles in fine-grained sediments plays a major role," (Krauskopf, 1967).

Since the outer electron structures are so similar, the elements of the lanthanide and actinide series show very similar chemical properties within their respective series; so similar that they generally occur intimately associated in nature. The generalization is less true for the actinides than for the lanthanides, because some of the former have stable higher valences (additional electrons coming from the shell under the valence shell).

Generally, the chemistry for all lanthanides and actinides in the M^{3+} and M^{4+} states are similar, and the ionic radii for most of the actinides and the lanthanides are comparable within 15%. This suggests similar potential for substitution in minerals, even though the charge may differ by one unit.

In the actinide series, the energies of the outer orbitals are about comparable over a range of atomic numbers, especially for uranium through americium and since the orbitals overlap spacially, bonding can involve any or all of them. Actinides, therefore, have a tendency to form complexes and bond covalently. In contrast, lantnanides bond almost exclusively ionically and form virtually no complexes or covalent compounds.

C. Lanthanide Geochemistry:

Reducing conditions in geomedia would immobilize lantnanides (Brookins, 1979). A lamprophyre dike near the WIPP site can be considered as a natural analog for a high temperature canister emplaced in bedded evaporite. Data indicate retention of most if not all elements originally present in the dike despite 1 to 2 meter contact zone effects on the evaporite sequence. The dike is enriched in lanthanides (Brookins, 1980).

Apparently there is little exchange of the lanthanides with clay minerals due to interaction with brine. The slight depletion of light (La, Ce) rare earths and enrichment of heavy rare earths is due to the formation of Mg-rich clay minerals such as chlorite-saponite, at the exposure of pre-existing smectites. The slight loss of La and Ce is due to incorporation of these elements into included salts or into oxide-hydroxide coatings (Register et al., 1980).

Preferential fixation of lanthanum and cerium into calcareous sediments is due to control by similar ionic radii for Ca^{2+} (in the sediments), La^{3+} and Ce^{3+}. Sea water shows a pronounced cerium depletion. It has been proposed that the depletion is due to formation of Ce^{4+} which is removed by precipitation with ferromanganese nodules (Register et al., 1980). (The section on Sorption presents additional information on lanthanide effects).

D. Alkali Metals (Rb and Cs) Geochemistry:

Monovalent elements like Cs would not form any complexes in ground water (Allard, 1979). "Rb/Sr dating of clay minerals penecontemporaneous with uranium mineralization indicates closed system conditions for Rb and Sr since the time of ore formation 135 to 140 million years ago. Because of the greater retentivity of Cs and Rb in most clays, an indirect argument can be made for these rocks being closed to Cs since time of formation as well," (Brookins, 1980). Most of the geochemical data on these elements deals with sorption effects. See the section on sorption for further discussions.

E. Alkaline Earths (Ca, Sr, Ba, Ra) Geochemistry:

Little discrimination between ^{83}Sr and ^{45}Ca in either precipitation or cation exchange was observed in soil, therefore Sr seems to behave like Ca in soils.

Maximum concentration of Sr (divalent) in ground water is limited by precipitation of non-soluble carbonate (Allard, 1979).

Na_2SO_4 has been proposed for use in waste canister overpacks to limit Sr mobility in brine environments.

Generally, uranium appears to be more mobile than radium around uranium deposits in Canada. Accumulations of radium are particularly prominent in ground waters which arise from sufficient depth, such that reducing conditions prevail. As Fe and Mn precipitate upon oxidation, radium becomes adsorbed on the oxides. Moreover, deep water usually contains large amounts of CO_2 which escapes when the water reaches atmospheric pressure. This CO_2 escape causes Ca- and Mg- carbonates to precipitate with the co-precipitation of Ra. This phenomena is particularly evident near mineral springs. Geochemical controls which depress Ra concentration in water are:

1. cation exchange with clays
2. co-precipitation with geochemically related elements, Ca and Mg.
3. adsorption onto Fe and Mn hydrous oxides (Dyck, 1978).

Typical radium concentration in oxidized ground water is about 1.0×10^{12} g/l (0.1 picograms/l). In brines the dissolved radium content increases ten to even several hundred picograms/l due to complexing with Cl^-. Ra in water increases under reducing conditions around deposits not because of dissolution of Ra itself, but due to dissolution of Fe-Mn hydroxides which removes a major host for Ra adsorption. So, radium increases with depth due to greater salinity of ground water and reducing conditions which dissolve Fe-Mn oxides (Dyck, 1978). This maximum concentration of Ra in ground water is limited by precipitation of a non-soluble sulfate (Allard, 1979).

Reconcentration and resulting enhanced radiation field of Th and Ra due to different migration rates of a parent/daughter chain is discussed by Burkholder and Cloninger (1978).

F. Iodine:

Iodine environmental chemistry is a topic in itself. It certainly is soluble (as are the other halogens) and mobile in the geochemical environment in many ways. Further, sorption of iodine is generally low (See Sorption Section) and iodine may migrate in halite by diffusion (Brookins, 1979). Mobility is decreased in reducing environments.

The toxicity arguments for iodine (229) are interesting. On one hand is the high geochemical mobility and the high biological (including human) affinity for the element. Counter to this is the extremely long half-life of I^{229} (very low specific activity).

Iodine should be assumed to be highly mobile geochemically. Barriers generally must be physical or time-distance related. The question of base toxicity must be settled by the toxicology/health physics community.

G. Metals:

Ruthenium (Ru)- Reducing conditions would increase retardation of Ru in a brine, possibly as a sulfide with some hydroxide (Brookins, 1979).

Humic acid promotes sorption of Ru. Nitrite ions strongly complex Ru^{2+} to form neutral or anionic complexes which are very weakly sorbed by sediments and thus decrease the sorption of Ru (Barney, 1979).

Ru did show a tendency to sorb on halite containing clay from brine simulant solution at pH = 6.5-7.9 (Dosch, 1979).

Antimony (Sb)- Owing to similar ionic radius Sb^{3+} can substitute for both Nb and Ta and vice versa.

Nickel and Cobalt (Ni and Co)- Co and Ni are estimated to be about 20 times as abundant in uranium ores as in unmineralized sandstone. Nickel enrichment is more pronounced in the clay-sized fraction than in the whole-rock samples (Brookins, 1980).

Nitrite ions strongly complex Co^{2+} to form neutral or anionic complexes which are very weakly sorbed by sediments. Thus NO_2^- decreases sorption of Co. Humic acid inhibits sorption of Co apparently by forming soluble complexes with Co^{2+} (Barney, 1979).

Lead (Pb)- Lead is relatively immobile due to insoluble sulfides and sulfates (Dyck, 1978). "In the weathering zones (oxidizing), Pb-rich uranium minerals lose lead and are ultimately replaced by uranophane and montmorillonitic clay" (Rimsaite, 1978).

Diffusion loss of lead from host uraninite appears to be an important process in the fractionation of lead from uranium, (Gancarz et al., 1980).

Other metals- For Eh-pH diagrams of Ru, Cd, In, Sb, Ag, Pd, Zr, Rh, Re, Mo, Sn, Te, Bi, Y and Nb refer to Brookins (1978).

H. Technetium:

Tc^{4+} is sparingly soluble in reducing environments. Reducing conditions would increase retardation of Tc in a brine or other geomedia, possibly by incorporation into carbonates or absorbed on clays (Brookins, 1979). Also under reducing conditions TcO_4^- may precipitate as an oxide. Augite adsorbs TcO_4^- (Bird and Lopata, 1980).

See Allard et al. (1979) and Brookins (1978) for Eh-pH diagrams for technetium, and also Section VI on Sorption.

V. GEOCHEMICAL PARAMETERS USED IN MATRIX

This section examines effects in terms of the geochemical parameters (Eh, pH, mineralogy, presence of anions, temperature) on the most significant group of elements, the actinides.

A. Effects of Eh on Actinide Geocnemistry

Eh (oxidation potential) is the single most important variable influencing the mobility of actinides in near surface environments. Reducing conditions in tne geomedia would immobilize the actinides (Brookins, 1979) oecause the reduced species form very insoluble oxides/hydroxides and sorption is greatly ennanced (Allard et al., 1979). Comparisons of actinide chemistry indicate that uranium is potentially the most mobile actinide and conditions leading to immobilization of uranium would also immobilize Np, Pu, Am and Th. Uranium chemistry proxies behavior of the group. The dominant mechanism speculated for uranium ore deposition (immobilization) is reduction notably by organic matter, ferrous iron compounds (minerals) and/or sulfur compounds (Allard, 1975; Rich et al., 1975; Barthel, 1974).

Under oxidizing conditions uranium is generally one of the most mobile trace elements, mostly owing to the high stability of its complexes, especially tne carbonate complexes. The uranyl ion is mobile in natural and alkaline solutions if carbonate is present and somewnat mobile in weakly acid solutions (due to sulfate, halogen and hydroxide complexes).

Carbon readily reduces uranium. However, under certain conditions, tne uranyl ion may be stable in the presence of reduced iron and sulfur. The uranous ion is oxidized in tne presence of oxygen, MnO_2, and possibly hematite.

Under mildly reducing conditions, complex formation and self-oxidation/reduction due to α-radiation-induced radiolysis may affect mobility.

B. Effects of pH on Actinide Geochemistry

The reduced forms of U, Np, Pu and Am are insoluble at pH = 6.5 to 8.5. The important uranyl minerals (carnotite and autunite) are least soluble at pH of 5 to 8.5 (less than 1-2 ppb of U should be present in saturated ground water). Solubilities increase significantly for pH values below 5 and above 9 for all species. Thorium is generally insoluble at normal environmental pH values, particularly for the pH range 7 to 8. There is some evidence that uranium may form a mobile species UO_3^+ under slightly reducing conditions at pH below 7.

At normal environmental pH values (6 to 8) carbonate and phosphate complexes contribute to the mobility of oxidized uranium. The effects of fluoride and sulfate are minimal with this pH range.

C. Effects of Mineralogy on Actinide Geochemistry

Mineral species influence the adsorption and oxidation/reduction potential of the rock and associated ground fluids. Adsorption is considered by some to be an important preconcentrating step for the ultimate immobilization of uranium by reduction to UO_2. Others perceive reduction as a precursor for adsorption. Common rock-forming minerals which are important because of their reducing and/or adsorption properties include: zeolites, clays, iron-manganese-titanium oxyhydroxides, biotite, hornblende, pyrite/marcasite, fossil carbon, CH_4, H_2S, petroleum, bitumens, graphite, and humic acid. The presence of the above materials reduces the potential for

actinide migration. The most effective agents for immobilization are carbon and hydrocarbon compounds.

Low temperature alteration of clay in association with carbonaceous matter and sulfides may be a significant mechanism for the precipitation of uraninite.

Manganese and iron oxides are potential sorbers. Also MnO_2 and possibly hematite can convert reducing fluids into uranium carriers.

D. Effects of the Presence of Anions on Actinide Geochemistry

($CO_3^{=}$, $HPO_4^{=}$, $SO_4^{=}$, F^-, Cl^-, OH^-, etc.).

Actinides, more than any other group of elements, form an extensive series of complexes with halogens, oxo-anions, carbonate, sulfate, and phosphate. Complexes of uranium have been studied because of their possible geochemical role in transport and ore formation. Under oxidizing conditions uranium is one of the most mobile trace elements, mainly due to the high stability and solubility of its complexes, especially with CO_3^{2-} but also with halogens, phosphate and sulfate. Complexing can change the oxidation potential and therefore the oxidation state of the actinides as well as greatly influencing the solubility, resulting in enhanced mobility.

The influence of complexes on uranium mobility is greatly decreased under reducing conditions. Under mildly reducing conditions, carbonate complexes may be effective uranium mobilizers. In general, the potential for complexing is greatly reduced because the actinides precipitate as very insoluble oxides and hydroxides. Under oxidizing conditions in the normal pH range of 6.5 to 8, both carbonate and phosphate complexes are important in the natural environment. There are contradictory statements in the literature concerning the stability of carbonate complexes at elevated temperatures. Langmuir (1978) observes that at 100°C and CO_2 at 10^{-2} atm, the uranyl carbonate complexes are minor at all pH's.

At pH values below 6 and especially below 4, uranyl complexes with halogens, sulfate and hydroxide become significant mobilizers. The effects of the carbonate complexes increases at alkaline pH values.

In summary, under normal near-surface environmental conditions, carbonate and possibly to a lesser degree phosphate complexes are the dominant complexing anions which enhance uranium (and other actinides) mobility. Reducing conditions and pH values from 7 to 8 would minimize, if not eliminate, the potential impact of complexes on actinide mobility given the usual near-surface concentration of complexing anions in ground water. Very high concentrations of carbonate, phosphate and halogens would greatly increase actinide mobility, probably in almost any geochemical environment. Complexing inhibits sorption.

E. Effects of Temperature on Actinide Geochemistry

"It has been established that the main effects of temperature are an acceleration of the hydrolysis of a number of the major components of the waste and an increase in radiation yields", (Spitsyn and Balakova, 1979). Hydrolysis of metal ions (Fe, Cr, Al) at certain temperatures leads to the formation of crystalline precipitates that prevent transfer of all the waste ions to the solid phase (tends to reduce adsorption by coating open fluid passageways?).

At 200°C and above, new crystalline phases appear in shale. The minerals formed would depend on the waste form, accessory minerals in the shale and on the temperature. Since shales are alkali-poor they should act as scavengers for alkali elements (e.g., Rb, Cs) which would react with the clays to form framework silicates, i.e., zeolites and/or feldspars. Pollucite ($CsAlSi_2O_6$) appears as a dominant reaction product in the 200°C experimental range.

Oxidized uranium minerals do not occur when waste forms are reacted with organic-rich shale at 200°C. It seems quite clear that highly reducing materials such as organic carbon and iron sulfides are sufficient to prevent oxidation of uranium.

Prototype nuclear waste materials react with shale rocks in the presence of water (at 100°-400°C) to form at least 20 reaction product phases. These materials act to buffer or control the further transport of radionuclides beyond the immediate reaction zone. Alumino-silicate minerals act as scavengers for cesium and strontium which becomes immobilized as pollucite, powellite and feldspar. Uranium and (by implication) the transuranic elements are strongly influenced by the redox characteristics of the accessory minerals in the rock.

"Shales act as chemical as well as physical barriers to the migration of radionuclides from the immediate vicinity of a waste canister," (even at elevated temperatures 100°-400°C) (Freeborn et al., 1980).

VI. SORPTION

Sorption is not well understood and it would appear that some of the examples of effective sorption blockage of waste spill migration may be misleading. Sorption, as a group of chemical/mineral interactions tends to be more rate-dependent than other processes discussed in this report. Perhaps sorption mechanisms are better thought of as delayers rather than barriers. In the case of surface spills, a one-shot chemical release into a homogeneously porous sorbing media such as organic-rich soil, sorption is an effective short-term barrier.

In subsurface systems the sorption process is less predictable:

1. Continued flow of toxic solutions can circumvent sorption by moving continuously and rapidly through the media such that sorption effects as studied in controlled experiments do not maximize.
2. Moving solutions equilibrate with sorption media and flush out toxins already sorbed.
3. Solutions flow preferably through few channelways in the bulk sorbing media, saturating rock adjacent to channelways and not utilizing the sorption capacity of the mass.
4. Addition of natural ions (e.g., brines) overpowers available sorbing media capacities for toxic retention and/or flushes out already-sorbed toxins.

Notice that sorption mechanisms are generally most effective under the gross conditions that immobilize the important radiotoxins geochemically i.e., reducing conditions, near neutral pH, and low dissolved salt. Mobilizers such as uranyl-sulfate,-floride and-carbonate complexes inhibit the sorption processes thus increasing their effect on mobility.

Sorption processes may include:

1. ion exchange,
2. adsorption reactions of ions or complexes,
3. reversible formation of non-soluble complexes,
4. reversible formation of non-soluble complexes and,
5. formation of colloid particles.

At least three major mechanisms of sorption appear to dominate over simple cation exchange:

1. Hydrolysis and carbonate complexation appears to enhance general sorption of radionuclides on normally very inert materials such as quartz (Beall and Allard, 1980).
2. Chemi-sorption mechanisms that take place on the surface of certain minerals involve complex formation between an exposed anion on the mineral surface and the cation from solution.
3. Oxidation/reduction reactions between the Fe^{2+}/Fe^{3+} couple and certain actinides (U, Pu, Np).

But in most systems, higher sorption was obtained for minerals with high surface area or cation exchange capacity. (Beall and Allard, 1980; Beall et al., 1980).

The pH of the aqueous phase seems to be one of the most important parameters that determines the sorption on a solid surface. Generally maximum sorption is at the near neutral pH range of 6.5 to 8.5.

There are significant differences in static vs. dynamic sorption behavior which suggest the importance of sorption kinetics. Increased sorption is obtained with increased contact time, which implies a kinetic factor, especially for tri- and tetravalent elements. Temperature increases from 25-65°F resulted in small increases of sorption (less than a factor of three) for clay, granite and ferrous minerals (Allard, 1979).

"The clay fraction of a natural formation will not retard significantly the migration rates of the corresponding radioisotopes if the contacting phase has high salinity," (Shiao et al., 1979, based on studies of monovalent and divalent ions on either Na or Ca montomorillonite). Shiao also studied Eu^{3+}, apparently as an analog to lanthanides and actinides, however, Lynch and Doscn (1980) note that for Eu^{3+}, mechanisms other than sorption are important when making experimental measurements.

"Tne hold up time in the backfill material is at the most some ten thousand years. The only long-lived radionuclides of biological interest that would be sufficiently delayed are ^{90}Sr, ^{137}Cs and ^{241}Am. Thus, the clay barrier is of minor importance in the long term perspective, as far as retention is concerned." (Allard et al., 1979). "The time needed for equilibration (for sorption) is much longer than the transit time of the solution through the pores of the rock. The kinetics of adsorption and de-adsorption may severely effect the dispersion of nuclides in geo-media." (Friedman and Fried, 1979).

Based on studies of Am on hornblende schist and Sr on glauconite· "Kinetic parameters may be as important to understanding the migration of a nuclide through a geologic media as the equipibrium-sorption value (Kd). Desorption may occur with a rate equal to or less than the rate for adsorption." (Rickert et al., 1979). Radionuclide dispersion through the geologic media surrounding a repository may be enhanced by high aqueous ion concentrations, especially divalent ions from dissolving waste canisters. Na and Ca ion loading decreased retention of Cs (10x), Sr (100x) and Eu (100x) by silicate minerals (Winchester, 1979).

Figure 17 provides additional information on uranyl adsorption as a function of pH. Table 10 gives experimental data on measured sorption of selected anions on a number of minerals.

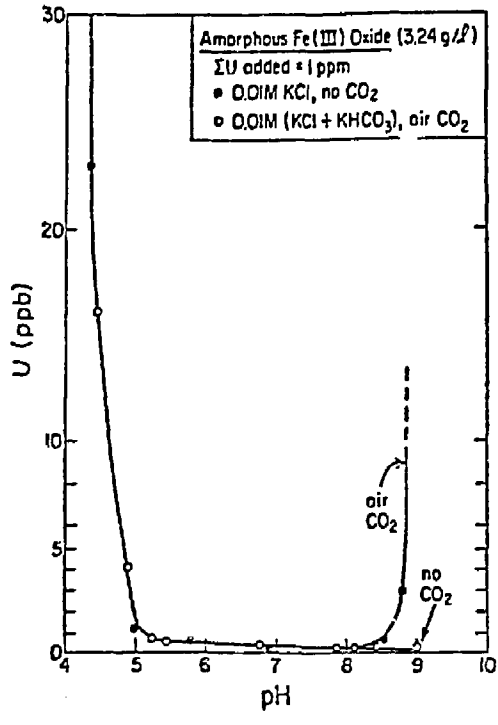

FIG. 17. Adsorption of uranyl onto X-ray amorphous ferric oxynydroxide as a function of pH (oxyhydroxide surface area 285 m^2/g, H_2O/Fe_2O_3 molar = 1.38, PZC = 8.6). The "air CO_2" curve ($P_{CO_2} = 10^{-3.5}$ atm) is extrapolated above the last data point, parallel to data trends for two similar experiments (not shown). (From Langmuir, 1978).

TABLE 10. Measured sorptions for $SeO_4^=$, TcO_4^- and I^- on a number of minerals. Each mineral was contacted with each anion separately. Results are given for only those minerals which showed measurable takeup of the anions. The ratios of the anions to minerals were 0.1 mole/kg, 1.0×10^{-2} mole/kg, and 1.0×10^{-5} mole/kg for $SeO_4^=$, TcO_4^-, and I^-, respectively except as noted.

