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GEOLOGICAL SURVEY

A Literature Review of Interaction of Oxidized

Uranium Species and Uranium Complexes with

Soluble Organic Matter

by

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Species and Uranium Complexes with Soluble Organic Matter

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Abstract

Organic material is commonly found associated with uranium ores
in sandstone-type deposits. This review of the literature summarizes
the classes and separations of naturally occurring organic material
but the emphasis is on soluble organic species. The main class of
materials of interest is humic substances which are high-molecular-
weight complex molecules that are soluble in alkaline solution.
These humic substances are able to solubilize (make soluble) minerals
and also to complex [by ion exchange and (or) chelation] many
cations. The natural process of soil formation results in both
mineral decomposition and element complexing by organic species.

Uranium in solution, such as ground water, can form many species
with other elements or complexes present depending on Eh and pH. In
natural systems (oxidizing Eh, pH 5-9) the uranium is usually present
as a complex with hydroxide or carbonate. Thermodynamic data for
these species are presented.

Interacting metals and organic materials have been observed in
nature and studied in the laboratory by many workers in diverse
scientific disciplines. The results are not easily compared.
Measurements of the degree of complexation are reported as
equilibrium stability constant determinations. This type of research
has been done for Mn, Fe, Cu, Zn, Pb, Ni, Co, Mg, Ca, Al, and to a
limited degree for U. The use of Conditional Stability Constants has
given quantitative results in some cases. The methods utilized in
experiments and calculations are reviewed.

I. Introduction

The association of certain metals with organic materials has been recorded for several decades. In 1938 Laatsch observed tannic substances in the translocation of iron and aluminum (Kononova, 1961). The association of uranium with organic material has been demonstrated in the Uravan Mineral Belt and the Grants, N. Mex. prefault ore, where entire logs in paleostream channels have been replaced with coffinite. Although the uranium-organic association has been documented from a variety of environments (peat enrichment, lignites of North Dakota, black shale, sandstone deposits and Precambrian conglomerates), the mechanisms of concentration/fixation/reduction of the uranium are poorly understood. The association of uranium with organic matter does not seem to be a chance spatial relationship. The coexistence may occur from the time of mobilization of the uranium from its original "source" rock (Schalscha and others, 1967; Baker, 1973) until it is concentrated in a reducing organic-rich environment.

A generalized model which incorporates the various factors encountered in the natural environment would be an aid in understanding the genesis of a uranium deposit. This model would include optimum pH values for the formation of soluble and insoluble uranium-organic complexes as well as organic-material-to-metal ratios determined in these complexes.

To be able to formulate this generalized model, it is necessary to understand the components present. This paper summarizes work

done by various researchers. It includes information on organic material, humic and fulvic fractions and their interaction with various metals and background information on aqueous uranium geochemistry is presented to give a more complete view of the fundamental components.

II. Organic Material

Organic material—Occurrence

The naturally occurring organic material of soils is formed from decomposing plant and animal remains and from biological and chemical reactions of the breakdown products. Organic material is commonly subdivided into humic and nonhumic substances.

Nonhumic substances are well characterized, specific chemical compounds such as hydrocarbons, carbohydrates, proteins, and other simple organic species. These compounds are readily degraded by microbial activity and have a rather short life span in the soil.

The humic fraction is the major organic constituent of most soils According to Schnitzer and Khan (1972) these are "amorphous, brown or black, hydrophilic, acidic, polydisperse substances of molecular weights ranging from several hundreds to tens of thousands. Important characteristics exhibited by all humic fractions are resistance to microbial degradation. The ability to form stable water-soluble and water-insoluble salts and complexes with metal ions and hydrous oxides, and to interact with clay minerals and organic compounds."

Observed humic accumulations (Swanson and Palacas, 1965) in near-surface soil layers from marsh deposits, bay and bayou beach

sands, mouths of streams that are golden-brown colored, ground-water seeps, and organic sediments in bodies of brackish and saline waters are common. The humics are leached from decaying land plant materials. Surface or subsurface water then transports the soluble and (or) colloidal material to various environments where flocculation or precipitation of the humic substances occurs.

Organic material--Nomenclature

There are many schemes of nomenclature for naturally occurring organic material. This variety of schemes is unfortunate. Each group of geologists, biologists, soil scientists and chemists has a different approach to organic material and a different view of its importance. To the geologist, organic material is merely ground cover. To the biologist, organic material is life forms and ecological systems. To the chemist, organic material is the chemical and molecular components. The entire frame of reference of the soil scientist lies within the realm of organics. It is not surprising that anyone reading the literature today might be confused with the various terms. The following scheme of nomenclature will be adopted in this study (refer to figure 1):

Organic material (OM): Material derived from decomposing
        biological material, either disseminated (such as, through a
        sandstone) or acumulated (as in peat bogs)

Soluble organic material (SOM): That portion of OM soluble in
        NaOH solution, that is, alkali extract, humic material,
        humus

Kerogen: That portion of OM insoluble in NaOH solution, that is,
        organic residue, humins

ORGANIC MATERIAL

NaOH EXTRACTION

SOLID RESIDUE
KEROGEN
HUMIN

NaOH SOLUBLE
SOLUBLE ORGANIC MATERIAL
HUMUS

ADJUST TO pH 1
WITH HCL

PRECIPITATE
HUMIC ACID SOLID

SOLUBLE
FULVIC ACID
SOLUTION

ETHANOL
EXTRACTION

ACETONE
EXTRACTION
POLYSACCHARIDES

EXTRACTED
HYMATOMELANIC
ACID

SOLID
HUMIC ACID
RESIDUE

ADJUST TO
pH 4.8

PRECIPITATE
β - HUMUS

SOLUTION
FULVIC
ACID
RESIDUE

Figure 1. Nomenclature and relationship of organic fractions used in this study.

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Humic acid solid (HAS): That portion of SOM precipitated by acidification to pH 2, commonly referred to as humic acid (HA)

Hymatomelanic acid: That portion of HAS solubilized by ethanol

Humic acid residue (HAR): That portion of HAS remaining after hymatomelanic acid is solubilized

Fulvic acid solution (FAS): The portion of SOM that remains in solution after acidification to pH 2, commonly referred to as fulvic acid (FA)

β-humus: Precipitate that forms in FAS when pH adjusted to 4.8

Polysaccharides: Precipitates that form when acetone is added to FAS

Fulvic acid residue (FAR): Solution remaining after precipitation of β-humus and polysaccharides.

One of the principal sources of organic material (OM) occurs as the result of soil formation. The accumulation of bacteriological decomposition of plant debris transforms various components of the biological environment into potentially important components of the geologic realm.

Molecular form of FAS-HAS

As shown in table 1 (Schnitzer and Khan, 1972) the elemental composition of HA and FA is predominantly carbon, oxygen, hydrogen, and nitrogen, with some sulfur. The FA's contain less carbon and more oxygen than the HA's and humins.

The similarity of the visible absorption of SOM, regardless of the SOM origin, indicates a similar, but highly heterogeneous complex structure. FA solutions are more intensly colored than equally concentrated HA solutions (Schnitzer and Khan, 1972).

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Even though the ultraviolet (UV) spectra of SOM are featureless, the characteristic shape of the spectra of SOM from various origins again indicates similar form of the organic complex. Chromophores (linkages or groups that confer color) found in SOM are C=C and C=O; auxochromes (groups that enhance chromophore color) found are predominantly COH and CNH_2.

Generalized structures for FA and HA, shown on figures 2 and 3, are popular models. These generalized structures are only schematic and several further points need to be made regarding them. The SOM is actually three dimensional, so that it has a variety of shapes and sizes which include voids as well as protrusions. This complex geometry allows the trapping of water and metal ions. In addition, various humic molecules can interact with each other. Measurements of the apparent molecular weight and size vary considerably depending on such things as pH and such variations are caused by this coagulation (Wershaw and Pinckney, 1971, Gjessing, 1965).

The generalized structures of figures 2 and 3 do not show the heteroatoms nitrogen and sulfur which are present in humic material. These atoms may be particularly important in the binding of metals due to their ability to form chelates. Finally figure 2 does not show the aliphatic (long chain-saturated carbon) component of as many as 14 carbon atoms (Ogner, 1973). Ogner found six CH_2 units to be the most common chain length, which would connect aromatic nuclei units together. This result is quite different from the mainly hydrogen bonded structure shown on figure 2. Figure 4 is our rendition of a HA which includes the above mentioned features.