Minerals	Approximate formula	Anions attached	Original concentration attached (mole/kg mineral)	Number of desorptions attempted	Concentration remaining on solid	Equilibrium pH of solution
Silicates						
Augite	$(Ca,Na,Mg,Fe^{+2},Mn,Fe^{+3},Al,Ti)_2[(Si,Al)_2O_6]$	$SeO_4^=$	4.0×10^{-2}	2	3.2×10^{-2}	8.2
		TcO_4^-	1.9×10^{-3}	1	1.4×10^{-3}	8.1
Hornblende	$(Na,K)_{0-1}Ca_2(Mg,Fe^{+2}Fe^{+3},Al)_5[Si_{6-7}Al_{2-1}O_{22}](OH,F)_2$	$SeO_4^=$	2.2×10^{-2}	2	1.6×10^{-2}	8.2
Biotite	$K_2(Mg,Fe^{+2})_{6-4}(Fe^{+3},Al,Ti)_{0-2}[Si_{6-5}Al_{2-3}O_{20}](OH,F)_4$	I^-	2.4×10^{-6}	0*	-	7.8
		TcO_4^-	9×10^{-5}	0	-	-
			5×10^{-6}**	0	-	
Vermiculite	$(Ca,Mg)_{0.7}(Mg,Fe^{+3},Al)_{6.0}[(Al,Si)_8O_{20}](OH)_4 \cdot 8H_2O$	$SeO_4^=$	3.2×10^{-2}	4	2.0×10^{-2}	6.8
Kaolinite	$Al_4[Si_4O_{10}](OH)_8$	TcO_4^-	3×10^{-4}	0	-	6.8
			8×10^{-6}**			
			8.0×10^{-5}***			

(Table 10 continued on next page)

TABLE 10 (continued)

Minerals	Approximate formula	Anions attached	Original concentration attached (Mole/kg mineral)	Number of desorptions attempted	Concentration remaining on solid	Equilibrium pH of solution
Sulfides, carbonates, Phosphates						
Galena	PbS	$SeO_4^=$	5×10^{-3}	0	-	6.1
		TcO_4^-	2.7×10^{-7}	0	-	-
		I^-	3.0×10^{-4}	0	-	-
Sphalerite	(Zn,Fe)S	$SeO_4^=$	3.9×10^{-2}	1	3.9×10^{-2}	-
		TcO_4^-	2.2×10^{-6}	0	-	-
Calcite	$CaCO_3$	$SeO_4^=$	9.7×10^{-3}	1	1.5×10^{-3}	8.2
Smithsonite	$ZnCO_3$	$SeO_4^=$	9.8×10^{-4}	0	1.5×10^{-3}	-
		TcO_4^-	3.2×10^{-5}	0	-	-
Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	$SeO_4^=$	2.5×10^{-2}	3	0	8.0
Metals, oxides						
Copper		$SeO_4^=$	see reference	0	-	-
		TcO_4^-	see reference			
		I^-	see reference			
CuO		$SeO_4^=$	1.3×10^{-2}	0	-	-
Cu_2O		I^-	see reference			
PbO		$SeO_4^=$	see reference			
		TcO_4^-	see reference			
		I^-	see reference			

* Spontaneous desorption occurred.

** 1×10^{-5} moles TcO_4^-/kg mineral.

(From Bird and Lopata 1980)

VII. HYDROTHERMAL ORES

Geochemical work has been focused for decades on the characterization of the hot aqueous solutions which transport and deposit metallic ore elements. Geochemical conditions which allow mobility of metal ions prior to ore deposition would jeopardize the stability and integrity of a waste disposal site. Ore solutions are generally characterized as follows:

- Aqueous solutions saturated with silica and often containing high [NaCl].
- Temperature range: 50 to 550°C.
- Pressure range: up to 2,000 atm.
- pH: neither strongly acid nor strongly alkaline.

Interestingly, the order of solubilities for ore minerals provides no explanation for the observed order of deposition. Of the various suggestions for explaining metal solubility in ore solutions, the most promising is increased solubility resulting from the formation of complex ions and molecules. Ore solution behavior may be characterized in terms of species mobility and immobility as follows:

A. Mobility (active ore solutions)

- Salinity 3%-50% dissolved solids by weight.
- Major aqueous components: Na, K, Ca, Cl.
- 0.1M carbonate; 0.1M sulfur species; 0.01M ammonia; weakly alkaline to somewhat acidic.
- Mechanicism for transport: sulfide complexes at low temperature; chloride complexes at high temperature with generally increasing stability above 200°C.

- Evolving fluids: Field and experimental studies and data from $^{87}Sr/^{86}Sr$ ratios indicate that anion exchange reactions, between solution and minerals, such as feldspar, micas and clays must proceed continually so that a solution changes in composition as it moves... A hydrothermal fluid is therefore an evolving or changing entity, influenced principally by temperature and the rock through which it passes (Skinner, 1979; Stanton, 1972).

It appears that a toxic metal waste disposal situation should assume some mobility of fluids and that the rates and distances of that mobility must be controlled.

B. Immobility (ore deposition)

- Chemical reactions between moving solutions and the rocks lining the channelways must be a major cause of precipitation. These are:
  a) Exchange reactions which change anion and cation concentration.
  b) Addition of reduced sulfur from black shale would cause an immediate precipitation of sulfide minerals.
  c) Change in oxidation state which can be influenced by metamorphic reactions (i.e., serpentinization) and the addition of carbonaceous matter or mixing with ground waters.
- Drop in temperature - reduced stability of complexes, e.g., chloride complexes.
- Drop in pressure - reduces the amount of dissolved gases, e.g., CO_2, NH_4, CH_4.
- Change in pH - (associated with above changes) hydrogen ion consumers are carbonates, feldspars, mafic minerals (Barnes, 1979).

C. Supergene Processes (Remobilization of metals in the weathering/ oxidizing environment)

The mobility of metal ions in the zone of weathering is determined by the composition of both the waters and the country rock. The fundamental process is oxidation, but since the oxidation of sulfides produces hydrogen ion and sulfate, both Eh and pH are important.

The host rock environment is especially important in the oxidation of sulfides in the supergene process. Some metals that would be leached from a siliceous host are retained in calcareous rocks (Park and McDiarmid, 1975).

Sulfide-free oxidizing meteoric waters leach such elements as zinc, molybdenum, and uranium from igneous rocks leaving behind stable oxidation products of Fe, Al, Ti, and Cr. Molybdenum, Zn and Ag are especially soluble in sulfate solutions, but under favorable conditions they form stable oxidation products in limestone. Similarly, copper, which is relatively mobile in sulfate waters that circulate through siliceous igneous rocks, forms practically insoluble carbonate minerals in calcareous environments. Iron and lead oxidize to stable compounds in both siliceous and calcareous rocks, and are generally retained in the zone of weathering. Most arsenic compounds, in contrast with those of antimony, are relatively soluble and consequently are leached from the zone of weathering. Copper and silver when mobilized in the oxidizing zone will largely redeposit under reducing conditions, generally at the water table as a sulfide mineral phase, thus the basis for the supergene ores or enrichments of these metals.

D. Hydrothermal alteration (Bulk-rock mineral changes due to hydrothermal activity)

Ore-bearing solutions evolve as they move. Given the proper country rock and conditions, the alteration reactions can significantly influence mobility. Certain alteration (silicification, dolomitization and

recrystallization) may prepare the ground (chemically and physically) for precipitation of ore. Example: silicification can convert a soft, impermeable rock to a more brittle rock subject to fracture and therefore more susceptible to ore solutions. Silicified rock terrain should be avoided for waste sites because of such tendency to allow fracture access of oxidizing ground waters. Conversely, such a rock mass could serve if disposal is in a permeable silicified rock confined by soft, reducing, relatively impermeable rock strata (silica alteration zones surrounded by clay alteration with pyrite). Alteration products are an integral part of the mineralization process. Detailed studies of mineral alteration associated with ore deposits provide clues for the conditions over which the deposit formed. A discussion of alteration reactions is beyond the scope of this project but may provide a fruitful avenue of investigation. Alteration reactions can significantly influence the Eh, pH and cation/anion characteristics of ore solutions. Hydrous silicates (clays, micas, etc.) are abundant products of alteration accompanied by volume increase relative to original rock, a factor often considered as a progressive natural sealant process around a hot waste package. Increased sorption effects ascribed to such clay alteration is not a likely benefit, however, as dealt with in Section VI of this report.

Tables 11 and 12 illustrate natural variation in hydrothermal solutions.

In summary, this section suggests that waste behavior generalizations can be drawn from the abundant literature on hydrothermal solutions. But these geochemical systems are even more complex than those affecting the behavior of the selected radwaste elements and further treatment will not be attempted here.

TABLE 11. Compositions of some modern and ancient hydrothermal solutions.

Concentrations in ppm. 1 = Salton Sea geothermal brine; 2 = Cheleken geothermal brine; 3 = oil field brine, Gaddis Farms D-1 well, Lower Rodessa reservoir, central Mississippi, 11,000 ft; 4 = fluid inclusion in fluorite, Cave-in-Rock District, Ill.; 5 = fluid inclusion in sphalerite, OH vein, Creede Colo.; 6 = fluid inclusions, core zone at Bingham Canyon.

	Modern solutions			Ancient solutions		
Element	1	2	3	4	5	6
Cl	155,000	157,000	158,200	87,000	46,500	295,000
Na	50,400	76,140	59,500	40,400	19,700	152,000
Ca	28,000	19,708	36,400	8,600	7,500	4,400
K	17,500	409	538	3,500	3,700	67,000
Sr	400	636	1,110	-	-	-
Ba	235	-[a]	61	-	-	-
Li	215	7.9	-	-	-	-
Rb	135	1.0	-	-	-	-
Cs	14	0	-	-	-	-
Mg	54	3,080	1,730	5,600	570	-
B	390	-	-	< 100	185	-
Br	120	526.5	870	-	-	-
I	18	31.7	-	-	-	-
F	15	-	-	-	-	-
NH_4	409	-	39	-	-	-
HCO_3^-	>150	31.9	-	-	-	-
H_2S	16[b]	0	-	-	-	-
SO_4^{2-}	5	309	310	1,200	1,600	11,000
Fe	2,290	14.0	298	-	-	8,000
Mn	1,400	46.5	-	450	690	-
Zn	540	3.0	300	10,900	1,330	-
Pb	102	9.2	80	-	-	-
Cu	8	1.4	-	9,100	140	-

[a] Not determined.
[b] Sulfide present; all S reported as H_2S.

(From Skinner, 1979)

TABLE 12. Representative Total (analytical) Concentrations in Hydrothermal Solutions.

	Complex-Forming Species (molalities)					Metals (ppm)				
Location	ΣCl	ΣSO_4	ΣS^{2-}	ΣNH_3	ΣCO_3	Zn	Pb	Cu	pH at T°C	
Ore Deposits										
Creede, Colo.	0.9-1.9	0.02-0.3	$10^{-3.8}$-$10^{-3.7}$	-	-	$10^{2.8}$	$10^{-3.3}$ (Fe: 1)	$10^{-2.8}$	5.4	250
Darwin, Cal.	>4.3	~0.01	-	-	0.15 ± 0.06	<7700	-	740	4.8-6.7	350
Yatani, Japan	0.1-0.2	10^{-6}-10^{-10}	~10^{-2}	-	-	-	-	-	~6	250
Providencia, Mex.	0.03->4.3	<0.7	-	-	-	220-890	-	<70-530	-	300
Echo Bay, N.W.T.	~7	10^{-2}-10^{-3}	-	-	to 0.1		(Ag: 0.1-1.)		4.2 ± .5	200
Kuroko Deposits, Japan	0.4-1.5	-	<$10^{-1.7}$	-	-	-	-	-	5.5 ± .5	250
Pasto Bueno, Peru	0.4 to 3.5	<H_2S	10^{-2}-10^{-3}	-	-				-	175-290
Tribag, Ontario	-								-	-
Messina, S. Africa	-								-	-
S.W.Wisconsin, U.S.	4.2->5.1	-	>10^{-3}	-	0.03-0.9	8700	~500	400	6.0 ± .3	150
Eureka, Col.	0.1-0.6	$10^{-2.2}$	$10^{-1.4}$	-	0.01-0.2	>1-<1000	>1-<1000	(Au 10^{-2}-10^{-3})	4.3-5.9	300
Geothermal Fluids										
El Tatio, Chile	0.2	-	$10^{-3.7}$	$10^{-3.9}$	$10^{-1.1}$	-	-	-	-	263
									7	25
Imperial Valley										
Salton Sea, Cal.	2.4	<$10^{-4.0}$	$10^{-3.7}$	$10^{-1.5}$	$10^{-3.0}$	380	70	3	-	240
									6.1	25
Cerro Prieto, Mex.	0.3	$10^{-3.8}$	-	-	$10^{-3.0}$	-	-	-	-	100
									7.9	25
Cheleken, U.S.S.R.	3.1	$10^{-2.8}$	$10^{-4.0}$	-	$10^{-2.4}$	0.19	3.6	0.9	5.5	54
	2.9	$10^{-2.5}$	-	-	$10^{-3.4}$	2.3-4.7	3.6	0.8	5.4	80
Central Miss. U.S.A.	5.9	-	-	$10^{-2.1}$		124	6.8			158
Eastern Kansas, U.S.A.	6.0	$10^{-1.9}$	$10^{-2.9}$	$10^{-3.0}$	$10^{-2.4}$	.06	1.7	.14	7.03	~20
	4.0	$10^{-2.9}$	$10^{-2.2}$	$10^{-3.4}$	$10^{-2.2}$	.13	1.1	<.1	6.88	~20

(After Skinner, 1979)

VIII. DEPTH

The gross changes of geochemical variables associated with increased depth are, of course, temperature and pressure increase (plus simple distance to the biosphere). But other major variables change with the temperature/pressure gradients, namely:

1. Porosity
2. Permeability
3. Eh
4. pH
5. Salinity (especially chloride)
6. Sorption

As shown in Fig. 18, pressure increase is equated with depth into the earth, along with examples of high, medium and low natural thermal gradients possible in crustal environments. Recall that in shallow/moderate depths, the pressure of an essentially open (to the surface) system would be atmospheric plus hydrostatic (groundwater) pressure. At moderate/great depths or in very weak rocks with sufficient time allowed, pressure will approach that of the overlying rock column (lithostatic).

A. Porosity/Permeability/Depth Relationships

Initial porosities for shales at the time of deposition range from 0.6 to 0.9 and most of the reduction in porosity occurs within the upper 300 m of burial. Sands are less variable (Fig. 19). At depths of 3000 m, porosity ranges from 0.2 to nearly 0.0 for sands or shales. Porosity reversals are noted in zones of sediments that have not followed the usual compaction-depth sequence because their low permeability has prevented the escape of interstitial water at normal rates with burial (Hanor, 1979).

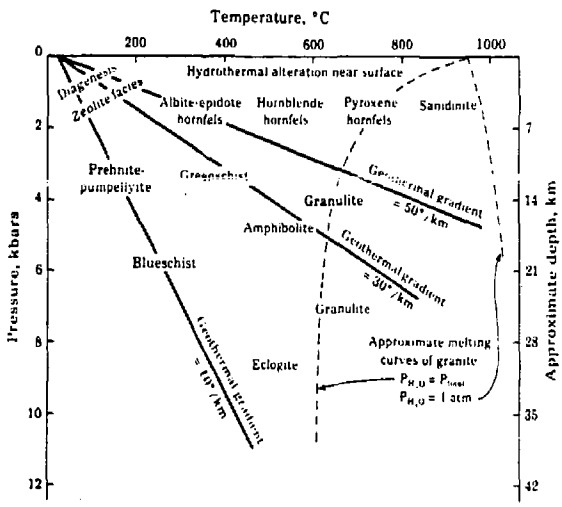

FIG. 18. Approximate pressure-temperature fields of the principal metamorphic facies. The three solid lines show possible values of the geothermal gradient: the mean of measured values is about 30°/km, the maximum about 50°/km, the minimum about 10°/km. The dashed lines show temperatures of incipient melting of granite, under water-vapor pressure equal to total pressure and water-vapor pressure equal to 1 atm. Between the two lines is the region where differential melting of high-grade metamorphic rocks may occur.

(In Krauskopf, 1967)

A significant volume of water is released during normal sediment compaction and diagenesis (lithification). Seventy-five percent of this water from shale is normally expelled during shallow burial from 0-1000 m, and a shale is likely to be essentially stabilized and "sealed" at depths of 300 m (Fig. 19). For sandstone, burial to 3000 m is required before 75% of this water is expelled (Hanor, 1979).

Note: Low porosity and permeability are not necessarily desirable for the immediate area of the waste disposal site. Generally a critical factor for the deposition of ores and sorption reactions to take place is relatively high surface area (i.e., a generally porous/permeable strata). Permeability can be an important control since most mineralogic changes (chemical changes that would aid precipitation and adsorption) are not isochemical. The rocks must be open for contact and for exchange with constituents in the solution. However, too porous/permeable strata would allow flow rates to be too high and not allow for enough time for potential contact (adsorption) and exchange. Likely, a high porosity coupled with low permeability, such as may exist in interbedded shale units or shales interbedded with certain sandstones, would be ideal.

In general, ore deposits are localized in rock strata of intermediate porosity and permeability. Often the process of ore deposition and alteration greatly influences these properties. High fracture permeability would be nearly always undesirable.

Generally, permeability and porosity decrease with depth of burial owing to pressure of overlying rocks and to the cementing action of mineral-laden waters. Many mines are dry in their lower levels. The lower depth limit varies considerably and may be anywhere from a few feet to several thousand feet below the surface.

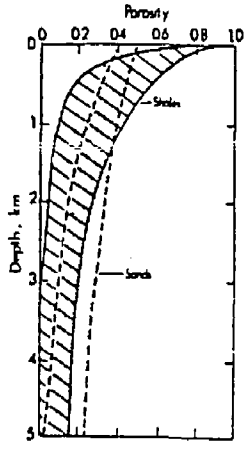

FIG. 19. Range in porosity of shales (ruled area) and sands (stippled area) as a function of depth of burial. Based on data of Perrier and Quiblier (1974).

Nevertheless, the preponderance of evidence indicates that solutions in large amounts do move through massive rocks at depth. Fluids under pressure are able to fracture and work their way through rock. Depth, due to increasing hydrostatic pressure may work against immobility. Studies support the contention that fluids are able to fracture rocks and pass through them to areas of lower pressure. (Park and McDiarmid, 1975).

One cannot help being impressed by the movement of large amounts of hot fluids through relatively impermeable rocks e.g., in the Big Geyser Area, California (and the many broadly mineralized and altered hydrothermal ore districts). Park and McDiarmid (1975) concluded that "ore-bearing fluids are able to move through dense rocks by working around individual grain boundaries or by other means."

B. Depth-related Salinity:

Salinity often increases with depth in sedimentary basins (Fig.21). Typically, the rate of salinity increase diminishes with depth, and maximum observed salinities level off to a value that is characteristic for each basin (Dickey, 1969; Hanor, 1979). Significant reversals in salinity with depth have been found in Cenozoic sands and shales of the Gulf Coast with lower salinity in sediments of abnormally high fluid pressures. In the Illinois Basin (Figs. 20 and 21) chloride increases with depth and there is an approximate depth sequence, observed in many other basins as well. Shallow waters are nigh in bicarbonate and sulfate, progressing to sodium chloride waters with increasing depth. In zones characterized by hydrostatic fluid pressure, salinities in shales are a factor of 1/4 to 1/10 lower than in adjacent sands. Most high-sulfate formation waters are confined to relatively shallow depths (Hanor, 1979).

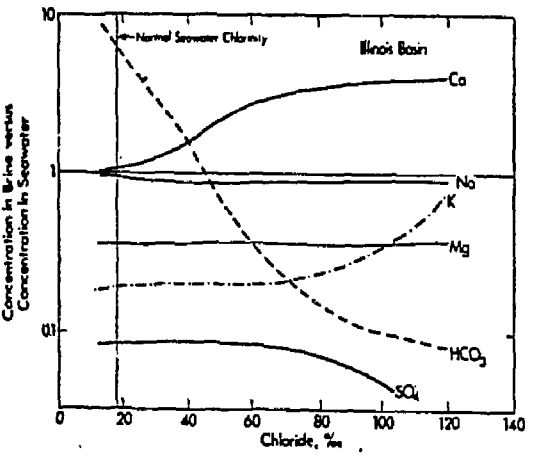

FIG. 20. Variation in major element concentration of waters in the Illinois basin as a function of dissolved chloride content. Values are normalized with respect to sea water of the same chloride content.