Table 1.--Elementary composition, in percent, of humic
substances from soils and other sources

(Data from Schnitzer and Khan, 1972)

C	H	N	S	O
		Soil HA's		
56.4	5.5	4.1	1.1	32.9
53.8	5.8	3.2	.4	36.8
56.7	5.2	2.3	.4	35.4
56.4	5.8	1.6	.6	35.6
60.4	3.7	1.9	.4	33.6
60.2	4.3	3.6	a	31.9
		Lake sediment HA		
53.7	5.8	5.4	a	35.1
		Coal HA		
64.8	4.1	1.2	1.2	28.7
		Biologically synthesized HA's		
54.5	5.1	8.5	a	31.9
		Soil FA's		
42.5	5.9	2.8	1.7	47.1
47.6	4.1	.9	.1	47.3
50.9	3.3	.7	.3	44.8
		Water FA		
46.2	5.9	2.6	a	45.3
		Soil humins		
55.4	5.5	4.6	0.7	33.8
56.3	6.0	5.1	.8	31.8

[a]Not determined.
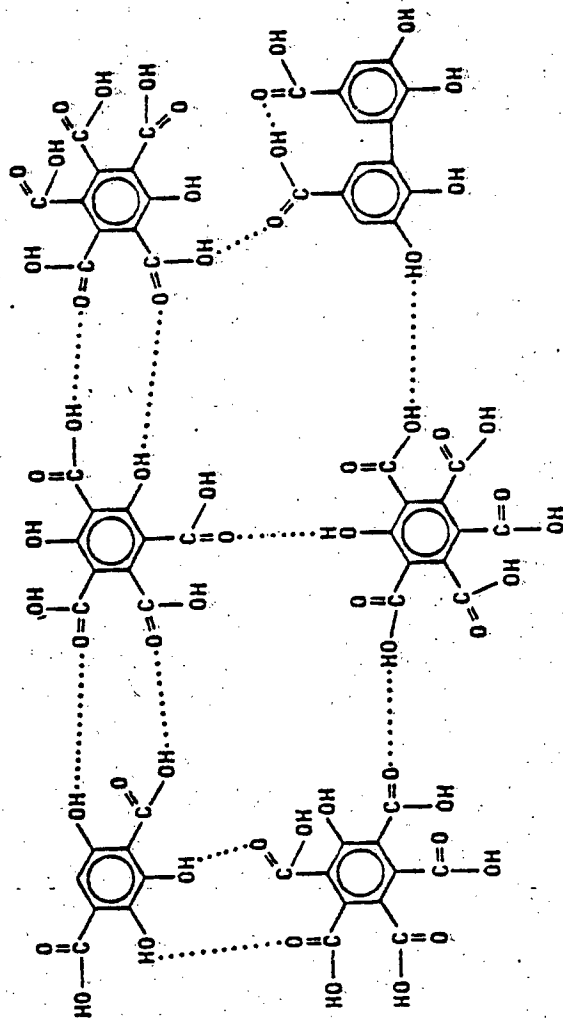
STRUCTURE OF FA AS PROPOSED BY SCHNITZER

Figure   2. Structure of FA as proposed by Schnitzer.
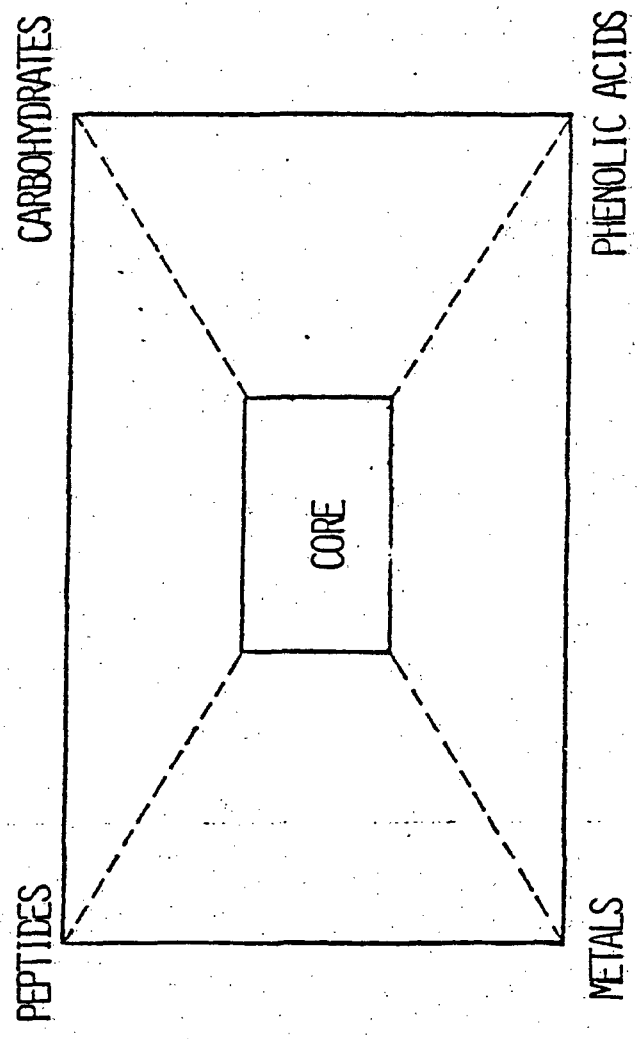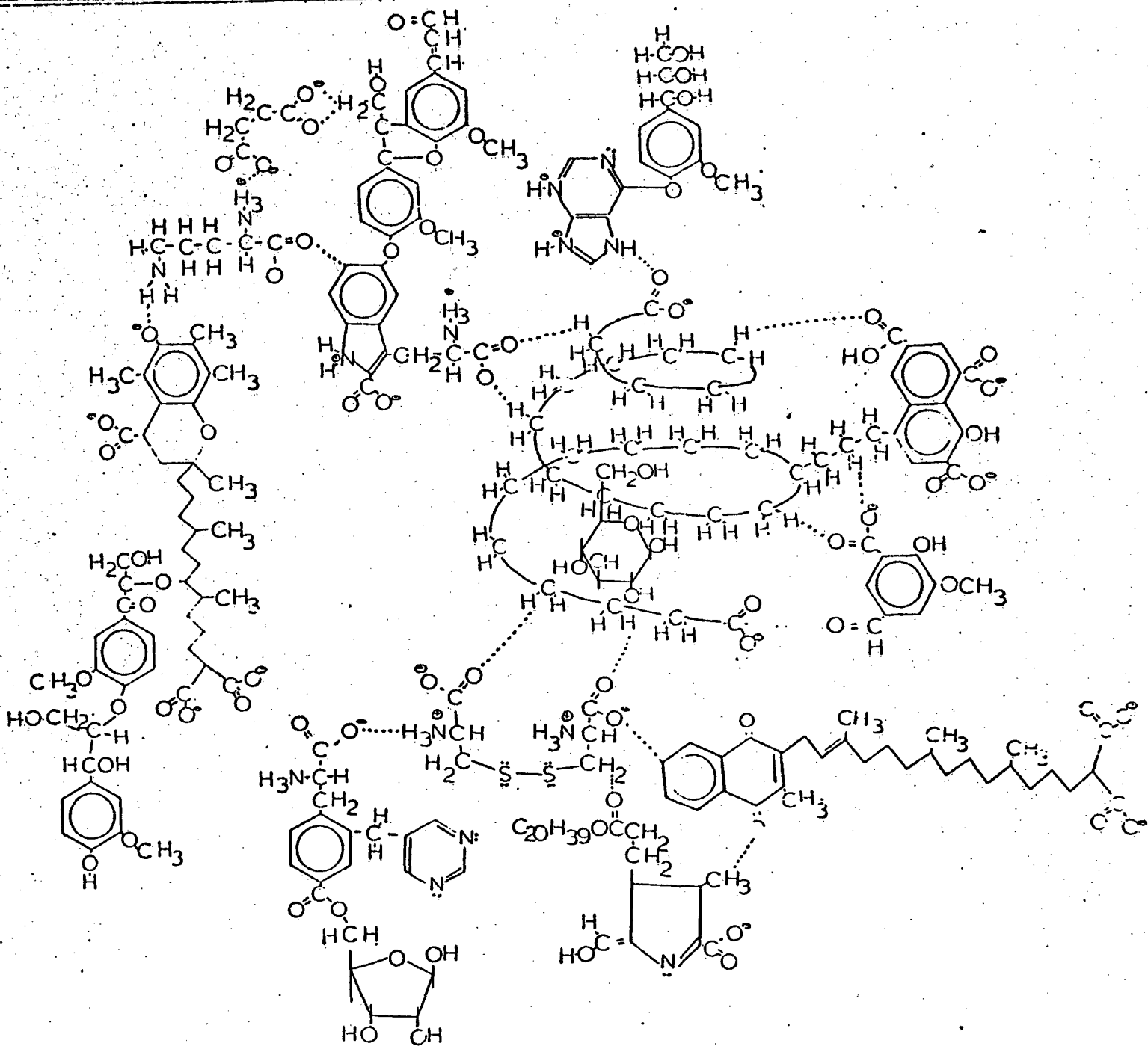
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Figure   3. Diagrammatic representation of HA by Haworth.