(Hanor, 1979)

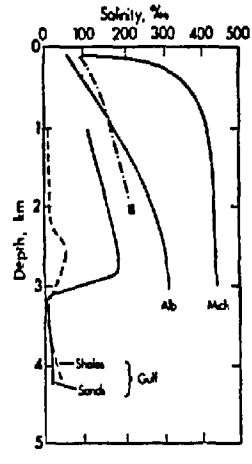

FIG. 21. Maximum observed salinities at various depths in the Illinois, Michigan, and Alberta basins. The two profiles on the left show the variation in salinity in shale sands in the Manchester field, Louisiana Gulf Coast (In Hanor, 1979).

C. Depth-related pH:

Temperature increases with depth, and pH is generally considered to decrease as temperature increases. Hanor (1979) states that the pH of pure water will be 5.8 at 150°C. The diagram (Fig. 22) from Krauskopf (1967) shows a confusing effect of temperature on pH. Because of the increased ionization constant of water to a maximum at 230°C, the neutral pH point is then 5.7. Krauskopf states that with increasing temperature water at first becomes <u>both</u> a better acid and a better base. It is likely that increased geochemical mobilities, dependent on decreasing pH, will result due to this depth function (this point deserves some review).

Field data from the Stripa Granite shows an increase of pH with shallow/moderate depth. At 10m, pH = 5.15 and at 801-838m, pH = 9.60 (Fritz et al., 1980). This is an unusually high natural pH. Thermal gradient in the Stripa area is low. Recall that relative to actinide mobilization significant pH variance either side of neutral will increase mobility.

D. Depth-related Eh:

The redox potential for deep ground water (approx. 500 m) in Stripa granite is largely determined and buffered by the presence of iron-containing minerals. For the expected pH ranges of 7.2 to 8.5, the Eh value would be in the range of -70 to -380 mV in <u>undisturbed</u> ground water from granitic terrain due to the Fe^{3+}/Fe^{2+} equilibrium. Under these conditions:

Pu exists as Pu^{3+} or Pu^{4+},

Np as Np^{4+},

Tc as Tc^{4+}, and

U probably as U^{4+}. (Allard et al., 1979)

The above reducing conditions would tend to minimize the mobility of the actinides.

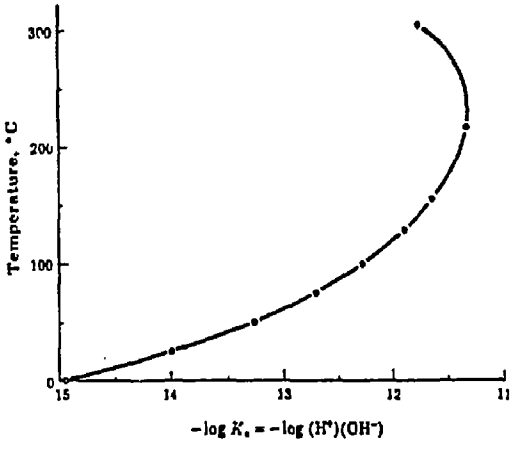

FIG. 22. Change of the ionization constant of water with temperature. (In Krauskopf, 1967).

The following discussion is from Park and McDiarmid (1975)

"In tectonically stable regions, the oxidation zone generally extends to the water table, especially if the country rocks are permeable. Recent faulting, fluctuating water table or impervious wall rocks may modify the pattern of oxidation.

The position and permanence of the water table is critical because sulfides are generally stable in the slightly alkaline, moderately reducing environment below the ground water table. In humid climates the sulfide zone (reducing) may be a few feet from the surface; in arid environments, where the water table is likely to be deep, the lower limit of oxidation may extend 2000-3000 ft. below the outcrop.

The role of permeability in oxidation is strikingly demonstrated at the Tsumeb Mine, SW Africa, where a nearly vertical ore pipe that cuts through steeply dipping sediments is oxidized in the upper and lower parts but is unweathered at the intermediate levels. The unoxidized part of the pipe is protected from ground water by relatively impermeable strata. Oxidation along the deep brecciated (fractured) stratum is so efficient that the lower part of the pipe is more thoroughly oxidized than much of the shallow weathered zone."

Note: What one gains geochemically from depth in terms of waste isolation may depend significantly on the rock strata in which the waste will be put. It is conceivable that a shale at a depth of 100 to 300 m would exhibit better properties in terms of sealing (very low solution mobility) than a sandstone or a granite at 1000 to 3000 m.

E. Other Depth Functions:

CO_2 content, which is of critical importance to the geochemical mobility of many radionuclides, is in a simple sense increased with the

increased pressure of depth. The actual source of much CO_2 is limited by depth. Diagenetic/metamorphic reactions (changing calcite and quartz into calcium-silicates + CO_2) which take place at shallow depth and moderate temperature (approximately 300°C) are limited by depth-pressure increase in a closed system. A temperature of about 600°C is necessary for this reaction at a pressure equivalent of 3000 meters depth (Fig. 23). Note that this effect increases rapidly through depths of 0 to 2000 meters.

Melting points of rocks decrease with depth due to fluxing by increased H_2O pressure.

F. Summary of Depth Implications to Waste Isolation:

The question of depth as related to burial of wastes can be answered with respect to the variation of geochemical functions as follows.

1. Low porosity and permeability generally associated with depth are not necessarily desirable for the immediate area of the disposal site.
2. Decreased pH at greater depths would likely provide increased geochemical mobilities. Relative to actinides, significant pH variation either side of neutral will increase mobility.
3. Reducing conditions associated with greater depths would tend to minimize mobility of the actinides. But these conditions depend on the type of rock strata in which wastes will be placed. Shales exhibit favorable geochemical conditions at relatively shallow depths.

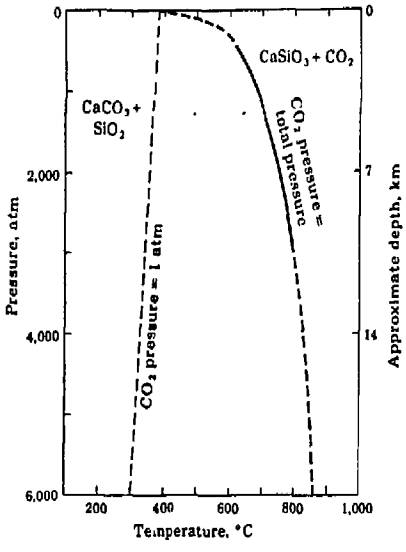

FIG. 23. Equilibrium curves for the reaction $CaCO_3 + SiO_2 \rightleftarrows CaSiO_3 + CO_2$ at $P_{CO_2} = P_{total}$ (heavy line) and $P_{CO_2} = 1$ atm (light line). Heavy solid line experimentally determined. Dashed lines extrapolated or theoretical. At P-T values between the two lines, calcite and quartz are stable if $P_{CO_2} = P_{total}$, and wollastonite is stable if $P_{CO_2} = 1$ atm.

(*In* Krauskopf, 1967)

IX CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

A. Conclusions

The geochemical approach leads to the conclusion that radioactive wastes could be immobilized in a quite normal, easily obtainable geologic/geochemical situation. That situation should consist of:

- Reducing Environment
- Moderate pH (6.0-8.5)
- Low CO_2
- Low salt (especially chloride)
- High porosity, low permeability

The above conditions do not imply considerable depth. For shale, which appears to be the rock-type most closely associated with optimal geochemistry, the optimum depth is likely to be less than 1000 ft.

The prime variable for radionuclide immobility is the Eh. Reducing conditions should prevail unless the isolation is to depend on physical/hydrological barriers rather than geochemical stability; and it is our contention that when coupled with those above, reducing conditions essentially ensure immobility even when physical/hydrological conditions are otherwise poor.

The very long-term stability (10^7-10^9 years) of important elements at Oklo (natural fission reactors) and of uranium ore deposits, indicates the effectiveness of low Eh in apparently varied and not necessarily optimum physical/hydrologic conditions. An isolation site in shale, if selected to provide long-term geologic stability relative to exhumation by erosion or disturbance by tectonic effects, could be quite shallow (less than 1000 ft).

Appropriate geochemical conditions may be present below any stable water table. Obviously very long-term prediction of water table levels or non-incursion of circulating oxidizing waters is difficult, thus moderate depth provides a time-rate insurance that is likely to be valid. This is significant also in terms of the geologic mobilities of iodine and radon.

Sorption is perhaps over-rated as a barrier process relative to long-term radioactive waste isolation. Sorption processes are effective in nomogeneously porous and permeable sorbing materials such as soils under slow solution flow (leaks) or one-shot situations (spills). In the long-term subsurface situation, sorption can be important but can also be rendered ineffective by expected natural processes. At best sorption should be considered a moderate-term delay (10^4 years) rather than a long term barrier. Interestingly, sorption is maximized under the same conditions that maximize other geochemical immobilizing processes so these processes are mutually supportive.

Organic and pyritic shales are generally the best waste host rocks in terms of parameters used in this study.

Base metal behavior, as seen in our brief look at theoretical hydrothermal ore deposition and geothermal systems, appears to be similar to the nuclides studied in their tendencies toward immobility under reducing conditions and some mobility in oxidizing systems. These distinctions are less clear-cut for hydrothermal metals in both the reducing and oxidizing situations, and the role of complexing is likely even more significant than for the nuclides studied. Empirical data (as in several tables following) suggests massive mobilities of base metals, probably even under reduced conditions. More empirical data would likely support the implication that metals are mobile even where they should theoretically stay put.

The m-factors identified in this report are easily interpreted and reproduced, but are not yet in a form useful for broad derivation and application to the hazard index formula. The +m, -m designations must be quantified numerically in order to interface with the Smith et al. (1980) geotoxicity hazard index. For that matter, the m-factors based on geochemical functions should be reducible to broader, more easily identifiable geologic conditions as related to specific sites.

In the geochemical review work for this report, we felt that it is not possible in a theoretical approach to ensure that the subtle geochemical effects on waste behavior are entirely allowed for. The analog (empirical) approach, if several models are used, is likely to be superior to the theoretical approach in allowing for geochemical/thermodynamic variables such as:

- Kinetics (reaction rates)
- Reaction potentials
- Reversibility of reactions and
- Threshold functions.

B. Suggestions for Further Work

We felt it impossible (as apparently did out literature sources) to attempt the evaluation of analog models without some traditional base in theory. It is difficult to accept the suggestion of immobility of a few natural examples without knowing "why?" Therefore, our results are definitely a hybrid of theoretical and analog reasoning and are likely in need of further analog input and testing. The suggestions for further work, given by each individual author, are presented in the following paragraphs.

Kresan feels that the following areas of work would be of particular importance.

Other Analogs:

1. Review of sedimentary basins especially in petroleum literature was barely touched in our study. Further review would provide considerable information on the geochemistry and porosity/permeability of sedimentary rocks and characteristics of fluids within these rocks. (Material referenced from Hanor (1979), in Fig. 24, shows temperature-related salinity functions.)
2. A geothermal springs analog built on a comparison of metal bearing and non-metal bearing geothermal waters could provide a more definite feel for metal mobilities (as summarized by Tables 13-17).
3. Replacement deposits, i.e., behavior of metal-bearing solutions as they react with certain minerals to precipitate ore have not been dealt with significantly in this report.
4. Stability and characteristics of alteration products over different temperature and pressure conditions should be studied. This could yield information on the chemical and physical properties of alteration products formed before or during ore deposition which may have influenced deposition. Alteration reactions can significantly influence pH, Eh and cation/anion concentrations, as well as permeabilities.

Concepts to Explore:

1. Assume a potential for the migration of aqueous solutions to predict minimizing the mobility of constituents using the natural characteristics of a sequence of rock strata.

 (Text continues on Pg. 93)

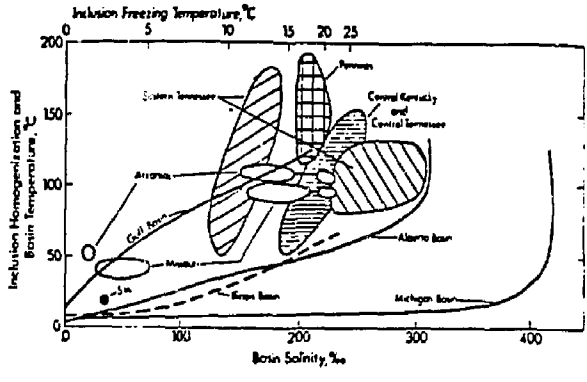

FIG. 24. Temperature-salinity relations in ore-forming fluids from Mississippi Valley type districts (patterned areas), as deduced from fluid inclusion data, and temperature-salinity relations for waters in the Illinois, Michigan, Alberta, and Mississippi Gulf basins. S.W. marks the position of surface seawater. (From Hanor, 1979)

TABLE 13. Estimated compositions (weight per cent) of three samples of sulfide-rich scale from pipes discharging Salton Sea brines at well No. 1 IID.

	W-769 (220 ± 30°C)	W-767 (170 ± 30°C)	W-768 (130 ± 20°C)
Si	M	M	M
Cu	M	M	M
Fe	5.0	7.0	6.0
Ag	7.0	1.3	2.8
As	0.18	0.10	0.10
Sb	0.72	0.17	0.25
Bi	0.11	0.004	0.009
Mn	0.055	0.42	0.34
Co	0.0050	0.0004	0.0006
Al	3.	1.0	1.4
Ga	0.0016	0.016	0.012
Yb	0.0002	0.0002	0.0002
Be	0.0036	0.046	0.037
Mg	0.014	0.0085	0.0080
Ca	0.55	0.60	0.55
Sr	0.008	0.003	0.003
Ba	0.014	0.020	0.0090
B	0.019	0.11	0.080
Pb	0.012	0.011	0.007
Sn	0.002	0.002	0.002
Na	1.	1.	1.
K	1.5	1.	1.5
Ti	0.0007	0.0015	0.0007

M = major constituent.

(In Stanton, 1972)

TABLE 14. Quantitative x-ray fluorescence analyses (weight per cent) and mineralogical assemblages of sulfide-rich scale from No. 1 IID well, Salton Sea geothermal area.

Sample No. †	Temp., °C	Cu	Ag	Fe	As	Sb	S	Mineral content
W-769 (1)	220 ± 30	10.0	1.2	3.8	0.23	1.05	6.6	bn,cp,Ag
W-769 (2)	220 ± 30	43.6	5.8	7.1	0.15	0.69	22.5	bn,cp,ccII, asp,Ag
W-767 (1)	170 ± 30	14.0	1.2	15.7	0.20	0.52	10.2	dg,py
W-767 (2)	170 ± 30	27.5	3.1	8.6	0.13	0.66	13.4	bn,ccII,Ag
W-767 (3)	170 ± 30	23.6	1.0	10.6	0.13	0.57	12.8	dg,bn
W-768 (1)	130 ± 20	10.1	1.0	25.4	0.30	0.55	9.9	dg,trace td
W-768 (2)	130 ± 20	13.4	1.2	18.8	0.23	0.53	10.8	dg,trace td
W-768 (3)	130 ± 20	19.2	1.6	11.3	0.15	0.56	12.2	dg,bn,py
W-768 (4)	130 ± 20	12.4	1.6	14.0	0.15	0.53	10.9	dg,bn
W-768 (5)	130 ± 20	11.5	2.1	12.0	0.14	0.45	11.6	dg,strm
W-768 (6)	130 ± 20	28.2	3.4	9.8	0.11	0.55	14.2	bn,cp,ccII, strm,Ag

† Individual bands in the scale are indicated by numbers in parentheses, band 1 being the first band deposited in each case. Mineralogical abbreviations: asp=arsenopyrite; bn=bornite; ccII=dense Cu_2S; cp=calcopyrite; dg=digenite; py=pyrite; strm=stromeyerite; td=tetrahedrite.

(In Stanton, 1972)

TABLE 15. Concentrations of Minor Elements in Waters From Geothermal Wells and Springs (ppm).

	Mn	Fe	Ni	Cu	Pb	Zn	Cd	Ag	Au	As	Sb	
Apapel Springs, Kamchatka		0.7	0.015	0.002	0.025	0.005				3	0.15-0.45	
Arima Springs, Japan	61	187		0.1	0.4	0.2						
Broadlands, New Zealand												Tl 0.007, W 0.087
Drillhole 2	0.0133	0.36	0.0002	0.0009	0.0013	0.001	0.00001	0.0007	0.00004	5.7	0.2	Br2 (V 0.0023, Ge 0.004
Drillhole 25		0.36	0.00005	0.0013	0.0055	0.0006	0.00002	0.00025				Sn 0.021, Be 0.00023
												Bi (Br 7) 0.0003
Cerro Prieto												
Mexicali, Mexico	0.64	0.2	0.002	0.005	0.0046	0.006		0.004	0.004	2	0.4	
Cheleken, USSR												
Wells (ii)	46.5	14.0	0.33	1.41	9.20	3.06	1.66					
(iii)		4.2		0.90	3.60	0.19	0.00					
Geysir, Iceland		0.0125	0.001			0.002						V 0.015, Mo 0.0175
												Ge 0.0236, Co 0.001
Matsao, Taiwan	42	220		0.05	0.6-0.9	13						
Drillhole E205										3.6		Al 2.3
Osoreyama, Japan												
Spring (a)	1.2	0.02			0.01					39.5		Al 0.7
(b)	5.4	21.1			0.01					0.04		Al 24.2
Red Sea, Atlantis II Deep												
56°Brine	82	81		0.26	0.63	0.54						Co 0.16
Interstitial Brine (26m-3m	134	83		1.5	0.3	7.1		0.04				Mo 0.03, Al 15
Salton Sea, California												
Drillhole No. 1, IID	1400	2290		8	102	540	2.0	1.4	0.0	12	0.4	Tl 1.5, Sn 0.5
												Hg 0.006, Al 4.2
												Sr 400, Ba 235
Tamagawa, Japan	4.2	105		0.01	1.0	2.8						Al 138, Hg 0.01
Uzon, Kamchatka												
Spring in Central Thermal Areas				0.1		0.1		0.015				Hg 0.012, Mo 0.014
												Ge 0.008
Wairekei, New Zealand (average										4.7	0.1	Be 0.00005
of several drillholes)	0.0007	0.012	0.001	0.0019	0.0045	0.0022	0.00055					Al 0.00015

(After Barnes, 1979)

TABLE 16. Examples of geothermal areas explored by drilling.

Area	Rock Types	Max. drilled depth (m)	Max. temp. (°C)	Main solutes (total dissolved solids, g/kg, surface sample)	Water pH (surface, cold)	Main gases present
Hveragerdi, Iceland	Quaternary basalt	1200	232	Na^+,Cl^-(0.9)	9.5	CO_2,N_2,H_2S,H_2
Reykjavik, Iceland	Tertiary basalt	2200	146	Na^+,Cl^-,HCO_3^-(0.4)	8.6	N_2
Reykjanes, Iceland	Quaternary and Recent basalt	1750	290	Na^+,Cl^-,Ca^{2+}(40)	5.8	CO_2,N_2
Wairakei, New Zealand	Quaternary rhyolite, andesite	2300	265	Na^+,CL^-,(4.5)	8.2	CO_2,H_2S
Broadlands, New Zealand	Quaternary rhyolite; Mesozoic graywacke	2420	300	Na^+,Cl^-,(4.1)	8.3	CO_2,CH_4,H_2S
Pauzhetsk, Kamchatka, U.S.S.R.	Quaternary dacite, andesite	800	190	Na^+,Ca^{2+},Cl^-,SO_4^{2-} (3.0)	8.9	CO_2,H_2S
El Tatio, Chile	Quaternary and Tertiary rhyolite, andesite; Mesozoic sediments	600	260	Na^+,CL^-(15)	7.0	CO_2,N_2,H_2S
Yellowstone Park, U.S.A.	Quaternary rhyolite	330	240	Na^+,Cl^-,HCO_3^-(1.7)	8.8	CO_2,H_2S
Steamboat Springs, Nevada	Granodiorite; Tertiary and Quaternary andesite, rhyolite	175	172	Na^+,Cl^-,HCO_3^-(2.0)	8.8	CO_2,H_2,H_2S
Matsao, Taiwan	Quaternary and Recent andesite; Miocene sandstone	1500	293	Na^+,Cl^-,Ca^{2+}(30)	2.5	CO_2,H_2S
Salton Sea, California	Tertiary sediments (Quarternary rhyolite)	2470	360	Na^+,Ca^{2+},K^+,Cl^-(350)	5.5	CO_2,CH_4,H_2S
Mexicali, B.C., Mexico	Sediments; Quaternary basalts, granite	2600	370	Na^+,Cl^-,K^+(17)	5.5	CO_2,H_2S
Ngawha, New Zealand	Cretaceous sediments (basalt)	600	235	B,Cl^-,Na^+,HCO_3^-(8)	7.5	CO_2,H_2S,NH_3
Kizildere, Turkey	Tertiary sandstones, limestones; schist, marble	1000	220	Na^+,HCO_3^-,SO_4^{2-},Cl^- (4.8)	9.0	CO_2,H_2S
Matsukawa, Japan	Quaternary and Tertiary andesite, dacite	1200	280	Na^+,So_4^{2-},Fe^{2+}(1-4)	3-6	CO_2,H_2S
Larderello, Italy	Mesozoic and Tertiary clays, limestone, anhydrite; Permian shist	1600	260	Steam only		CO_2,H_2S, H_3BO_3,NH_3
The Geysers, California	Mesozoic graywacke; serpentine, basalt	2800	285	Steam only		CO_2,N_2, CH_4,H_2S

(After Barnes, 1979)

TABLE 17. Estimated composition of dissolved matter (in ppm) of brines produced from two bores in tne Salton Sea area, California.