Figure 4. A "generalized" humic acid molecule, with a more complete structure than previously rendered[11]

$C_{249} O_{82} H_{320} N_{13} S_2$

MW = 5000

From ultimate and functional group analyses, between 68 and 91 percent of the oxygen in humus and humins is accounted for in carboxyl, phenolic hydroxide, alcholoic hydroxide, carbonyl, and methoxyl groups (table 2). Greater than 90 percent of this oxygen is thus accounted for as functional groups in soil FA (Schnitzer and Khan, 1972). The oxygen in humic substances is predominantly in the carboxyl groups (-COOH) and to a lesser extent in phenolic hydroxyl (ph-OH) and carbonyl (RC=O).

Soluble organic material (SOM) is composed of between 1 and 6 percent nitrogen (Schnitzer and Khan, 1972). After acid hydrolysis of SOM, 20-55 percent of SOM nitrogen is amino acid nitrogen (table 3) and 1-10 percent is amino sugar nitrogen. Small quantities of purine and pyrimidine bases (guanine, adenine, cytosine, thymine and uracil have been identified in the acid hydrolyzates). Amino sugar nitrogen is the form of glucosamine and galactosamine.

A large percentage of SOM nitrogen is not released by acid hydrolysis. This nitrogen is either chemically bonded to or firmly adsorbed on the humic materials (Schnitzer and Khan, 1972).

Solubilizing properties of organic material

Baker (1973) extracted soluble organic materials from a podzol soil. He then allowed a 0.1 percent weight/volume aqueous solution of the soluble organic material to react with mineral grains for 24 hours. Many of the metal humates formed had low solubility in water, but their solubility increased in the presence of the SOM solution. Schalscha and others (1967) used salicylic acid, which occurs naturally in small amounts, to dissolve iron from minerals. The

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Table 2.—Distribution of oxygen in humic substances

(Data from Schnitzer and Khan, 1972)

Carboxyl	Phenolic OH	Alcholoic OH	Carbonyl	Methoxyl	Percent oxygen
			Soil HA's		
43.8	10.2	13.6	21.4	1.5	90.5
26.1	24.9	15.2	7.8	a	74.0
13.6	38.0	12.7	4.1	a	68.4
42.2	24.7	.9	23.4	a	91.2
44.8	17.1	a	14.8	1.4	78.1
			Coal HA		
41.1	16.2	a	a	9.4	74.4
			Soil FA's		
57.5	19.3	11.5	5.8	a	94.1
65.0	11.8	12.9	11.1	1.7	102.5
61.0	9.1	16.4	3.7	1.0	91.2
			Soil humins (kerogen)		
36.0	9.9	a	22.7	1.9	70.5
26.1	12.1	a	28.7	1.5	68.4

[a]Not determined.

Table 3.—Nitrogen distribution in HA, FA, and a humin fraction

(Data from Khan and Sowden, 1971)

Type of material	N content in percent	N distribution after acid hydrolysis, in percent of total N in material			
		Amino acid N	Amino sugar N	Ammonia N	N accounted for
HA	4.07	28.3	1.3	19.8	49.4
FA	3.87	26.4	3.6	15.1	45.1
Humin	4.60	36.1	1.3	22.1	59.8

resultant complex had a distinctly red color and a large stability constant. Soluble decomposition products of aerobically incubated lucerne soil were utilized by Bloomfield and Kelso (1973) in their study of mobilization of metals. They found that vanadium and uranium were extensively solubilized by larger molecular weight constituents of lucerne decomposition products.