Constituent	Bore No. I IID	Bore No. 2 IID
Sodium	50,400	53,000
Potassium	17,500	16,500
Lithium	215	210
Rubidium	137	70
Cesium	16	20
Ammonia (NH_4)	409	
Calcium	28,000	27,800
Magnesium	54	10
Barium	235	250
Strontium	609	440
Chloride	155,000	155,000
Fluorine	15	Not reported
Bromine	120	Not reported
Iodine	18	Not reported
Sulfate (SO_4)	5.4	Total sulfur = 30
Sulfide sulfur	16	--
Boron	390	390
Iron	2,090	2,000
Manganese	1,560	1,370
Silver	0.8	2
Copper	8	3
Lead	84	80
Zinc	790	500
Arsenic	12	Not reported
Antimony	0.4	Not reported
CO_2 as HCO_3	150	690
Silica	400	400
Total reported	258,360	258,765

(From Stanton, 1972)

2. Solutions evolve as they move through wall rock. Any model dealing with potential mobility/transport of radionuclides must incorporate potential changes in the solution during flow.

...cs from Wachter regarding further work:

1. Purely analog data may be collected from diverse sources to test the conclusions regarding Eh, pH, CO_2, etc. effects as opposed to gross physical/hydrological effects.

   Uranium exploration data apparently show some randomness in results, often with low uranium concentrations even in oxidizing uranium systems.

   Table 18 shows one of a series of coal-waste materials tested under known Eh, pH conditions. Actinide/lanthanide mobilities are negligible even though present in the test material in moderate concentrations. Tables 19 and 20 further illustrate these test results, indicating significant mobilities of other toxins.

   Tables 21 through 24 show the incidents of certain metallic toxins in about 500 wells tested in Arizona.

2. The m-factors approach should be restructured to reflect more easily obtained information. The m-factors should be based on semi-quantitative definition of geologic/geochemical factors or limits imposed by analog models.

3. Drillers' experience, when integrated for a given rock-type in a given area, may yield interesting depth-analog data. Waltz and Decker (1981) indicate in the Johnson Drilling Journal that fracture permeability (especially for all except near-vertical fractures) decreases markedly at depths as shallow as 400 feet in the Colorado Front Range Granite.

Purely analog work, the collection and interpretation of the type of data illustrated here, would as (suggested by the samples in Tables 18-24) apparently be rewarding and further test the conclusions of this report.

TABLE 18. Chemical Composition of Lurgi Ash and Slurry Supernatant Solutions of the Ash from an Illinois No. 6 Coal at several ph's.

		Chemical composition of 10% slurry supernatant							
		Air (mg/L)				Argon (mg/L)			
Constituents	Solid Ash (mg/kg)	pH 7.55*	pH 5.10	pH 3.82	pH 2.68	pH 8.82*	pH 7.20	pH 5.35	pH 3.79
Ag	<0.4	-	-	-	-	-	-	-	-
Al	108,121	<0.3	2	14	132	<0.3	<0.3	<0.3	92
Au	<.001	-	-	-	-	-	-	-	-
As	3	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
B	355	4.0	4.5	4.5	5.5	4.5	3.0	4.5	8.0
Ba	950	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Be	12	<.02	<.02	.01	.03	<.02	<.02	<.02	.01
Br	<1.0	-	-	-	-	-	-	-	-
Ca	16,652	290	480	400	570	440	370	430	500
Cd	<1.6	.02	.03	.03	.06	.01	<.03	.02	.05
Ce	140	-	-	-	-	-	-	-	-
Cl	100	<25	<25	<25	<25	<25	<25	<25	<25
COD†	-	2	2	2	81	2	2	16	140
MCE+	-	28	28	0	23	10	3	6	4
Cr	212	<.02	.02	.05	.12	.01	.01	.06	.16
Co	34	<.05	.05	.08	.19	<.05	<.05	<.05	.17
Cu	57	.01	.02	.13	.73	.01	.05	.01	.05
Cs	11	-	-	-	-	-	-	-	-
Eu	1.9	-	-	-	-	-	-	-	
F	<10	.31	.30	.09	.04	.51	.34	.16	.02
Fe_{total}	143,780	.06	.19	.24	560	.06	.11	101	880
Fe^{+2}	-	.03	.11	.10	533	.13	.05	110	864
Ga	26	-	-	-	-	-	-	-	-
Ge	7.0	-	-	-	-	-	-	-	-
Hf	6.1	-	-	-	-	-	-	-	-
Hg	.05	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002	<.0002
K	14,611	42	49	51	26	39	43	48	61
La	47	-	-	-	-	-	-	-	-
Li	42	1.8	1.9	2.0	2.0	1.6	1.8	1.9	2.1
Lu	1.5	-	-	-	-	-	-	-	-
Mg	3,739	10.5	14	15	22	9.5	11	13.5	23

(Table 18 continued on next page)

Table 18. (cont.)

Constituents	Solid Ash (mg/kg)	Chemical composition of 10% slurry supernatant: Air (mg/L) pH 7.55*	pH 5.10	pH 3.82	pH 2.68	Argon (mg/L) pH 8.82*	pH 7.20	pH 5.35	pH 3.79
Mn	1,859	.45	1.94	2.7	3.8	.11	.90	2.3	3.7
Mo	30	<.03	<.03	<.03	<.03	<.03	<.03	<.03	<.03
Na	1,929	34	37	38	40	32	37	37	40
NH_4	-	17	8	12	11	10	10	10	17
Ni	89	.03	.13	.23	.50	<.07	.04	.14	.42
Pb	45	.1	.1	.1	.2	.1	.1	.1	.2
P	87	-	-	-	-	-	-	-	-
PO_4	-	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01
Rb	162	-	-	-	-	-	-	-	-
S_{Total}	6,100	-	-	-	-	-	-	-	-
S^{-2}	1,500	<.2	<.2	<.2	<.2	<.2	<.2	<.2	<.2
SO_4	8,100	820	943	808	338	730	735	700	710
Sb	4.2	.2	.3	.3	.6	.3	.3	.3	.5
Sc	29	-	-	-	-	-	-	-	-
Se	<1	<.1	<.1	<.1	<.1	<.1	<.1	<.1	<.1
Si	229,946	5	29	60	130	4	9	27	120
Sm	8.21	-	-	-	-	-	-	-	-
Sn	-	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Sr	370	1.8	1.9	2.1	2.9	1.5	1.7	1.9	2.6
Ta	1.1	-	-	-	-	-	-	-	-
Te	-	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	21	-	-	-	-	-	-	-	-
Ti	6,295	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Tl	4.6	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
U	17	-	-	-	-	-	-	-	-
V	184	-	-	-	-	-	-	-	-
W	1.5	-	-	-	-	-	-	-	-
Yb	2.9	-	-	-	-	-	-	-	-
Zn	400	.12	5.5	12	17	.01	.11	6.5	20
Zr	170	-	-	-	-	-	-	-	-
EC (mmhos/cm)	-	1.17	1.50	1.95	5.60	1.20	1.39	1.80	5.20
Eh (electrode mv)	-	+223	+246	+407	+349	+109	+161	+102	+243

*Natural pH of supernatant.

**Chemical oxygen demand.

***Methylene chloride extractable organics.

(From Griffen et al., 1980)

TABLE 19. Discharge Severities for Constituents in Coal Utilization Solid Wastes Exceeding Health- or Ecology-Based Solid Waste MATE Values.

Parameter	MATE Health (mg/kg)	MATE Ecology (mg/kg)	Lurgi No. 5	Lurgi No. 6	Lurgi Rosebud	H-Coal	SRC	Fly ash	Bottom ash (slag)	High-temp. char	Medium-temp. char	High-S refuse	Low-S refuse
Ag	50	10											
Al	16,000	200	478	541	506	86	338	368	423	86	68	283	485
Au	N	N											
As	50	10	1		2		7	5				1	7
B	9,300	5,000											
Ba	1,000	500	2	2	8				1				
Be	6	11	2	2			2	3					
Br	N	N											
Ca	48,000	3,200	7	5	19	2	2	8	14	1	2	9	7
Cd	10	0.2	8	8	8	2	6	9	10	2	2	7	9
Ce	250,000	N											
Cl	260,000	N											
Cr	50	50	3	4	1		2	3	2				2
Co	150	50											
Cu	1,000	10	5	6	5	1	10	14	4	1	1	3	4
F	7,500	N											
Fe	300	50	3,020	2,876	1,201	473	2,703	2,688	2,745	479	117	1,723	496
Ga	15,000	N											
Ge	1,700	N											
Hf	150	N											
Hg	2	50											
K	N	4,600	3	3	1		2	5	3			2	4
La	340,000	N											
Li	70	75											
Mg	18,000	17,000			1								
Mn	50	20	101	93	46	4	8	19	23	4	3	15	15
Mo	15,000	1,400											
Na	160,000	N											
Ni	45	2	97	44	2	10	7	80	28	10	6	24	27
Pb	50	10	18	4	4	3	6	11	2	1		6	5
P	3,000	0.1	2,180	870	20,950	440	10,040	8,730	7,860	870	870	8,290	13,970
Rb	360,000	N											
S Total	N	N											
Sb	1,500	40											
Sc	160,000	N											
Se	10	5						3					
Si	30,000	N	8	8	8	1	4	6	7	1	2	5	9
Sm	160,000	N											
Sn	N	N											
Sr	9,200	N											
Ta	15,000	N											
Te	300	N											
Th	130	N											
Ti	18,000	160	40	39	40	6	11	32	28	6	27	29	52
Tl	300	N											
U	12,000	100											
V	500	30	6	6	1	1	4	8	2			1	1
W	3,000	N											
Zn	5,000	20	75	20	2	4		28	3	2	2	15	25
Zr	1,500	N											
Total discharge severity			6,054	4,531	22,805	1,033	13,152	12,020	11,155	1,463	1,100	10,412	15,118

Discharge severity = concentration/MATE

(From Griffen et al., 1980)

TABLE 20. Elements with Concentrations Exceeding Recommended Water Quality Levels Under the Laboratory Test Conditions.

		Natural pH		
Sample	pH range	Air	Argon	Constituents
Lurgi Ash (Ill. #6 Coal)	8.8-2.7	7.6	8.8	B, Ca, Cd, K, Mn, NH_4, Pb, SO_4, Sb
Lurgi Ash (Ill. #5 Coal)	10.9-3.1	8.3	10.9	B, Ca, K, Mn, NH_4, Pb, SO_4, Sb
Lurgi Ash (Rosebud Coal Mont.)	11.1-3.1	8.4	11.1	B, Ca, Cd, F, K, Mo, NH_4, Pb, SO_4, Sb
SRC	10.2-2.9	6.4	7.5	B, Ca, Fe, Mn, NH_4, SO_4
H-Coal	11.3-2.3	8.8	11.3	B, Ca, NH_4
Char (1200°F)	9.7-2.4	7.2	7.6	B
Char (1800°F)	8.1-2.5	8.1	7.5	B, Ca, Mn, NH_4
Low-sulfur gob	9.2-2.4	9.2	9.2	None
High-sulfur gob	8.9-2.5	7.5	7.4	K, NH_4, SO_4
Slag	8.8-2.8	3.8	5.7	NH_4
Fly ash	10.0-2.5	4.1	4.3	B, Ca, SO_4

(From Griffen et al., 1980)

TABLE 21. Highest concentration of copper and samples exceeding the U.S. Public Health recommended limit of 1.0 ppm for the counties of Arizona.

County	Highest Value	Samples Exceeding 1.0 ppm	
	ppm	No.	%
Apache	0.58	0	0.0
Cochise	0.14	0	0.0
Coconino	4.36	1	3.6
Gila	0.50	0	0.0
Graham	0.25	0	0.0
Greenlee	0.04	0	0.0
Maricopa	0.46	0	0.0
Mohave	2.63	1	2.9
Navajo	0.43	0	0.0
Pima	22.60	4	2.1
Pinal	4.26	1	0.7
Santa Cruz	0.01	0	0.0
Yavapai	1.23	1	9.1
Yuma	0.10	0	0.0
All Counties	22.60	8	1.2

TABLE 22. Highest concentration of zinc and samples exceeding the U.S. Public Health recommended limit of 5.0 ppm for the counties of Arizona.

County	Highest Value	Samples Exceeding 5.0 ppm	
	ppm	No.	%
Apache	1.73	0	0.0
Cochise	2.78	0	0.0
Coconino	1.91	0	0.0
Gila	0.57	0	0.0
Graham	0.33	0	0.0
Greenlee	0.03	0	0.0
Maricopa	0.68	0	0.0
Mohave	0.864	0	0.0
Navajo	4.54	0	0.0
Pima	3.0	0	0.0
Pinal	15.14	2	1.5
Santa Cruz	0.01	0	0.0
Yavapai	0.34	0	0.0
Yuma	0.28	0	0.0
All Counties	15.14	2	0.3

(From Dutt and McCreary, 1970)

TABLE 23. Highest concentration of lead and samples exceeding the U.S. Public Health Service mandatory limit of 0.01 ppm for the counties of Arizona.

County	Highest Value	Samples Exceeding 0.01 ppm	
	ppm	No.	%
Apache	0.088	7	30.4
Cochise	0.045	0	0.0
Coconino	0.187	3	10.7
Gila	0.000	0	0.0
Graham	0.000	0	0.0
Greenlee	0.000	0	0.0
Maricopa	0.177	8	11.0
Mohave	0.029	0	0.0
Navajo	0.254	2	7.4
Pima	0.518	18	9.6
Pinal	0.175	3	2.2
Santa Cruz	0.043	0	0.0
Yavapai	0.000	0	0.0
Yuma	0.113	3	12.0
All Counties	0.518	44	6.5

TABLE 24. Highest concentration of cadmium and samples exceeding the U.S. Public Health Service mandatory limit of 0.01 ppm for the counties of Arizona.

County	Highest Value	Samples Exceeding 0.01 ppm	
	ppm	No.	%
Apache	0.494	1	4.4
Cochise	0.003	0	0.0
Coconino	0.002	0	0.0
Gila	0.000	0	0.0
Graham	0.000	0	0.0
Greenlee	0.000	0	0.0
Maricopa	0.204	2	2.7
Mohave	0.000	0	0.0
Navajo	0.004	0	0.0
Pima	0.080	8	4.2
Pinal	0.011	1	0.7
Santa Cruz	0.000	0	0.0
Yavapai	0.000	0	0.0
Yuma	0.004	0	0.0
All Counties	0.494	12	1.8

(From Dutt and McCreary, 1970)

X. REFERENCES

A. Fission Product Behavior

Allard, B. et al. (1980), "Possible Retention of Iodine in the Ground," in Northrup, ed., p. 673-680.

Allard, B. et al. (1979), "Disposal of Radioactive Waste in Granitic Bedrock," in Fried, ed., p. 48-73.

Allen, E. J., (1978), "Criticality Analysis of Aggregations of Actinides From Commercial Nuclear Waste in Geological Storage," ORNL/TM-6458 U.S. DOE - August.

Andelman, J. B. and T. E. Rozzell (1970), "Plutonium in the Water Environment," in Radionuclides in the Environment, S. E. Fierling, ed., Am. Chem. Soc., Washington, D.C. p. 118.

Apt, K. E., ed. (1977), "Investigations of the Natural Fission Reactor Program," Los Alamos Report No. 7032-PR.

Barney, G. S. (1979), "Variables Affecting Sorption and Transport of Radionuclides in Hanford Subsoils," in McCarthy, ed., p. 435-438.

Barthel, F. H. (1974), "Review of Uranium Occurrences in Permian Sediments in Europe, with Special Reference to Uranium Mineralizations in Permian Sandstone," in IAEA Proc., Athens, May 1974, p. 277-289.

Beall, G. W. and B. Allard (1980), "Prediction of Sorption Behavior of Actinides on Geologic Media," in Abstracts, Materials Research Society, p. D94.

Beall, G. W. et al. (1980), "Chemical Reactions in the Bedrock-Groundwater System of Importance for the Sorption of Actinides," in Northrup ed., p. 625-631.

Beall, G. W. et al. (1979), "Sorption Behavior of Trivalent Actinides and Rare Earths on Clay Minerals," in Fried, ed., p. 201-213.

Bird, G. W. and V. J. Lopata (1980), "Solution Interaction of Nuclear Waste Anions with Selected Geological Materials," in Northrup, ed., p. 419-426.

Bondietti, E. A. and C. W. Francis (1979), "Chemistry of Tc-99 and Np-237 in Contact with Unweathered Igneous Rocks," in McCarthy, ed., p. 417-418.

Bredehoeft, J. D. et al. (1978), "Geologic Disposal of High-Level Radioactive Wastes - Earth Science Perspectives," U.S. Geol. Survey Circular 779.

Breger, I. A. (1974), "The Role of Organic Matter in the Accumulation of Uranium," in IAEA Proc., Athens, May 1974, p. 99-124.

Brookins, D. G. (1980), "Geochemistry of Clay Minerals for Uranium Exploration in the Grants Mineral Belt, New Mexico," AIME Preprint 80-112, 12 p.

Brookins, D. G. (1980), "Clay Minerals Suitable for Overpack in Waste Repositories: Evidence from Uranium Deposits," in Northrup, ed., p. 427-435.

Brookins, D. G. (1979), "Thermodynamic Considerations Underlying the Migration of Radionuclides in Geomedia: Oklo and Other Examples," in McCarthy, ed., p. 355-366.

Brookins, D. G. (1978), "Application of Eh-pH Diagrams to Problems of Retention and/or Migration of Fissiogenic Elements at Oklo," in IAEA Natural Fission Reactors Proc., p. 243-265.

Brookins, D. G. (1976), "Uranium Deposits of the Grants, New Mexico Mineral Belt," ERDA/DOE Rept. GJO-1636-1, Grand Junction, Colo.

Burkholder, H. C. and C. DeFigh-Price (1978), "Diffusion of Radionuclide Chains Through an Adsorbing Medium," in Am. Inst. of Chem. Eng. Symp. Series No. 179, Vol. 74.

Burkholder, H. C. and M. O. Cloninger (1978), "The Reconcentration Phenomenon of Radionuclide Chain Migration," in Am. Inst. of Chem. Eng. Symp. Series No. 179 Vol. 74, p. 83-90.

Chipman, N., G. Simpson, W. Rodger, R. Frendberg, and H. Lawroski (1980), "Environmental Effects From Disposal of Defense High Level Radioactive Wastes in a Generic Geologic Repository", in Northrup, ed., p. 813.

Claassen, H. C. (1978), Hydraulic Processes and Radionuclide Distribution in a Cavity and Chimney Produced by the Cannikin Nuclear Explosion, Amchitka Island, Alaska, U.S. Geol. Survey, Prof. Paper 712-D.

Cohen, B. L. and H. M. Jow (1978), "A Generic Hazard Evaluation of Low-Level Waste Burial Grounds," Nuclear Technology, Vol. 41, p. 381-388.

Cowan, G. A. (1978), "Migration Paths for Oklo Reactors Products and Applications to the Problem of Geological Storage of Nuclear Wastes," in IAEA Natural Fission Reactors Proc., p. 693-699.

Cotton, F. A. and G. Wilkinson (1967), Advanced Inorganic Chemistry, John Wiley, N. Y.

Dahl, A. R. and J. L. Hagmaier (1974), "Genesis and Characteristics of the Southern Powder River Basin Uranium Deposits, Wy. U.S.A.," in IAEA Proc., Athens, May 1974, p. 201-216.

Dall'Aglio, M. et al. (1974), "Geochemical Factors Controlling the Formation of the Secondary Minerals of Uranium," in IAEA Proc. Athens, May 1974, p. 33-48.

Dosch, R. G. and A. W. Lynch (1980), "Radionuclide Transport in a Dolomite Aquifer," in Northrup, ed., p. 617-624.

Dosch, R. G. (1979), "Radionuclide Migration Studies Associated with the WIPP Site in S. New Mexico," in McCarthy, ed., p. 395-398.

Duffy, C. J. (1978), "Uranium Solubilities in the Oklo Reactor Zones," in IAEA Natural Fission Reactors Proc., p. 229-234.

Dyck, W. (1978), "The Mobility and Conclusions of U and Its Decay Products in Temperate Surficial Environments," in Kimberley, ed.

El Shazy, E. M. et al. (1974), "Origin of U in Oligocene Qatrani Sediments, Western Desert, Arab Republic of Egypt," in IAEA Proc. Athens, May, 1974 p. 467-477.

Erdal, B. R. et al. (1980), "Parameters Affecting Radionuclide Migration in Geologic Media," in Northrup, ed., p. 609-616.

Erdal, B. R. et al. (1979), "Sorption and Migration of Radionuclides in Geologic Media," in McCarthy, ed., p. 423-426.

Erickson, K. L. (1980), "Radionuclide Sorption Studies on Abyssal Red Clays," in Northrup, ed., p. 641-646.

Erickson, K. L. (1979), "Radionuclide Sorption Studies on Abyssal Red Clays," in Fried, ed.

Ermolenko, N. K. (1972), Trace Elements and Colloids in Soils, 2nd. ed., (Translated from Russian), Israel Prog. for Scientific Translation and U.S. Dept. of Commerce.

Freeborn, W. et al. (1980), "Shale Rocks as Nuclear Waste Repositories: Hydrothermal Reactions with Glass, Ceramic and Spent Fuel Waste Forms," in Northrup, ed., p. 499-506.

Fried, S. et al. (1980), "The Radiolytic Oxidation and Reduction of Plutonium," in Northrup, ed., p. 655-664.

Fried, S., ed. (1979), Radioactive Waste in Geologic Storage, Am. Chem. Soc. Symp. Series 100, Sept. 1978, Miami Beach, FL.

Fried, S. et al. (1976), "Migration of Actinides in Geologic Formations," in Proc. on Internat. Symp. of Management of Wastes from the LWR Fuel Cycle, July 11-16, 1976, Denver, p. 697-701.

Friedman, A. M. and S. Fried (1979), "Kinetic Effects in Migration," in Fried, ed., p. 191-199.

Fre'jacques, C. and R. Hagemann (1979), "Conclusions from Studies of the Oklo Natural Reactor," in Proc. on Internat. Symp. of Management of Wastes from the LWR Fuel Cycle, July 11-16, 1976, Denver.

Fritz, P. et al. (1980), "Geochemistry, Origin and Age of Groundwater in the Stripa (Sweden) Test Mine," in Northrup, ed., p. 543-552.

Galley, J. E., ed. (1968), "Subsurface Disposal in Geologic Basins - A Study of Reservoir Strata," Am. Assoc. of Petrol Geol. Memoir 10.

Gancarz, A. et al. (1980), "^{99}Tc, Pb and Ru Migration Around the Oklo Natural Fission Reactors," in Northrup, ed., p. 601-608.

Griffen, R. A. et al. (1980), "Chemical and Biological Characterization of Leachates from Coal Solid Wastes," Illinois Inst. of Natural Resources, Env. Geol. Notes, 89, Champaign, Ill.

Haire, R. G. and G. W. Beall (1979), "Consequences of Radiation From Sorbed Transplutonium Elements on Clays Selected for Waste Isolation," in Fried, ed., p. 291-295.

Hinkebein, T. E. and P. F. Hlava (1979), "Interactions of Simulated Waste Radionuclides and Rocks," in McCarthy, ed., p. 419-422.

Hinkebein, T. E. and P. F. Hlava (1978), "Microstructural Interactions of Geologic Media With Waste Radionuclides," Sandia, SAND 78-0108.

Hoffman, D. C. (1979), "A Field Study of Radionuclide Migration," in Fried, ed., p. 149-166.

I.A.E.A. (1978), Natural Fission Reactors, Proceedings from Dec. 1977, Paris Meeting, Second Int. Conf. on Oklo., Publication TC-119/33.

I.A.E.A. (1977), Site Selection Factors for Repositories of Solid High-Level and Alpha-Bearing Wastes in Geologic Formations, Technical Reports Series No. 177.

I.A.E.A. (1974), Formation of Uranium Ore Deposits, Proc. of a Symp., Athens, May, 1974.

I.A.E.A. (1967), Disposal of Radioactive Waste Into the Ground, Proc. of a Symp., May 29-June 2, 1967.

ICRP (1975), "*Report of the Task Group on Reference Man*," International Commission of Radiation Protection, Publication #23, Pergamon Press, NY.

Jakubick, A. T. (1979), "Analysis of Pu-release Consequences on the Environmental Geochemistry," in McCarthy, ed., p. 427-434.

Janse, A. J. A. (1969), "Gross Brukkaros, A Probable Carbonatite Volcano in the Nama Plateau of SW Africa," Geol. Soc. of Am. Bull., Vol. 80, p. 573-586.

Jayaram, K. M. V. et al. (1974), "A Study of the Influence of Microflora on the Genesis of Uranium Occurrences of Udaisagas, Udaipur District, Rajasthan," (India), in IAEA Proc. Athens, May 1974, p. 89-98.

Katayama, N. et al. (1974), "Genesis of Uranium Deposits of the Tono Mine, Japan," in IAEA Proc., Athens, May 1974, p. 437-452.

Kimberley, M. M., ed. (1978), Short Course in Uranium Deposits: Their Mineralogy and Origin, Mineralogical Association of Canada, Toronto.

Kimberley, M. M. (1978), "Origin of Stratiform Uranium Deposits in Sandstone, Conglomerate, and Pyroclastic Rock," in Kimberley, ed.

Kocher, D. C. (1979), "A Dynamic Model of the Global Iodine Cycle for the Estimation of Dose to the World Population from Releases of Iodine -129 to the Environment," NUREG/CR-0717, ORNL/NUREG-59.

Komarneni, S. and R. Roy (1980), "Super Overpack: Tailor-made Mixtures of Zeolites and Clays," in Northrup, ed., p. 411-418.

Langford, F. F. (1978), "Origin of Unconformity-Type Pitchblende Deposits in the Athabasca Basin of Saskatchewan," in Kimberley, ed.

Langmuir, D. (1978), "Uranium Solution-Mineral Equilibrium at Low Temperatures with Application to Sedimentary Ore Deposits," Geochim. Cosmochim. Acta, Vol. 42, 1978, p. 547-569.

Langmuir, D. (1978), "Uranium Solution-Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits," in Kimberley, ed., p. 17-55.

Langmuir, D. (1977), "Uranium Solution - Mineral Equilibria at Low Temperatures with Applications to Sedimentary Ore Deposits," ERDA/DOE Rept., GJO-1659-3 (GJBX-54), Grand Junction, Colo.

Lynch, A. W. and R. G. Dosch (1980), "Interaction of Radionuclides With Geomedia From the Nevada Test Site," in Northrup, ed., p. 633-640.

Magne, R. et al. (1974), "Solubilization and Insolubilization of Uranium From Granites by Heterotrophic Bacteria," in IAEA Proc. Athens, May 1974, p. 73-88.

Meyer, G. L. (1976), "Recent Experience with Land Burial of Solid Low-Level Radioactive Waste," in Symp. Proc., March, IAEA/OECD-NEA, Vol. II.

Miller, L. J. (1958), "The Chemical Environment of Pitchblende," Geology, Vol. 53, p. 521.

Morton, R. D. (1974), "Sandstone-Type Uranium Deposits in the Proterozoic Strata of NW Canada," in IAEA Proc., Athens, May 1974, p. 255-273.

McCarthy, G. J., ed. (1979), Scientific Basis for Nuclear Waste Management, Vol. 1, Plenum Press, NY.

McMillan, R. H. (1978), in "Origin of Stratiform Uranium Deposits," Kimberley, ed., p. 199.

NAS (1978), "Geological Criteria for Repositories for High-Level Radioactive Wastes," Panel on Geological Site Criteria, Nat. Acad. Sci., Wash., DC.

Nandet, R. (1978), "Summary of the Data on the Stability and the Re-Mobilization of Uranium and Rare Earths," in IAEA Natural Fission Reactors Proc., p. 643-673.

NEA (1977), "Objectives, Concepts and Strategies for the Management of Radioactive Waste Arising From Nuclear Power Programmes," Sept. Report by an NEA Group of Experts, Nuclear Energy Agency.

Northrup, C. J. M., Jr., ed. (1980), Scientific Basis for Nuclear Waste Management, Vol. 2, Proc. from Fall, 1979, Internat. Symp. on the Sci. Basis for Nuclear Waste Management, Mat. Res. Soc., Boston, Plenum Press, NY.

Nowak, E. J. (1980), "The Backfill as an Engineered Barrier for Nuclear Waste Management," in Northrup, ed., p. 403-410.

NWTS Program Office (1980), Proceedings of the 1980 Nat. Waste Terminal Storage Program Information Meeting, Dec., ONWI-212, U.S. DOE.

Ogard, A. et al. (1980), "Are Solubility Limits of Importance to Leaching?" Abst. Mat. Res. Soc., p. 041.

Pecora, W. T. (1956), "Carbonatites: A Review," Geol. Soc. Am. Bull., Vol. 67, p. 1537-1556.

Poston, J. W. (1978), "Measures of Equivalent Hazard of Radionuclides: A Survey," May, Union Carbide Corp./Office of Waste Isolation, DOE.

Poty, B. P. et al. (1974), "Fluid Inclusions in Uranium Ores From Intragranitic Deposits in Limousin and Forez, France," in IAEA Proc., Athens, May 1974, p. 569-581.

Register, J. K. et al. (1980), "Clay Mineral-Brine Interactions During Evaporite Diagenesis: Lanthanide Distribution in WIPP Samples," in Northrup, ed., p. 445-451.

Rich, R. A., H. D. Holland and U. Petersen (1975), "Vein-Type Uranium Deposits", ERDA/DOE Report, GJO-1640, Grand Junction, Colo.

Rickert, P. G. et al. (1979), "Nuclide Migration in Fractured or Porous Rock," in Fried, ed., p. 167-189.

Rimsaite, J. (1978), "Application of Mineralogy to the Study of Multi-State Uranium Mineralization in Remobilized Uranium Deposits, Saskatchewan," in Kimberley, ed., p. 403-430.

Roberts, L. E. J. (1978), "Radioactive Waste, Policy and Perspectives," British Nuclear Energy Society, Nov. 9.

Ruffenach, J. C. (1978), "The Natural Reactors of Oklo: Study of Uranium and Rare-Earth Migration in a Core Sample and Its Application to the Dating of the Nuclear Reactions," in IAEA Natural Fission Reactors Proc., p. 441-471.

Shiao, S. Y. et al. (1979), "Ion-Exchange Equilibrium Between Montmorillonite and Solutions of Moderate-to-High Ionic Strength," in Fried, ed., p. 297-324.

Silbey, D. F. and J. T. Wilband (1977), "Chemical Balance of the Earth's Crust," Geochim. Cosmochim. Acta, Vol. 41, p. 545.

Silva, R. J. et al. (1979), "Studies of Actinides Sorption on Selected Geologic Materials," in Fried, ed., p. 215-240.

Smith, C. F., J. J. Cohen, and T. E. McKone (1980), "A Hazard Index for Underground Toxic Material," UCRL-52889, Lawrence Livermore Laboratory, June 1980.

Smyth, J. R. et al. (1980). "Microautoradiographic Studies of the Sorption of U and Am on Natural Rock Samples," Radioactive Waste Management Vol. 1, No. 1, p. 13, Harwood Academic Pub., NY.

Stanton, R. L. (1972), Ore Petrology, McGraw-Hill, NY.

Spitsyn, V. I. and V. D. Balukova (1979), "The Scientific Basis For, and Experience with Underground Storage of Liquid Radioactive Wastes in the USSR," in McCarthy, ed., p. 237-248.

Szalay, A. (1967), "The Role of Humic Acids in the Geochemistry of Uranium and Their Possible Role in the Geochemistry of Other Cations," in Chemistry of the Earth's Crust, ed., Vinogradov - Israel Prog. of Sci. Transl., Jerusalem, p. 456-471.

Temple, A. K. and R. M. Grogan (1965), "Carbonatites and Related Alkalic Rocks at Powderhorn, Colorado," Econ. Geol., Vol. 60, p. 672-693.

Vidale, R. J. (1978), "The Highest Temperatures Recorded by the Oklo Mineral Phase Assemblages and Rock Textures," in IAEA Natural Fission Reactors Proc., p. 235-241.

Wacks, M. and R. Post (1980), The State of Waste Disposal Technology, Mill Tailings and Risk Analysis Models, Vol. I and II, Engineering Experiment Station, U. of Ariz., Tucson.

Wahlberg, J. S. and R. S. Dewar (1965), "Comparison of Distribution Coefficients for Sr Exchange From Solutions Containing One or Two Competing Cations," U. S. Geol. Surv. Bull. 1140-D.

Wahlberg, J. S. et al. (1965), "Exchange Adsorption of Strontium on Clay Minerals," U.S. Geol. Surv. Bull. 1140-E.

Wahlberg, J. S. and M. J. Fishman (1962), "Absorption of Cesium on Clay Minerals," U.S. Geol. Surv. Bull. 1140-A.

Walton, R. D. and G. A. Cowan (1975), "Relevance of Nuclide Migration at Oklo to the Problem of Geologic Storage of Radioactive Waste," in IAEA Libervill Symp. Oklo Pnenomena (June), p. 499-509.

Waltz, J. and T. L. Decker (1981) "Hydro-fracturing Offers Many Benefits," Johnson Drillers Journal, August, p. 4-9.

White, A. F. (1979), "Geochemistry of Ground Water Associated With Tuffaceous Rocks, Oasis, Valley, Nevada," U.S. Geol. Surv. Prof. Paper, 712-E.

Winchester, J. W. (1979), "Long Term Geochemical Interactions of High Active Waste With Crystalline Rock Repository Media," in McCarthy, ed., p. 345-347.

Winograd, I. J. (1975), "Hydrologeologic and Hydrochemical Framework, South-Central Great Basin, Nevada-Calif. with Special Reference to the Nevada Test Site," U.S. Geol. Surv. Prof. Paper 712-E.

Wyllie, P. J. and O. F. Tuttle (1960), "System $CaO-CO_2-H_2O$ and The Origin of Carbonatites," Journal of Petrology, Vol. 1 No. 1.

B. Hydrothermal Ores

Baes, D. F. and R. E. Mesiner (1976), The Hydrolysis of Cations, John Wiley, NY.

Barnes, H. L. ed. (1979), Geochemistry of Hydrothermal Ore Deposits, John Wiley, NY.

Barnes, H. L. and C. K. Czamanskye (1967), "Solubilities and Transport of Ore Minerals," in Barnes, ed., Geochemistry of Hydrothermal Ore Deposits, Wiley, p. 334-381.

Chapman, R. E. (1973), Petroleum Geology, A Concise Study, Elsevier, p. 304.

Dana, E. S., 1966, A Textbook of Mineralogy, John Wiley, NY, P. 851.

Degen, E. T. and D. A. Ross (1969), Hot Brines and Recent Heavy Metal Deposits in the Red Sea, Springer-Verlag.

Dickey, P. A. (1969), "Increasing Concentration of Subsurface brines with Depth," Chem. Geol., v. 4, p. 361-370.

Dutt, G. R. and T. W. McCreary (1970), "The Quality of Arizona's Domestic Agricultural and Industrial Waters," Rept. 256, Agric. Exp. Sta., Univ. of Ariz.

Gardner, L. R. (1974), "Organic vs. Inorganic Trace Metal Complexes," Geochim. Cosmochim. Acta, Vol. 38, p. 1297-1302.

Hanor, J. S. (1979), "The Sedimentary Genesis of Hydrothermal Fluids," in Barnes, ed., Geochemistry of Hydrothermal Ore Deposits, p. 137-172.

Hawkes, H. E. and J. S. Webb (1962), Geochemistry in Mineral Exploration, Harper-Row, NY.

Helgeson, H. C. (1964), Complexing and Hydrothermal Ore Deposition, Pergamon Press, NY.

Krauskopf, K. B. (1967), Introduction to Geochemistry, McGraw-Hill, p. 72.

Lebedev, L. M. and I. B. Nikitina (1968), "Chemical Properties and Ore Content of Hydrothermal Solutions at Cheleken," Dokl. Akad. Nauk; 555 R, Engl. Transl. Earth Sci. Sec. 183, p. 180-182.

Park, C. F. and R. A. MacDiarmid (1964), Ore Deposits, Freeman, San Franciso,CA.

Park, F. P. Jr. and R. A. MacDiarmid (1975), Ore Deposits, Freeman, San Franciso, CA.

Perrier, R. and J. Quiblier (1974), "Thickness Changes in Sedimentary Layers During Compaction History, Methods of Quantitative Evaulation", Amer. Assoc. Petrol. Geol. Bull. v. 58, p. 507-520.

Schmidt, G. W. (1973), "Interstitial Water Composition and Geochemistry of Deep Gulf Coast Shales and Sands," Am. Assoc. Petrol. Geol. Bull. v. 57, p. 321-337.

Skinner, B. (1970), "The Many Origins of Hydrothermal Mineral Deposits" in Barnes, ed., Geochemistry of Hydrothermal Ore Deposits, John Wiley, p. 1-21.

Smith, R. M. and A. E. Martell (1976), Complexes, Volumes 1-4, Plenum Press, NY.

Stanton, R. L. (1972), Ore Petrology, McGraw-Hill.

Weissberg, B. (1969), "Gold and Silver Ore Grade Precipitates from New Zealand Thermal Waters", Econ. Geol., Vol. 64, p. 95-108.

Weissberg, B. et al., (1979), "Ore Metals in Active Geothermal Systems", in Barnes ed., Geochemistry of Hydrothermal Ore Deposits, Wiley, p. 738-780.

White, D. E. (1965), "Saline Waters of Sedimentary Rocks," Am. Assoc. Petrol. Geol. Mem. 4, p. 342-366.

White, D. E. (1968), "Environments of Generation of Some Base Metals Ore Deposits," Econ. Geol., Vol. 63, p. 301-335.

White, D. E. (1974), "Diverse Origins of Hydrothermal Ore Fluids," Econ. Geol., Vol. 69, p. 954-973.

White, D. E. et al. (1963), "Chemical Composition of Subsurface Waters," U.S. Geol. Surv. Prof. Paper 440-F.

XI. APPENDICES

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A. Additional Discussion, Oklo

The rare-earths are similar in charge, ionic radius and electronegativity to U^{4+} and data, consistent with Eh-pH interpretation indicate complete retention. Pu, Np and some Am were also retained in host pitchblende while Bi, plus Pb, formed from Th and U decay, were locally redistributed but nevertheless retained. Eh-pH diagrams are not especially useful for alkali, alkaline earths or halide elements, although Ba (and thus Ra) as barite exhibits a wide stability field (Brookins, 1978).

Natural rare-earths have not been subject to any major remobilization at Oklo (Ruffenach, 1978).

Absence of detectable zonation in the isotopic compositions of the uraninite might be caused by a low solubility of uraninite in the Oklo body resulting in insignificant U transport. If O_2 and CO_2 are in equilibrium with solid assemblage magnetite, hematite and graphite, total uranium mobilities would be less than 10^{-9} in the pH range 5 to 6.8 (Duffy, 1978).

Only local migration or "even retention" of alkali and alkaline earth elements in the overall Oklo system is suggested. Migration of Sr and Rb (possibly Ba and Cs) has effected movement locally out of reactor zone (Brookins, 1980).