The relative stability of metal-organic complexes has an effect on the competition of metals for the various complexing sites on the organic structure. Because the functional complexing groups of the SOM are so prevalent, it is conceivable that SOM is a better complexer than reducer of metal ions (Baker, 1973). Bloomfield and Kelso (1973), however, suggest that fixation of Mo, V, and U by organic matter follows the reduction of these metals.

Oxygenated water was necessary for solubilizing uranium in laboratory experiments of Szalay and Samsoni (1969). Anions present in water also affected dissolution of uranium. Distilled water that was free of air, oxygen, and carbon dioxide dissolved only small amounts of uranium. Aerated water and water containing 2 percent $NaHCO_3$ were much better solvents. An increase in carbonate content above this value did not seem to increase the solvent activity of the solution.

Metal-organic relationships

There are two major sources for the organic material that occurs in ground water. The first major source is the regions of soil formation from which soluble organic material is leached and transported via the ground-water system. Schnitzer (1969) found that

SOM occurs in all soils and accounts for 25 to 75 percent of the total organic matter. Other accumulating and decomposing plant debris would also serve as surface or near-surface sources of organic material. The second major source is from accumulated plant debris that has been buried and is decomposing at depth. This second surce of organic material can be found disseminated throughout a sedimentary body. The disseminated pieces can be as small as grain coatings or as large as entire trees.

The complexing of Cu^{2+}, Fe^{3+}, and Al^{3+} by SOM was characterized in part by Schnitzer and Skinner (1963A). From various analytical procedures a molecular weight of SOM was determined (Schnitzer and Desjardins, 1962). Ferric iron, Al^{3+}, and Cu^{2+} formed water soluble 1:1 molar complexes with soluble organic material (SOM) at pH 3, and 2:1 water-soluble complexes at pH 5. The formation of water-insoluble 6:1 complex was also suggested.

Khan (1969) found that addition of low concentrations of metallic compounds to an organic solution would produce metal-organic complexes. Metal hydroxide formation was not observed. As the concentration of metallic cations was increased a portion was complexed and the excess was precipitated at the usual pH of hydroxide precipitation of the metal cation. However, iron and aluminum cations did not precipitate as humates when added at the low concentrations. As titration of the metal ions with dilute base proceeded, the precipitate of aluminum- and iron-humate complexes was hydrolyzed and began to dissolve as the pH rose above 7. In a strongly alkaline medium the complexes were completely hydrolyzed,

resulting in formation of aluminate anion and ferric hydroxide.

As much as 60 weight percent of the FAS studied by Schnitzer (1969) was composed of functional groups such as carboxyls, hydroxyls, and carbonyls which are attached to a predominantly aromatic skeleton. Schnitzer and Skinner (1963A and B) selectively blocked various functional groups. From their results they postulated that there are two types of reactions that account for practically all of the metal retention by the organic material (OM). The major reaction (I) involves simultaneously both the acidic carboxyl and phenolic hydroxyl groups. In the minor reaction (II) only the connected carboxyls participate.
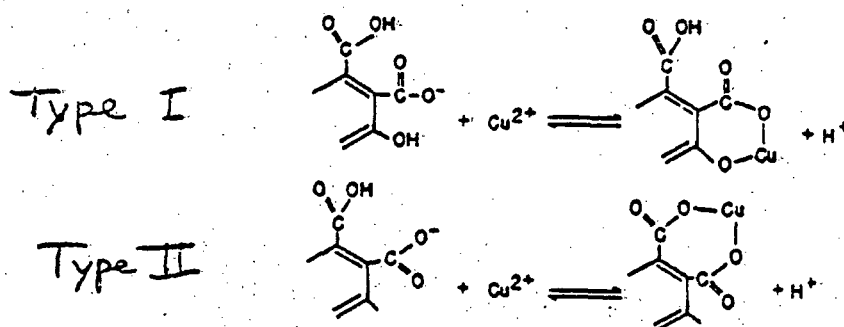
The Type I carboxyl is ortho to a phenolic-OH group; the Type II carboxyl is adjacent to another carboxyl group rendering it less acidic than Type I.

Fulvic acid solution in soils can dissolve and transport substantial amounts (as much as 84 mg Fe/g FAS and 40 mg Al/g FAS) of metal under acidic conditions (Baker, 1973).