Assuming quantitative retention of U, then Ru and Te have been removed from rocks below the reaction zones and redeposited above roughly 10 meters away. The hot aqueous fluids moderating the reactors may have been responsible for transporting these elements (Gancarz et al., 1980).

Some observational evidence indicates migration of Tc. Eh-pH diagrams would suggest retention, however, thermochemical data are not as complete as desirable (Brookins, 1978).

Redistribution of Pb should be (and was) local because in the pH range at Oklo, PbS is stable in the sulfide field and $PbSO_4$ in the sulphate field. RuS_2 is stable in the pyrite field; RuO_2 in the hematite field; Ru^{4+} substitutes for Fe^{3+} and Ti^{4+} (Brookins, 1978).

Molybdenum and Cd exhibit no stable phase above the pyrite/hematite fence (text Fig. 5) in the pH range of 7 to 8.5. Mo_3O_8 is stable at pH less than 5.5 and $Cd(OH)_2$ only above pH = 9.5 to 10.0 (Brookins, 1978).

The wide stability field of $Y_2(CO_3)_3$, shows that Y^{3+} is only released at pH = 5.5 when the carbonate species dissolves. In the case of REE's and Y, a major factor is the high degree of ionic substitution of Y and REE for U^{4+} in host pitchblende (Brookins, 1978).

The heavy rare-earths (gadolinium and dysprosium) migrated further and to a greater extent that the light ones (neodymium and samarium). The proportion of fission products carried outside of the reactor is only a few percent but the contamination is still detectable several meters from the core (Naudet, 1978).

Zr is stable as $ZrSiO_4$, ZrO_2 or in host pitchblende (Zr^{4+} for U^{4+}) or possibly (U,Zr) SiO_4 (Brookins, 1978).

Nb is retained due to the large stability field of Nb_2O_5 and possible retention in host pitchblende or as oxide-hydroxide phases in gangue minerals (Brookins, 1978).

Rhodium is a native element and Sn is an oxide under Oklo conditions (Brookins, 1978).

Under high pH, Bi may be present as the native metal, as Bi_2O_3 Bi_2S_3, depending on Eh. In the Oklo Eh-pH range, Bi_2S_3 is of prime importance. Bi_2S_3 is more stable than pyrite under slightly oxidizing conditions. The ionic radii of Bi^{3+} (1.10Å) is quite different from Pb^{2+} so it can be argued that Bi will behave independently of lead. The

ionic radii of Bi^{3+} is such that, even under slightly oxidizing conditions, it may have been retained in the pitchblende structure to a greater extent than Pb^{2+}.

NpO_2 exhibits a wide stability range in terms of pH and the dioxide is stable to relatively high Eh values. Np^{4+} has a similar ionic radius to both U^{4+} and Pu^{4+}. Providing U^{4+} to U^{6+} oxidation does not cause extensive damage to the pitchblende crystal structure, Np should be retained in the host pitchblende (Brookins, 1978).

Retention of Am as observed at Oklo may be due to: (1) Am^{3+} substitution for U^{4+} due to similar ionic radii; (2) $Am(OH)_3$; (3) retention of Eu and Am as carbonates (Brookins, 1978).

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B. Additional Discussion, Uranium Deposition

1. Vein-Type Deposits

Vein-type uranium deposits include various geologic associations namely pegmatites, aplites, calcite-fluorite-apatite veins or masses, and quartz-fluorite veins. Elemental correlation with uranium vein-type deposits are: S, Cu, Mo, F, Zr, K, Ni, Bi, V, P, Nb, Ta, Cl, Co and rare-earths.

Most vein uranium deposits contain pitchblende associated with some quartz, calcite and/or sulfides (pyrite, marcasite) and hematite.

Fluid inclusion studies suggest pitchblende deposition at low average temperatures of about 190°C, low formation pressures of about 1 kilobar and low to moderate salinity, but high CO_2 concentration. Decrease in the $[CO_2]$ of fluids during the pitchblende stage, suggesting transport as uranyl carbonate complexes, is shown in some districts.

Alumina zeolite minerals, i.e., natrolite, scolecite, and laumontite in association with uranium are indicative or high temperature depositional conditions. Some fluid inclusion studies indicate temperatures up to 500°C.

Formation temperatures have been shown in the range of 200-350°C (Poty et al., 1974) for some vein-type pitchblende deposits but most vein-type deposits formed below 150°C (Rich et al., 1975).

Fluid inclusion studies indicate that the Beaverlodge-type, vein uranium deposits were formed under conditions of decreasing temperature from 410° $\pm$ 30°C to 80° $\pm$ 10°C accompanied by decreasing salinity.

Apparent precipitation mechanisms for the hydrothermal ores are reduction in temperature and pressure (a rapid decrease in confining pressure is sometimes indicated). Rich et al., (1976) favor formation of vein-type deposits by reduction mechanisms, as in the Colorado Plateau deposits. It seems unlikely that CO_2 evolution will move

hydrothermal solutions strongly in the direction of pitchblende precipitation. The main effect of the high CO_2 pressures in uraniferous hydrothermal solutions will probably turn out to be the stabilization of uranyl complexes via a proportionately higher bicarbonate concentration. The presence of hematite as a vein and wall rock mineral in most vein-type uranium deposits is consistent with uranium transport in the +6 valence state. The deposition of sulfides and arsenides with or shortly after uraninite is consistent with the reduction of U^{+6} to U^{+4} and the deposition of the very sparingly soluble UO_2 at low Eh. The isotopic composition of sulfur in sulfides and carbon in carbonates is consistent with the reduction deposition model.

Hematite-rich aquifers can raise the fugacity of oxygen in hydrothermal solutions until equilibrium with hematite has been reached. Calcite ($CaCO_3$) together with gypsum and anhydrite ($CaSO_4$) in red beds is not uncommon. It has been shown that at geologically reasonable CO_2 pressures, solutions saturated with respect to $CaSO_4$ and $CaCO_3$ can have O_2 - fugacity values well within the hematite stability field. This suggests that reducing solutions can react with hematite in red beds, resulting in an increase in O_2 - fugacity sufficient to convert initially reducing solutions into potential uranium ore fluids (Rich et al., 1975).

MnO_2 is a very potent oxidant because the Mn_3O_4--MnO_2 equilibrium has such a high O_2 - fugacity. In the presence of MnO_2 hydro- thermal solutions should become highly efficient carriers of U^{+6}.

Common geologic reducing agents: Fe^{+2}, S^{-2}, and C° (in biotite, hornblende, pyrite, graphite, fossil carbon or hydrocarbon) are capable or removing molecular oxygen efficiently from surface and subsurface solutions (Rich et al., 1975).

Distinction may be made between "hydrothermal" or "metamorphic" reactions. McMillan (1978) notes pertinent metamorphic reactions of probable importance in certain uranium deposits, e.g., metamorphic reactions which involve oxidation of ferrous iron and concomitant reduction of uranyl ions, e.g.:

$$3Ca(Mg,Fe)_5Si_8O_{22}(OH)_2 + 2Ca_2Al_3Si_3O_{12}(OH) +$$

(actinolite) (epidote)

$$2K(Mg,Fe)_3AlSi_3O_{10}(OH)_2 + 7H_2O + 8CO_2 + O_7 + 2Na^+ +$$

(biotite)

$$(UO_2)^{2+} + 2(CO_3)^{2-} =$$

$$3Al(Mg,Fe)_5AlSi_3O_{10}(OH)_8 + 2NaAlSi_3O_8 + 3Fe_2O_3 + 10CaCO_3$$

(chlorite) (albite) (nematite) (calcite)

$$+ 21SiO_2 + UO_2 + 2K^+ + 2(OH)^-$$

(quartz) (pitchblende)

2. Redox Reactions Involving Carbon Compounds

Uranium mineralization associated with V, Se and Mo occurs entirely within reduced rocks in the Grants, New Mexico District. In these deposits organic carbonaceous matter may be the main reductant. Organic carbon may be interpreted to serve as reductant for soluble U^{6+} species in solution. This in turn requires no dependence on sulfide-sulfate redox reactions to cause uranium mineralization. Reduction of U^{6+} with concomitant oxidation of C° is adequate to explain the uranium ore-calcite association. Some of the early formed organic deposits have been destroyed by uplift and penetration by oxidizating waters, although presently recognized redox fronts may have been

essentially stationary since the early Tertiary (5×10^7 years-scale) (Brookins, 1980). Uranium concentration in fossil logs has been noted to reach 16.5% (Breger, 1974).

Humic acid, carried by ground water would have precipitated as humates upon reaching the low Eh, higher pH water table and within areas of stagnation in interbedded sands and muds. These humates presumably precipitated uranium from alkaline ground water to form coffinite and uraninite. Brookins has shown thermodynamically that uranyl dicarbonate may coexist with pyrite under certain conditions but no uranyl species are thermodynamically stable in the presence of carbonaceous matter (Kimberley, 1978).

Evidence suggests that methane may have been the active reductant in ground waters carrying uranium in the Athabasca Formation, Saskatchewan (Langford, 1978).

Interaction of CH_4 with oxidized, uranium bearing ground water may have occurred at 200°C and 1000 bars. In the presence of the mineral buffer quartz-fayalite-magnetite, CH_4 and CO_2 predominate in a gas phase in equilibrium with carbon (graphite).

Several uranium deposits are located above or near producing oil fields for example, Lance Greek, Wyoming and Cement, Oklahoma. Reductants include H_2S, petroleum, humic acid and bitumins. The uranium was originally mobilized in salt solutions. Some uranium has precipitated as organo-uranium complexes in asphalt (Von Backstrom, IAEA, 1974).

3. Redox Reactions Involving Sulfate/Sulfide

Sulfide/sulfate equilibrium and hematitic oxidized rocks indicate precipitation of oxidation-mobilized uranium, to form roll-type ore at Grants, New Mexico. Deposition was apparently controlled by sulfide/sulfate equilibria (Brookins, 1980).

Also for Wyoming roll-type deposits the assumption is that most of the reduction of U^{6+} takes place at the iron redox front defined by the Eh-pH boundary between pyritiferous-bearing reduced rocks and hematitic bearing oxidized rocks. As solutions percolating through the rocks encounter this redox front, oxyions of uranium, vanadium, selenium, molybdenum and arsenic are reduced. Organic matter is very common in the reducing zones. Decreasing En is generally concomitant with decreasing pH, as pyrite is oxidized.

Oxidation of pyrite by increasingly oxidizing ground water flow causes sulphite to form. Sulphite disproportionation into SO_4^{2-} and HS^- developed the final reducing mechanism for uranium precipitation in the ore rolls (Dahl and Hagmaier, 1974).

Pyrite and uranyl carbonate complexes => uraninite and some combination of CO_2, iron oxides, SO_4^{2-}, and lower pH (Morton, 1974).

Uranium mineralization was accompanied by formation of Pb, Zn, Cu, Ni and Co sulfides or arsenides in Hungarian deposits indicating other redox reactions of sulfide/sulfate character (Barthel, 1974).

4. Clay Reactions

Brookins (1980) reviews the complex interactions and interrelationships between silicates (namely clays) iron, sulphur, soluble ions, i.e., U, Se, Mo, As and organic carbon under certain Eh-pH and temperature conditions. This generally relates to near surface environments of 25° to 60°C; 60°C is characteristic of the clay-rich, uranium-producing Morrison Formation's burial temperatures. "Chlorite-pyrite reactions may be very important for recognizing areas favorable for (existing) uranium mineralization". Uranyl dicarbonate + H_4SiO_4 + H_2O + Mg^{2+} + montmorillonite = coffinite + (HCO_3^-) + Mg-chlorite. H_4SiO_4 + Mg^{2+} are present due to organic acid attack on pre-existing minerals. Should HS^- (or H_2S) be present, it will conceivably

react with Fe^{2+} released from altering montmorillonite to form pyrite or marcasite. "Reactions involving organic carbonaceous matter, clay mineral formation, and pyrite (or marcasite) formation penecontemporaneous with the uranium mineralization can be advocated." "Uranium ore zones (Grants, New Mexico) in reduced rocks are typically enriched in some combination of chlorite, mixed layer illite-montmorillonite, illite and Mg-montmorillonite and are usually depleted in the Na-rich montmorillonite more typical of barren rocks". (Brookins, 1980).

5. Precipitating Ligands

Precipitating ligands, where CO_2 pressure in soil and ground water are relatively low because of the absence or paucity of organic activity in the soil are: (with resultant uranium mineral) vanadate (carnotite and tyuyamunite), phosphate (autunite group), silicate (uranophane), arsenate. NOTE: Low CO_2 pressure may be due to other factors other than paucity of organic material.

Calcrete (caliche-like) deposits in Australia, as mechanisms for uranium deposition, involve the transport of uranyl dicarbonate under high CO_2 pressure to the valley floor. Loss of CO_2 pressure results in precipitation of calcrete; oxidation of V^{+4} to V^{+5} (likely as the water moves through the calcrete) results in precipitation of carnotite (Langford, 1978). So the presence of V^{+5} in an oxidizing environment may enhance precipitation of uranium carbonate complexes yielding carnotite. Favorable conditions are initiated by the loss of CO_2 and precipitation of calcrete.

C. Additional Discussion of Uranium Mobility

Uranium transport generally occurs in oxidizing surface and ground waters as uranyl species, most often as UO_2^+ or uranyl fluoride phosphate or carbonate complexes which are formed by high CO_2 pressures (IAEA, 1974). UO_2^+ is apparently a weak complexer -- the existence of soluble U^{+5} greatly increases the mobility of U for a wide range of natural conditions, as indicated by evidence for stable UO_2^+ complexes in reduced waters at pH values below 7.

Solubility curves for autunite and carnotite versus pH show minimum [U] (about 10^{-7} M) at pH = 6. The adsorption curve for uranium by kaolinite also shows a *minimum* [U] at *pH* = 6 (10^{-8} moles). "Inferences made from Eh-pH diagrams indicate that uranium, vanadium, selenium, molybdenum, arsenic and antimony may have been transported as a group," (Brookins, 1980).

Uranium decay products generally do not form soluble compounds so isotopic disequilibrium is generally due to removal of uranium under oxidizing conditions or uranium addition under reducing conditions (decay products include: Pa-234, Th-230, Ra-226, Rn-222 and Pb-210). Uranium is the most mobile (non-gaseous) element of this series (Dyck, 1978).

Uraninite is 8 times more soluble in pure water at 100°C than 25°C, however, the decreasing stability of uranyl carbonate complexes above 25°C would induce precipitation of UO_2 upon elevated temperature.

The solubility of UO_2 in pure water at 750 bars increases to ∿ 75ppm at 275°C and then appears to decrease. The maximum is 260°C for UO_2/UO_3; with a rapid decrease below 200°C. Solubility of uranium in solutions in equilibrium with uraninite and schoepite at 25°C increased with increasing oxygen fugacity and/or with decreasing pH. (In pure water $P_{CO2} = 0$). pH has a profound effect but increases in U with decreasing pH becomes less important at temperatures above 100°C (Rich et al., 1975).

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D. Actinide Geochemistry

1. Uranium

Reducing materials such as organic carbon and iron sulfides are sufficient to prevent the oxidation of uranium (at elevated temperatures (200-300°C) in shale). Uraninite, U^{+4} is stable in the presence of hematite, which is the only redox oxide in many shales. Uraninite is found in association with hematite in geological environments. Thus hematite alone is not sufficient to oxidize uranium, although it would not reduce any uranium already present in the hexavalent state (Freeborn et al., 1980).

UO_2 in solutions containing very low oxygen levels (reducing conditions) may also form hydrate films due to local oxidants such as O_2 and H_2O_2 produced by strong radiation.

Uranium solubility is influenced by: (1) water temperature (directly proportional); (2) pH, (greater solubility at high and low pH's, minimum solubility in neutral pH range of about pH = 6 to 8.5); (3) gas content (increased O_2 and CO_2 content increases solubility); (4) electrochemical (mobility of uranium is greatly enhanced at high Eh values); (5) anionic composition of solution, (dicarbonate ions are most efficient at increasing U mobility since they cause formation of soluble and stable uranyl complexes under oxidizing conditions). Anions like the halogens, $SO_4^{=}$ and HPO_4^{-} have similar but profound less effect.

For example: $UO_2(CO_3)_2^{2-} \rightleftharpoons UO_2^{2+} + 2CO_3^{2-} \quad K = 10^{-14.6}$

Uranium may precipitate in the sexivalent (uranyl) state by a variety of anions, including bicarbonate if certain conditions prevail.

The dominant mechanism speculated for uranium precipitation in ore deposition is by reduction, notably by organic matter or Fe^{+2}, to form UO_2 or one of its hydrates (extremely insoluble hydroxides).

2. Thorium

Th resembles hafnium in terms of geochemical behavior. Th^{4+} is the dominant oxidation state. Thorium dioxide hydrate forms positively charged colloidal particles. The high charge on Th^{4+} makes it susceptible to complex formation.

Thorium-230 is somewhat more mobile than Th-232, just as U-234 is somewhat more mobile than U-238, because increased radiation damage of the crystal lattice due to a shorter half- ife produced microfractures and dislocations preferentially around Th-230 in mineral crystal structures (Dyck, 1978).

In sandstone, Th is mainly concentrated in the resistant heavy minerals. In the sedimentary cycle, Th behaves similarly to Sc. Because of the very high ionic potential of Th^{4+}, only very small amounts of Th can be kept in ionic solution in near neutral waters owing to the precipitation of highly insoluble Th(OH) (Brookins, 1980).

Thorium is extremely immobile in the surficial environment due to precipitation as hydroxide (Dyck, 1978).

Thorium undergoes extensive hydrolysis in aqueous solution at pH higher than 3; the species formed are complex and dependent on the conditions of pH, nature of anions, concentration, etc. Complex species, which may also be hydrolyzed and polymerized, can form (Cotton and Wilkinson, 1967).

3. Protactinium

Pa^{+5} is the dominant oxidation state. Aqueous chemistry of Pa^{+5} is somewhat like tantalum and niobium. Pa occurs in pitchblende with uranium.

In aqueous solution polymeric ionic species and colloidal particles form resulting in precipitation (generally insoluble).

4. Neptunium, plutonium, americium

The dioxides of Np, Pu and Am are insoluble at normal environmental pH. Chloride forms soluble compounds/complexes with Np, Pu and Am, but the fluorides are generally insoluble. It is expected that carbonates species can enhance mobility of Np, Pu, Am, i.e., analogous to uranium, however little appears to be known. Am does form a carbonate anion which is soluble under controlled and simple laboratory conditions.

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E. Effects of Eh on Actinide Geochemistry

The dioxides of U, Np, Pu and Am are insoluble at normal environmental pH. At pH = 7, U^{4+} concentration is negligible; at 25°C, U^{6+} concentration is 10^{-5} M to 10^{-8} M.

Mineralization in the Grants Belt, New Mexico, occurs entirely within reduced rocks. In these occurrences, organic matter may be the main reductant (Brookins, 1980).

It is generally thought that most reduction of U^{6+} and deposition of U^{4+} in the Wyoming roll deposits took place at the iron redox front defined by the Eh-pH boundary between pyritiferous reduced rocks and hematitic oxidized rocks.

The presence of organic matter and iron sulfides is sufficient to prevent the oxidation of uranium at elevated temperature (200-300°C) in shale. U^{4+} is stable in the presence of hematite. Thus hematite alone is not sufficient to oxidize uranium. Uranium already present in the hexavalent state is not reduced in the presence of hematite (Freeborn et al., 1980).

Uranyl dicarbonate may coexist with pyrite under certain conditions but no uranyl species are thermodynamically stable in the presence of carbonaceous matter (Kimberley, 1978).

Oxidation of pyrite by incursing ground water would cause sulphite to form. Sulphite disproportionates into SO_4^{-2} and HS^- which may reduce and precipitate the uranium ore in a roll deposit (Morton, 1974).

Brookins (1980) suggests that complex reactions involving carbonaceous matter, clays, iron, sulfur and soluble ions, like uranyl may create reducing conditions and result in the precipitation of uranium with chlorite.

Soviet researchers believe that reducing fluids can nevertheless carry hexavalent uranium in the form of uranyl carbonate complexes under high partial pressures of CO_2. A drop in CO_2 pressure is then the mechanism precipitating uranium in the oxide form (IAEA, 1974).

The aqueous chemistry of Pu (also Np and Am) is complicated by the fact that all four oxidation states can coexist in appreciable concentration in solution.

There is evidence for a stable UO_2^+ complex in reduced water at pH values below 7. UO_2^+ is apparently a weak complexer but the existence of soluble U^{+5} greatly increases the mobility potential of U for a wide range of natural conditions (Brookins, 1980).

F. Effects of pH on Actinide Geochemistry

Concentration of U^{4+} at pH of 7 is negligible at 25°C. Concentration of U^{4+} at pH of 4 is 10^{-6} M. Concentration of U^{6+} at pH of 7 is $10^{-5.1}$ M. Concentration of U^{6+} at pH of 4 is 10^{-2} M (or 4g/liter) (Krauskopf, 1967).

The important uranyl minerals are least soluble at pH's within the range 5 to 8.5. Above pH = 8.5 more soluble uranyl carbonate complexes form and below pH = 5 more soluble hydroxide of UO_2^{2+} and other cations form.

The solubility of carnotite and autunite show a minimum (about 10^{-7} moles) for pH = 6. Hydroxide complexes of U may reach significant concentration in reduced ground water above a pH = 8 (Langmuir, 1978).

Thorium undergoes extensive hydrolysis in aqueous solutions at a pH higher than 3, forming a very insoluble hydroxide (Cotton and Wilkinson, 1967; Dyck, 1978).

There is evidence for a stable UO_2^+ complex in reduced water at pH values below 7.

Tyuyamunite is several times more soluble than carnotite but also has a minimum solubility near 1 ppb U at about pH = 7 (Langmuir, 1978).

At pH values of 0 to 4 uranium sulfate and uranium fluoride complexes are important soluble species (Langmuir, 1978; Brookins, 1980).

At common ground water concentrations of sulfate and 100 ppm, $UO_2SO_4^\circ$ may be a significant species up to pH = 7. Silica forms a relatively weak complex $(UO_2SiO(OH)_3^+$ which is most important at pH = 6 (Langmuir, 1978).

Within the pH range (6.6 to 8.3) of ground waters in the Wind River Formation, Wy., both uranyl phosphate and carbonate complexes can predominate.

Rich et al. (1975) have found that $UO_2F_6^{4-}$ is stable up to a pH = 6.7 at 25°C and UO_3 forms a soluble fluoride complex, possibily UF_2^{2+} which is stable up to pH = 4.

Transport of uranium by $(UO_2(HPO_4)_2)^{2-}$ for total dissolved contents of phosphorous equal to 0.1 ppm (10^{-6} M) is likely near pH = 7. However, the most suitable conditions for the precipitation of autunite is at atmospheric CO_2 pressure and pH near 7 (Langmuir, 1978).

G. Effects of Mineralogy on Actinide Geochemistry

Reducing materials such as organic carbon and iron sulfides are sufficient to prevent the oxidation of uranium at elevated temperatures (200-300°C) in shale. Uraninite is stable in the presence of hematite, which is the only significant oxidizing mineral in many shales. Uraninite is commonly associated with hematite in the geologic environment. Thus hematite alone is not sufficient to oxidize uranium (Freeborn et al., 1980).

Most vein uranium deposits contain pitchblende associated with at least some quartz, calcite and/or sulfides and hematite. Uranium (UO_2) in metasomatic and regional metamorphic terrains is associated with calc-silicate and calcite-fluorite-apatite assemblages.

Brookins (1980) observes that uranium ore zones at the Grants, New Mexico deposits from reduced rocks are typically enriched in some combination of chlorite, mixed-layer illite-montmorillonite, illite, or Mg-montmorillonite and usually depleted in the Na-rich montmorillonite more typical of barren zones. He proposes that reactions involving organic matter, clay mineral formation and pyrite formation are penecontemporaneous with uranium mineralization.

Uranium is concentrated in petrified logs up to 16.5% (Breger, 1974).

Mineralogical effects are treated further in this report under the discussions of sorption.

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H. Effects of Anions on Actinide Geochemistry

1. Carbonate

For Eh values above -0.05v, increases in CO_2 pressure in ground water to 10^{-2} atm increases the solubility of UO_2 by more than 1000 times (due to increased activity of carbonate).

It is not possible to equivocally state whether uranium dicarbonate or $(UO_2(HPO_4)_2)^{2-}$ is the dominant species for transport of uranium (4+) in the pH range of 7-8 (Langmuir, 1978).

Carriers for U(4+) (stable at 150°C) include: $(UO_2(CO_3)_2(H_2O)_2)^{2-}$, $(UO_2(CO_3)_3)^{4-}$, $Na_2(UO_2(CO_3)_2)$, $Na_4(UO_2(CO_3)_3)$.

At a common ground water CO_2 pressure of 10^{-2} atm, and 25°C, the uranyl carbonate complexes are the major species in pure water down to pH = 5, and down to pH = 5.8 at CO_2 pressure = $10^{-3.5}$ atm.

With increasing temperature, the carbonate complexes become less important, therefore at 100°C and CO_2 at 10^{-2} atm, the uranyl carbonate complexes are minor at all pH's (Langmuir, 1978). (Note: There is some debate as to the stability and influence of carbonate complexes at elevated temperatures.)

Carbonate, sulfate and fluoride complexes inhibit sorption of uranyl ion in the pH range of 5 to 8.5 on clays, phosphorites and iron and titanium oxyhydroxides (Langmuir, 1978).

Thermodynamically, uranyl dicarbonate may coexist with pyrite under certain conditions (Kimberly, 1978).

Fluid inclusion studies of vein-type uranium deposits universally exhibit high CO_2 content in the fluids. There is debate as to the interpretation of this observation. Some investigations propose that a loss of CO_2 by boiling

or effervescence is the mechanism for the precipitation of uranium complexed by carbonate. Others suggest that high CO_2 pressure in uraniferous hydrothermal solutions enhances the solubility and, therefore the mobility of uranium out that precipitation of ore is due to reduction. Still others question the stability of the uranium carbonate complexes at elevated temperatures (Kimberly, 1978; Rich et al., 1978; Pocy et al., 1974; Langford, 1978; Langmuir, 1978; IAEA, 1974).

The solubility of oxidized uranium (4+) is greatly increased by the formation of carbonate complexes: $UO_2(CO_3)_2^{=} \rightleftharpoons UO_2^{++} + 2CO_2^{=}$ $K = 10^{-14.6}$, $UO_2(CO_3)_3^{4-} \rightleftharpoons UO_2(CO_3)_2^{=} + CO_3^{=}$ $K = 10^{-3.8}$. At 0.01M total carbonate, the uranium concentration in solution would be ten times as much as estimated for a carbonate-free solution. The effect of the carbonate complex would increase rapidly as the amount of $CO_3^{=}$ is increased, either by dissolving more carbonate or by raising the pH (Krauskopf, 1967).

Carnotite (and other uranyl minerals) is most stable (least soluble) at low CO_2 pressure such as in ground water in semi-arid areas. Ground water in equilibrium with carnotite could conceivably hold less than 1 ppo of uranium at pH = 5.5 to 7.5 (Langmuir, 1978).

The Soviets have noted that reducing fluids can nevertheless carry hexavalent uranium as uranyl carbonate ions. They suggest that a drop in CO_2 pressure is then enough to precipitate uranium in the oxide form (IAEA, 1974).

The role of carbonate complexes for other actinides is expected to be analogous but perhaps to a lesser mobilizing degree than for uranium. Little mention of other actinide carbonate complexing was noted in the literature

reviewed. Am does form a carbonate anion which is soluble, given controlled and simple laboratory conditions.

In the actinide series the energies of the outer orbitals are about comparable over a range of atomic numbers, especially for uranium through americium, and since the orbitals overlay spatially, bonding can involve any or all of them. Actinides, therefore have a tendency to form complexes and bond covalently.

The presence of $NaHCO_3$ increases the uranium concentration in solutions equilibrated with UO_2 and UO_3 througnout the hydrothermal range (Rich et al., 1975).

Silva et al. (1979) state that the solubility of Am and Cm carbonate is very low (10^{-41}).

2. Phosphate

It is not possible to unequivocally state whether uranium dicarbonate or $(UO_2(HPO_4)_2)^{2-}$ is the dominant species for transport of U in the pH range 7-8 (Langmuir, 1978).

Transport of uranium by $(UO_2(HPO_4)_2)^{2-}$ for total dissolved contents of phosphorus equal to 0.1 ppm (10^{-6}M) is likely near pH = 7; at lower concentration of total dissolved phosphorus (0.01-0.001 ppm) uranium dicarbonate will be more important (Langmuir, 1978).

Over the pH range of most natural waters, practically all the phosphorus is present as $H_2PO_4^-$ and HPO_4^{2-} on their metal complexes regardless of the oxidation potential. Phosphorus concentration in ground water rarely exceeds 1 ppm.

For typical ground water concentrations of 0.1 ppm phosphorus, the $(UO_2(HPO_4)_2)^{2-}$ will predominate over the hydroxyl complexes in pure water from pH = 4 to above 10 (Langmuir, 1978).

A 100-fold increase in uraninite solubility results at pH = 6 when a typical ground water phosphate level of 0.1 ppm is introduced and the Eh exceeds 0.05 v.

The most suitable conditions for precipitation of autunite is at atmospheric CO_2 pressure and pH values near 7. In the absence of vanadium the least soluble and most oxidized uranyl minerals are the autunites. Phosphate concentration must exceed $[VO_4]$ by roughly 500 times before potassium autunite will precipitate instead of carnotite (Langmuir, 1978).

3. Halogens

A major mechanism proposed for uranium, thorium and rare earth transport in the hydrothermal environment is halide complexing. The abundance of salts in uraniferous carbonaceous clay and fluid inclusions is cited as evidence for the role of brines in uranium mobility at elevated temperatures (El Shazy et al., 1974; IAEA, 1974; Kimberly, 1978).

Langmuir (1978) says "brines are excellent scavengers for uranium."

Uranous fluorides are important at typical fluoride concentrations in reducing ground waters below pH = 4. They enhance solubility (Langmuir, 1978). In pegmatites, volatile fluorides which are easily hydrolized, include: UF_4, UF_6, UO_2F_2 and $U[SiF_6]_2$.

Rich et al. (1975) find that $UO_2F_6^{-4}$ is stable up to a pH = 6.7 at 25°C and that UO_3 forms a soluble fluoride complex, possibly UF_2^{2+}, which is stable up to a pH = 4. The same authors suggest that in the pH range of most hydrothermal solutions, fluoride complexes are unstable and therefore, not a particularly important transport mechanism.

In the system U-O-H_2O-HCl the concentration of uranium in a solution saturated with respect to $UO_3 \cdot H_2O$ or $UO_3 \cdot 2H_2O$ (about 10 ppm in a neutral solution) rises rapidly with decreasing pH and rises very slowly

with the addition of NaOH (Rich et al., 1978). For hydrothermal solutions, Rich et al. (1975) suggest that the effects of NaCl is probably small in the pH range where neutral complexes are dominant. NaCl would increase the solubility of UO_2 and UO_3 hydrates in the alkaline range due to the effect of increasing ionic strength on the activity coefficients of the carbonate complexes and in acid solutions where $UO_2(OH)^+$ and UO_2^{2+} are dominant species.

Halogen complexes inhibit sorption and may favor desorption under acid conditions (Langmuir, 1978).

4. Sulfate/Sulfide

Sulfate complexes also inhibit sorption and may favor desorption under acid conditions (Langmuir, 1978).

Mineralization, after remobilization of uranium, to form roll-type ore at Grants, New Mexico was apparently controlled by sulfide/sulfate equilibria (Brookins, 1980).

In the Wyoming roll deposits the reduction of U^{6+} is thought to take place at the iron redox front defined by the Eh-pH boundary between pyritiferous reduced rocks and hematite oxidized rocks. The following references discuss sulfur as a reductant: Dahl and Hagmaier, 1974; Morton, 1974; Barthel, 1974; von Backstrom in IAEA, 1974.

At pH values of 0 to 3 uranium sulfate complexes are important soluble species. At common ground water concentrations of sulfate, 100 ppm, $UO_2SO_4^\circ$ may be significant up to pH = 7 (Brookins, 1980; Langmuir, 1978).

The formation of sulfate complexes of Np^{4+} and NpO^{2+} is strong enough to cause dissociation of NpO_2^+ (Cotton and Wilkinson, 1967).

5. Silica

Silica forms a relatively weak complex $UO_2SiO(OH)_3^+$ which is most important at pH = 6. In general, the uranyl silicate complex is unimportant (Langmuir, 1978).

Very high silica and low total phosphate concentrations are required to precipitate uranophane instead of autunite (Langmuir, 1978).

6. Hydroxide

Under conditions of low total dissolved carbonate and phosphate, hydroxide complexes may be important (Langmuir, 1978, Brookins, 1980).

Thorium is extremely immobile in the surficial environments due to precipitation of insoluble hydroxide (Dyck, 1978). Significant hydroxide complexes are UO_2OH^+, $(UO_2)_2(OH_2^{2+})$, $(UO_2)_3(OH)_5^+$ (Langmuir, 1978).

The uranyl ion forms a soluble hydroxide at pH = 4 with a concentration of 5 g/l of uranium in water. In acidic solutions at 25°C, U^{6+} is presently largely as $UO_2(OH)^+$ and UO_2^{+2} (Rich et al., 1975).

Only at pH's above 8 would hydroxide complexes reach significant concentration in reduced ground water (Langmuir, 1978).

The maximum concentration of tetravalent elements in solution is limited by the precipitation of hydroxides, which might be changed into dioxides (Allard, 1979). The tendency for hydrolysis is: Am > Pu > Np > U and $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$ (Cotton and Wilkinson, 1967).

I. Sorption Effects on Uranium

Decreasing sorption factors on various media.

8×10^4 to 10^6 for Ti $(OH)_4$ (amorphous).

1.1×10^6 to 2.7×10^6, amorphous Fe^{3+} oxyhydroxide.

10^4 to 10^6, peat.

4×10^3, fine-grained goethite.

15, phosphorites.

6, montmorillonite.

2, kaolinite.

Data are for a pH range of 5 to 8.5 in the absence of strong uranyl-sulfate, -fluoride and-carbonate complexes which inhibit adsorption. These data suggest tnat clays are relatively unimportant as concentrators of uranium but may be an important preconcentrating step leading to the formation of both uranyl and uranous minerals. The zeolites--heulandite, stillbite, clinoptilolite, and mordenite--are indicative of low temperature depositional conditions. Uranium has been adsorbed strongly on zeolites within Miocene sandstone and conglomerate in the Tono mine, Japan (Katayama et al., 1974).

"Sorption is generally a more important control on concentrations of trace metals, such as U at low temperatures, than is mineral precipitation or solution. Uranyl sorption in fact is probably an essential preconcentration step in the formation of many reduced and oxidated uranium ores." (Langmuir, 1978).

Sorption media include:

1. Organic matter
2. Ferric, manganese, and titanium oxyhydroxides, and;
3. Clays

"The pH range of minimum solubility of the uranyl minerals is also the pH range of maximal sorption on most important natural colloidal materials." "Once uranyl has been adsorbed, it may be reduced to U^{4+} in uraninite or coffinite by mobile reductants such as H_2S, CH_4 or by the sorbent itself if the latter is organic matter. If reduction does not follow adsorption, uranyl can be desorbed by increasing alkalinity at constant pH or raising the pH." (Langmuir, 1978).

J. Sorption Effects on Selected Elements - Actinides and Lanthanides

The sorption of U, Pu, Am (in 0.68N NaCl solution) onto abyssal red clay was relatively insensitive to pH at values between 6 to 8 but was greatly diminisned at pH 2.7 (Erickson, 1980). Am, Pu and Cm are adsorbed by argillite and hornfels. However, differences of up to five orders of magnitude for sorption of lanthanides and actinides is attributed to solution composition (Lynch and Dosch, 1980). "Information from uranium deposits suggests that chlorite will form during the mineralization process from pre-existing montmorillonite or illite or mixed-layered illite-montmorillonite accompanied by fixation of V, Mo, Se, As, REE, Th, and U," (Brookins, 1980). Sorption of U, Np, and Pu is highly dependent on oxidation state. From reduced ground water in granite, the following oxidation states would predominate (and enhance sorption): Tc^{4+}, U^{4+}, Np^{4+}, Pu^{3+} and Pu^{4+} (Allard et al., 1979). Sorption of Np on fresh rock surface in air is strongly correlated to the Fe^{2+} containing minerals (pyrite and biotite). "This is possibly the most important sorption mechanism for nuclear waste isolation since the higher valence actinides tend to be the most mobile. This could mean that NpO_2^+, UO_2^{2+}, TcO_4^- and PuO_2^{2+} could be reduced to less mobile NpO_2, UO_2, TcO_2 and PuO_2 states, respectively, by Fe^{2+} (Beall, 1980). In experiments with U, Np, Pu, Am and Cm in solutions equilibrated with rock material, precipitation or colloid formation were the major reactions for Pu, Am and Cm and perhaps a minor reaction for U. In general, the chemical behavior of Am and Cm in solutions are quite similar to the trivalent lanthanides. The solubility of Am and Cm carbonates may be very low (10^{-41}). If so, carbonate ion, as well as, hydroxide ion may cause precipitation of Am and Cm. Pu probably precipitates as the hydroxide (or

hydrated oxide). Results of contact experiments with basalt, shale and quartz monzonite showed the following (Silva et al., 1979):

1. rapid sorption during first two weeks;
2. U was moderately adsorbed onto basalt and less onto shale and quartz monzonite; and
3. Np was strongly adsorbed onto shale and only slightly onto basalt and quartz monzonite.

Intense radiation (10^{10} rad) damage to the clay structure does not apparently result in the release of soluble species (Haire and Beall, 1979). The same mechanisms which dominate sorption of the lanthanides also dominate sorption of the actinides (Erickson, 1980). Attapulgite clay has a significantly higher affinity for actinides than do kaolinite and montmorillonite. Kaolinite and montmorillonite have very rapid exchange reactions with actinides and rare earths that take less than 15 minutes to come to equilibrium. Attapulgite clay sorption in contrast takes as long as nine days to come to equilibrium (Beall, 1979). Certain actinides and lanthanides show "tendencies" to sorb by factors of 20-1000x onto halite with clay from simulant brine solutions at pH = 6.5 to 7.8 (Dosch, 1979). Increased solution concentration of Na and Ca decreased sorption of rare earths on kaolinite and montmorillonite (Beall, 1979).

Cerium and Eu sorption tended to increase with increasing ionic strength of solution. This may be due to enhanced tendency to form radio colloids as the sulfate ion concentration increases. Sorption of Ce and Eu were appreciably higher for granite and argillite under de-oxygenated conditions, while the values for tuff were unchanged (Erdal et al., 1980).

Alkaline Earths (Ca, Sr, Ba, Ra). Some retention of Sr by clay is noted by Spitsyn and Balukova (1979). Sr fixation is much greater in certain mixtures of zeolites than can be expected from the individual minerals. These mixtures involve the poor Sr fixers as well as clinoptilolite with mordenite or phillipsite which are the best for Sr sorption (Komarneni, 1980). Sr showed little tendency to sorb on any sample from brine simulant solution at pH = 6.5 to 7.9 (Dosch, 1979). Increased sorption of Sr and Ba is noted on glass as temperatures are increased from 22 to 70°F (Erdal et al., 1979). Humic acid promotes Sr retention. Na^{+}, Mg^{2+} and Ca^{2+} compete with Sr^{2+}, thereby decreasing Sr adsorption (Barney, 1979).

Ra is adsorbed more than Sr on granite and bentonite, perhaps because the $RaSO_4$ solubility product is lower than for $SrSO_4$ (Allard, 1979).

Cs and Rb. Vermiculite (superior to montmorillonite but not as good as zeolites) has a high capacity for Cs sorption and fixation, depending on Cs concentration in the solution and the charge density of the (clay) layers. Amorphous iron and Mg oxides have good sorption capacity for divalent and trivalent ions. Yet, crystalline oxides and hydroxides showed no sorption for Cs and Rb (Komarneni et al., 1980). Sorption of Cs^{+} on bentonite and crushed granite was about equivalent at 25°F in aerated systems. Temperature increases from 25°F and 65°F reduced Cs sorption on bentonite, which would correspond to an ion exchange process. Cs sorption seems independent of particle size (Allard, 1979). In terms of radiotoxicity, 10 to 30 Ci/kg of rock is retained by sorption of Cs on clay (Spitsyn and Balukova, 1979). At low Cs concentrations, sorption is very high, but at high concentration, results show a proportional decrease in the relative amount of Cs adsorbed

(McKinley, 1980). Cs sorption on "smectite" clay is not affected by pH, and increased temperature increases retention somewhat. Sorption of Sr, Cs and Ba decreased in water with higher dissolved salt. Sorption for Cs, Sr and Ba were generally less in de-oxygenated water than for atmospheric water for tuff and argillite; little change was noted for granite (Erdal et al., 1980).

Cs showed little tendency to sorb on any samples from brine simulant solution at pH = 7.5 to 8.2 (Dosch, 1979). Both K^+ and Na^+ compete with Cs^+ for sorption sites and their presence, therefore, decreases Cs sorption. Humic acid promotes sorption (Barney, 1979).

Iodine. I^- showed little tendency to adsorb on any samples in contact with brine simulant solution at pH = 6.5 to 7.9 nor in ground water at pH = 7.5 to 8.2 (Dosch, 1979). Sorption of I^- on crushed granite and bentonite is low (Allard, 1979). Some sorption of I^- is apparent on galena and copper metal under suitable Eh conditions. The PbO system sorbs I^- from very dilute solutions (Bird and Lopata, 1980). Fe and Al-hydroxides, clay minerals and Cu-, Pb-, Ag- compounds show retention factors of 100 to 1000 for I^- in reduced ground water. Increased salt (4M NaCl) in water has a mixed effect on retention (Allard et al., 1980). The diffusivity of both Am and Pu through illitic sea floor sediment is less than the relatively uneffected iodide ion by a factor of one million. "It must be caused by either a chemical transformation of the simple cationic species in solution, such as hydrolysis and attendant formation of an insoluble hydroxide, or by a very strong interaction with the constituent minerals of the sediments." (Fried, 1980).

Technetium. Sorption of Tc, under reduced oxygen and CO_2 conditions were consistently higher by more than a factor of 40 than under atmospheric

conditions. Tests were made on granite, tuff and argillite (Erdal et al., 1980). Tc snowed little tendency to adsorb on any samples in contact with brine simulant solution at pH = 6.5 to 7.9 or pH = 7.5 to 8.2 (Dosch, 1979). Sorption of TcO_4^- is low on granite and bentonite (in an aerated system) (Allard et al., 1979). Organic complexes of Tc^{4+} with EDTA and Tc^{5+} with DPTA reduced total Tc sorption in soil (pH ~ 8.2), thereby increasing mobility through soil. Sorption of Tc on abyssal red clay (oxidizing conditions) was essentially zero at pH = 8.3 and 2.6 (Erickson, 1980). TcO_4^- was removed from solution by argillite (Eleana Shale) under oxidizing conditions, yet hornfels had no affinity for TcO_4^-. Sorption in shale is attributed to the organic content (Lynch and Dosch, 1980). The effects of Eh are shown by increased Tc sorption (by factors of 100-300 in deaerated water. Reduction of Tc resulted in a dramatic increase in sorption on the solid phase (Allard et al., 1979).

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K. Eh, pH and Mineralogical Effects on Actinide Sorption

Eh: sorption is generally maximized under reducing conditions. There is good evidence to suggest that uranyl sorption is an important "preconcentrating" step leading to formation of both uranyl and uranous minerals (Langmuir, 1978). Sorption and reduction go hand-in-hand.

Sorption of Np on a fresh rock surface is strongly correlated with the Fe^{2+} containing minerals (pyrite and biotite). Oxidation/reduction reactions between Fe^{2+}/Fe^{3+} and actinides may be a major mechanism for sorption (Beall, 1980).

pH: Sorption is maximized between a pH = 6 to 8.5 for both reduced and oxidized species. Sorption is greatly decreased at pH values below 5 but only slightly decreased at pH's above 8. Changes in pH may result in desorption.

The desorption of U, Am, Pu on red clay is maximum at pH = 6 to 8 but was greatly reduced at pH = 2.7 (Erickson, 1980).

Adsorption of Am and Np is pH dependent with maximum adsorption at pH = 6.5 to 8; lower at pH = 4 and slight decrease above pH = 8. Sorption of Np and Am on biotite and kaolinite decreased from a 4M NaCl solution at pH below 5 (Beall et al., 1980).

Pu, Am, Np show "tendencies" to sorb by factors of 20-1000 times "onto halite with clay" from simulant brine solutions at pH = 6.5 to 7.8 (Dosch, 1979).

Concentration factor of U in humic acid relative to U in solution at a pH $\sim$ 5 is 10,000 to 1 (Dyck, 1978).

If reduction of the uranyl species does not follow adsorption, uranyl can be desorbed by increasing the pH (Langmuir, 1978).

pH dependence for Am and NP sorption with low sorption at pH = 4, maximum at pH = 6.5 to 8 and then levelling out or slight decreases at higher pH.

Order of increasing sorption capacity among the common igneous minerals is: quartz < feldspar with augite and olivine < kaolinite and biotite. In the case of biotite and kaolinite a decrease in sorption occurs in a 4M NaCl solution of pH below 5 (Beall et al., 1980).

Mineralogy/Sorption: Some data suggest that clays are relatively unimportant as concentrators of uranium during ore deposition but may be important preconcentrators, leading to formation of uranyl and uranous minerals. Experimental data by Langmuir (1978) shows the following heirarchy for enrichment by adsorption:

Amorphous $Ti(OH)_4$ > amorphous Fe^{3+} oxyhydroxide > peat > fine-grained goethite > phosphorites > montmorillonite > kaolinite.

Uranium is adsorbed on zeolites within a Miocene sandstone and conglomerate at the Tono Mine, Japan (Katayama et al., 1974).

Am and U^{4+} were sorbed on the glass phase and on clay in tuffaceous alluvium and on zeolites in tuff (Erdal et al., 1979).

Attapulgite clay has a significantly higher affinity for actinides than kaolinite and montmorillonite. Nevertheless, kaolinite and montmorillonite have very rapid exchange reactions with actinides and rare earths that take less than 15 minutes to come to equilibrium. Attapulgite clay in contrast takes as long as nine days to reach equilibrium (Beall, 1979).

L. Conditions for Hydrothermal Ore Formation

1. pH

pH varies as a function of temperature pressure and dissolved solids. The pH of pure water will decrease on simple heating from 7.0 at 25°C to 5.8 at 150°C, due to changes in the dissocation constants with temperature (Hanor, 1979). Note, however that the neutral pH point changes from the normal 7.0 to 5.7 at 230°C.

Relationships between bulk brine composition and pH can be generalized:

High SO_4 - HCO_3 waters	pH ≈ 8.0 ± 0.5 pH
High Na-Cl waters	pH ≈ 7.1 ± 0.5 pH
High Na-Ca-Cl waters	pH ≈ 6.7 ± 0.5 pH

This compositional sequence roughly corresponds to increasing depth or a progressive release of H^+ with depth (with diagenesis) (Hanor, 1979).

Field evidence suggests that ore-bearing fluids are nearly neutral and that strong acids and bases are exceptional. However, deep (hot) pH effects are confusing due to above mentioned changes in pH and neutral point. The chemical character of fluids near the surface is not a reliable indication of chemical properties at greater depths because of contamination by surface or reactions with wall rocks and changes in temperature and pressure. For example, sulfur present may be oxidized near the surface, thus forming sulfuric acid and lowering the pH (Park and McDiarmid, 1975; Weissberg, 1969).

Salton Sea Brines have an overall pH = 5.5 at 25°C. Red Sea Brines have pH = 6.5 (Stanton, 1972). Fumarolic (volcanic) gases and their associated hot water solutions seem to have an extremely low pH.

The concentration of both sulfide and carbonate ions is pH dependent. Oxidation of any insoluble sulfide leads to the formation of acidic solutions. The degree of acidity depends on the nature of the metal ion,

particularly the extent of its hydrolysis, or on the insolubility of its hydroxide. Iron sulfides produce the most acidic of all such solutions in the weathering environment because of the precipitation of Fe_2O_3.

2. Eh

New Zealand geothermal waters have an Eh = -0.50 to -0.60 V, based on the observed iron sulfide mineralogy and a deep water pH = 6.1.

Eh values are commonly calculated from pH, temperature and relative concentrations of members of a redox pair, like sulfide/sulfate or CH_4/CO_2, because direct measurements of deep waters or of fluid inclusions are extremely difficult. In general ground water above the water table is oxidizing whereas that below the water table has a low Eh. Fumarolic gases and associated heated waters have an Eh sufficiently low for deposition of sulfides.

3. Pressure

Most ore deposits form at depths of less than 20 km; this limit is set by the facts that temperatures at 20 km are of the order of 600°C and fractures cannot long remain open because of the plastic behavior of rocks under weight of overlying material. So 2,000 atm is the upper limit for deposition in veins but most ores are formed at pressures of the order of a few hundred atmospheres.

Most veins and replacement deposits form over a temperature range from 50 to 550°C. Ores generally do not form at a single temperature but over a temperature interval. Deep artesian and subartesian waters can reach very high temperatures (T > 300°C) as a result of normal thermal gradient (temperature increase expected with depth). The Red Sea brines are probably 100 to 150°C. Salton Sea brines are hotter. Fluid inclusion studies indicate

a temperature range of 50 to 550°C for ore deposits, e.g., limestone lead-zinc deposits <100°C to 200°C; deposits associated with subsurface igneous activity 150° to 400°C; pegmatite ores > 500°C.

4. Temperature

Temperature influences pH. The pH of pure water will decrease (become acidic) simply from heating, e.g., pH = 7.0 at 25°C; pH = 5.8 at 150°C, (Hanor, 1979).

At temperatures of 200-300°C, the assemblage potassium-feldspar-kaolinite should react to form muscovite-quartz. So, a given mineral assemblage may become unstable under the elevated temperature conditions in a radioactive waste disposal site (Hanor, 1979, p. 158). This is an example of one of scores of possible hydrothermal alteration reactions controlled in part by temperature.

"Evidence to date suggests that high temperatures (>80°C) and high salinities (>200°/$_{oo}$) or high dissolved sulfide concentrations favor the partitioning of metals into sedimentary fluids. Such conditions permit the formation of stable aqueous-metal complexes (Cl^- and HS^-) and appear to enhance the diagenetic destruction of the minerals or organic compounds which contain the metals. Active Salton Sea brines have temperatures of 40-60°C although the original inflow temperatures are above 100°C." (Weissberg, 1979). Stanton (1972) suggests maximum temperatures of inflow in the range 130 to 220°C where the active Red Sea Brines measure 34-56°C. "Most volcanic area thermal waters are dilute salt solutions at 200-300°C with very low concentrations of base metals, silver and gold," (Park and McDiarmid, 1975). High temperatures tend to promote disorder in a mineral structure and under these conditions other elements are readily absorbed and retained, (Park and McDiarmid, 1975). This statement identifies a potential avenue of research in

adsorption effects at elevated temperatures as a function of rock type and other variables.

5. Supercritical Solutions

Above the critical temperature of water, gases behave more like liquids; gases may therefore carry considerable amounts of metallic elements; high density steam has solvent properties simila to those of liquid water.

Park and McDiarmid (1975) note that in the Valley of Ten Thousand Smokes different mineral assemblages formed around the vents as the temperature dropped; the early phases of mineral deposition being characterized by magnetite; the later phase by galena and sphalerite.

Temperature affects:

1. the solubility (products) of sulfides and oxides;

2. the formation and stability of complex ions; and

3. the hydrolysis constants of ligands, such as Cl.

"In most cases, but not all, a decline in temperature will cause a reduction in solubility." Therefore, cooling and associated decrease in solubility and complex stability is a likely mechanism for ore deposition and has been so considered in classic ore study. Cooling may be due to:

1. mixing with cold near-surface water,

2. adiabatic decompression and/or

3. heat loss to wall rock (Skinner, 1979).

The average geothermal gradient in older sedimentary basins is 15-40°C/km. As fluids are expelled from deep sediments, sediment porosities in thermally insulating zones decrease. Geothermal gradients should then also decrease as the basin cools off (Hanor, 1979). So geothermal gradient of a sedimentary basin is a function of age. Older basins may be better candidates for waste disposal sites because they are cooler.

6. Composition of Solutions

The composition of ore solutions can be inferred from investigations of fluid inclusions (remnants of depositing solutions contained within ore-associated minerals), wall rock interactions (alteration), and presently active heated waters. In all cases, solution compositions are probably altered by near-surface interactions and so do not necessarily represent exactly the original mobilizing solution. Nevertheless, these solutions may still contain metal ions or associate closely with ore deposits such to provide valuable information on the general geochemical characteristics of original solutions.

Ground water (i.e., supergene enrichment), sea water (i.e., manganese modules), and igneous solutions (i.e., fumaroles) can transport significant quantities of metals. The Salton Sea and Red Sea brines are significant carriers of metal ions. The salinities of both are slightly more than 25% and contain a great abundance and variety of metal ions. Fumarolic gases contain large amounts of HCl, H_2SO_4 and HF.

Fluid inclusions studies indicate the solutions to be aqueous with CO_2, hydrocarbons and sulfur gases present in varying amounts. The solutions are almost always highly saline (0 to 40% by weight) and contain as major components Na^+, K^+, Ca^{4+}, Mg^{++}, Cl^-, and $SO_4^=$ plus minor components Li^+, Al^{+3}, BO_3^{-3}, PO_4^{-3}, SiO_3^{-2}, HCO_3^- and CO_3^{-2}. Elements commonly added to the wall rock adjacent to ore deposits include: Si, C, Mg, Na, K, Ca and Fe. Fumarolic waters commonly contain insufficient sulfur for the precipitation of all available sulfophile metals as sulfides.

7. Complexing in Ore Solutions

Chloride and bisulfide complexes are the two most plausible agents for increasing the solubility of metals. Helgeson (1965) has studied chloride complexes, and Barnes and Czamanske (1967) discuss sulfide complexes. Chloride complexes are probably significant mobilizers when there is (1) abundant chloride ion, (2) the pH is a little on the acidic side of neutral, and (3) temperatures are moderately elevated. Bisulfide complexes appear to form when there is abundant (1) sulfide (HS^-), (2) the solution is alkaline, and (3) has a low Eh. Stable bisulfide complexes, especially for copper and zinc, lead to substantial increases in sulfide solubility. Most of the summarizing material above is drawn from Krauskopf (1967) and Stanton (1972).

8. Geothermal Systems

NOTE: Suggested focus for further work - A comparison of the geochemical characteristics of metal-bearing vs. nonmetal-bearing geothermal and brine systems may elucidate the conditions favorable for mobility of ore-bearing solutions, especially for systems in the near-surface environment. Much data should be available on geothermal springs and prospects as a result of the recent DOE efforts to investigate potential sites for geothermal power.

Metal deposits have been observed forming from metal-bearing brines in the Red Sea, Salton Sea, New Zealand, Caspian Sea and other places. A detailed literature summary of the known characteristics of these systems and a comparison with non-metal bearing geothermal springs might reveal general conditions which favor metal mobility in crustal materials.

Metal concentrations in the New Zealand geothermal waters are very low. Their great enrichment in precipitates indicates that high metal concentrations in water are not required to form ore-grade materials. Critical factors are deposition rate and time (Weissberg et al., 1979).

In the Valley of Ten Thousand Smokes different assemblages formed around the vents as the temperature dropped, the early phase being characterized by magnetite, the later phase by galena and sphalerite. Incrustations contained: Fe, Pb, Zn, Mo, Cu, As, Sb, Sn, Ag, Ni, Co, Bi, S, O, F, Cl, Se, Te (Park and McDiarmid, 1975).

Several tons per year of base and precious metals in sludges are removed for disposal from the Salton Sea geothermal test plant site (personal communications, Union Oil Co.).

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M. Complexes

1. General

Formation of complex ions, charged particles consisting of several atoms, increases solubility of some metals by many orders of magnitude (Park and McDiarmid, 1975). "Complex ions, formed between metals and ligands in solution, serve as shields, or carriers for the metals consequently inhibiting precipitation of sulfide minerals" (Skinner, 1979).

"The relative abundance of anions in shale interstitial waters is: $HCO_3 > SO_4 > Cl$ or $SO_4 > HCO_3 > Cl$, in contrast to waters in sands, which are dominated by chloride" (Hanor, 1979).

"The ore-carrying capacity of hydrothermal solutions is determined more by the activity of these ligands than by abundance of the metals in host rock which varies over a comparatively narrow range" (Barnes, 1979). Note: Barnes is suggesting that the most significant factor in the mobility of ore solutions is the stability and characteristics of certain complexes, mainly sulfur and chloride complexes.

In terms of ore element mobility, chloride complexes are very significant above 200-250°F for mobilizing metals. Above 300°F organic complexes are dissociated and so are not significant. Organic complexes can be very important at low temperature however (Gardner, 1974). Sulfide complexes are relatively more important below 250°F than above.

Chloride Complexes. The relative stability of Cl^- complexes is: $Cu > Zn > Pb > Ag > Hg$.

1. Pb is mobile up to 600 ppm in solution @ 100-374°F.
2. The formation of lead chloride complexes ($PbCl^+$ and $PbCl_4^=$) in the solution is responsible for this solubility (Helgeson, 1964).

Red Sea and Salton Sea brines are very high in chloride. White (1968) notes that metals are presumed to be soluble due to chloride complexing, since not enough sulfur is present to account for the mobility of the metals.

Skinner (1979) says "from present evidence the role of chloride complexes seems more important than other complexes."

Water in regions of recent volcanic activity is commonly characterized by an abundance of NaCl grading into acidic sulfate-chloride waters (Park and McDiarmid, 1967).

NaCl and KCl are abundant in many deep artesian brines. Chloride complexes have an even greater stability (capacity for remaining in solution as ions) than NaCl, HCl or KCl in the temperature-pressure range of 100-374°F and 1-2000 atm. These complexes are virtually dissociated @ 25°F (Stanton, 1972).

Sulfur Complexes. Sulfur complexes are thought to be one of two kinds (the other being chloride) of complex ions that seem to be most important in hydrothermal solutions. In order for the sulfide complexes to form, the concentration of reduced S in solution must greatly exceed that of the metal species (Skinner, 1979). But Salton Sea brines have metals much more abundant than sulfur.

Sulfur is a significant complexer in alkaline pH's. Examples are:

Zinc - 2700 mg/l Zn dissolves in a aqueous solution @ 25°F, P_{H_2S} = 7 atm and pH = 8.2. If the solution becomes even weakly acidic, the complexing and hence solubility, decreases markedly.

Copper - up to 1300 mg/l of Cu dissolves in aqueous solutions @ 204°F, 24 atm pressure and 4.1 M NaHS (mechanism thought to be bisulfide complexes) (Stanton, 1972).

2. Metal Complexes

Copper Complexing. Near-surface waters carry copper as several complexes including $Cu(OH)_2$; $Cu(CO_3)_2^{2-}$; $CuSO_4$ and $CuCl^+$. The recent discovery of copper porphyrins in deep-sea sediments suggests that organic complexes should be added to the list. Transport by chloride complexes can account for the "low-temperature" formation of red bed (sedimentary) deposits. In anionic (reducing) marine waters, the bisulfide complexes have been calculated to be the dominant inorganic aqueous Cu species present.

Chloride complexing with copper is most significant for weakly acidic solutions @ 250-350°F and total sulfur from 0.1 to 1.0 M. Bisulfide complexes become relatively more important below 250°F. Solubilities of Cu may easily reach into the 1000's of ppm Cu in solution above 250°F - presumably due to chloride complexes.

Zinc: The dominant complex of Zn in hydrothermal solutions is $ZnCl_2$.

Lead: Various complexes with HS^- dominate over temperature which range from 25°F to 300°F in neutral to acidic solutions. At total S < 1.0 M, $Pb(HS)_3^-$ can exist at temperatures below 50°F and in neutral to slightly alkaline solutions.

Mercury: 1ppm Hg dissolves as bisulfide complexes in equilibrium with metacinnabar at 25°F in near-neutral solutions of total S = 0.1 M. The solubility increases approximately two times by 100°F and 4 to 7 times by 200°F.

Iron: Increasing association of Fe with Cl^- is characteristic of Fe^{+2} at higher temperatures. Solubility increases steeply above 250°F so that tens to

thousands of ppm of Fe are stable in Cl^- complexes at 350°F in the pH range in which muscovite is stable. At lower temperatures, ferrous chloride complexes become ineffective for moving iron in the quantities observed. Bisulfide complexes provide an alternative. Experimental studies show that bisulfide complexes are sufficiently stable at temperatures up to at least 300°F. Organic and/or ammine complexes may be significant at low temperatures.

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