III. Uranium in Solution

Uranium-system

In the $U-O_2-H_2O$ system there are two stable solids, uraninite (UO_2) and schoepite ($UO_2(OH)_2H_2O$) (fig. 5). Soluble or mobile forms occur in acid and distinctly alkaline solutions. The main stable ions are UO_2^{2+}, $UO_2(OH)^+$, and HUO_4^- (fig. 6). Pure or nearly pure water such as found in the $U-O_2-H_2O$ system is therefore a poor transporting medium for uranium under earth surface conditions.

Ground water is seldom, if ever, pure. Water in contact with various minerals and air dissolves and carries carbonate and bicarbonate ions relatively readily. Total dissolved CO_2 content ($CO_{2(aq)}+CO_3^=+HCO_3^-+H_2CO_3$) in natural waters commonly is 100-300 ppm. The addition of CO_2 to the $U-O_2-H_2O$ system decreases the solid field and introduces new soluble carbonate species.

The solid phases in the $U-O_2-H_2O-CO_2$ system are uraninite and schoepite plus rutherfordine (UO_2CO_3) (fig. 7).
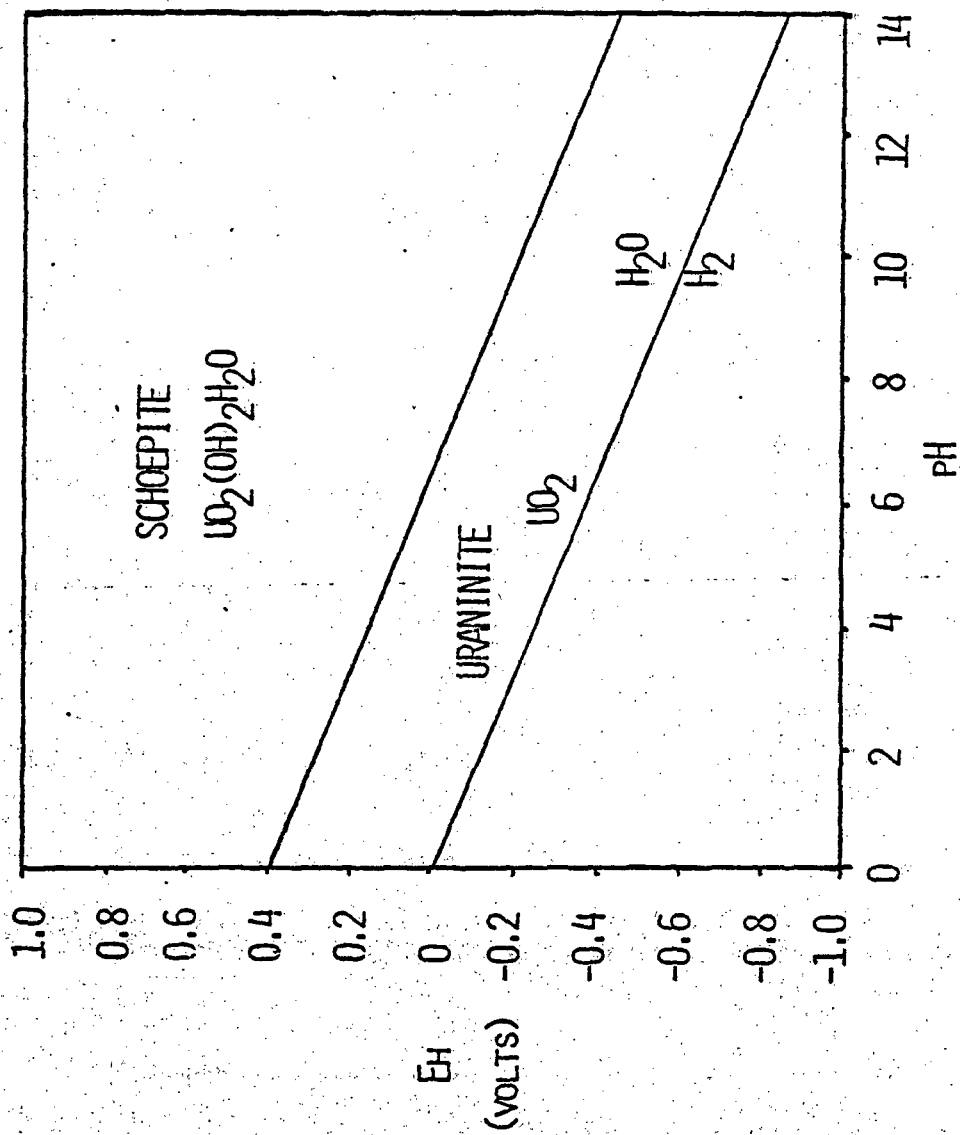
Figure 5. Aqueous equilibrium diagram of $U-O_2-H_2O$ system at $25^{\circ}C$ and 1 atm.
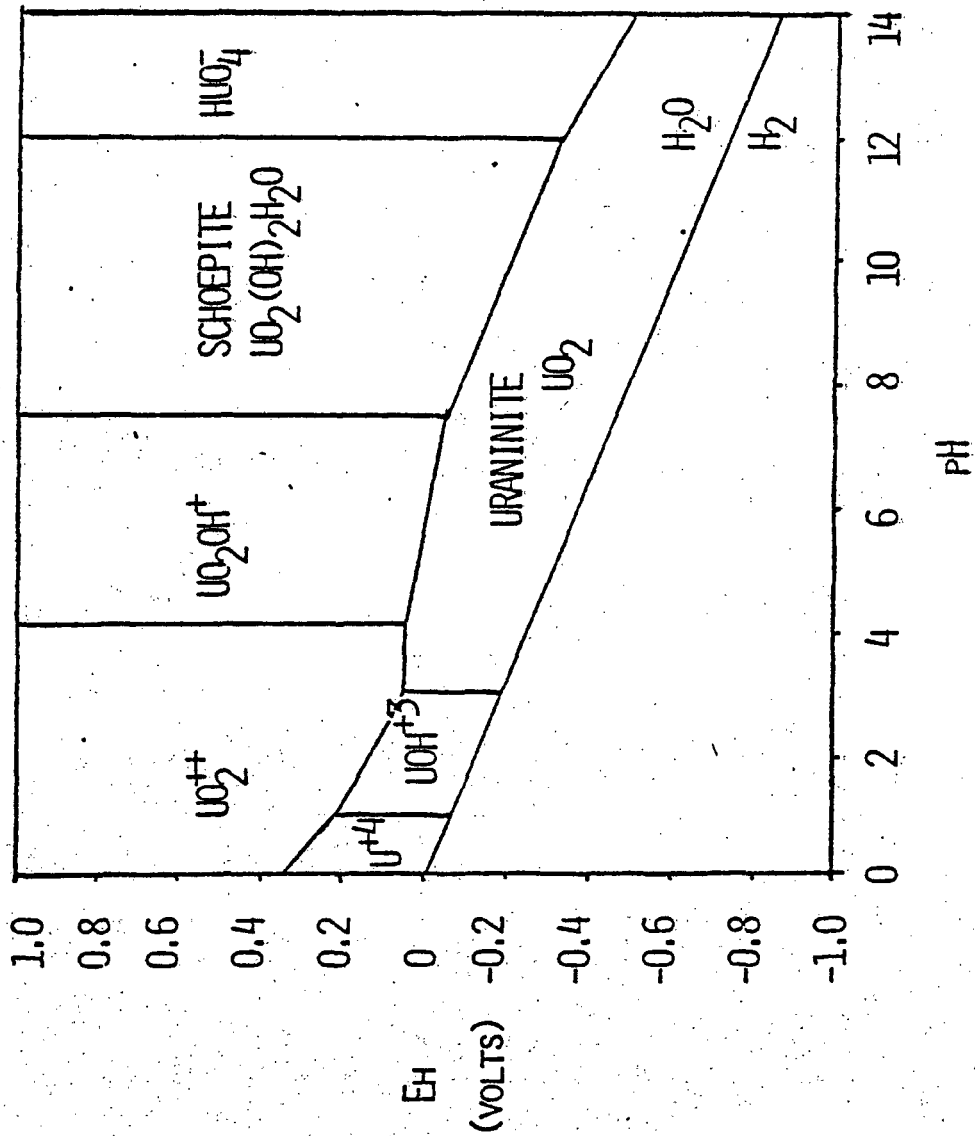
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Figure 6. Equilibrium diagram of the $U-O_2-H_2O$ system at $25^{\circ}C$ and 1 atm.

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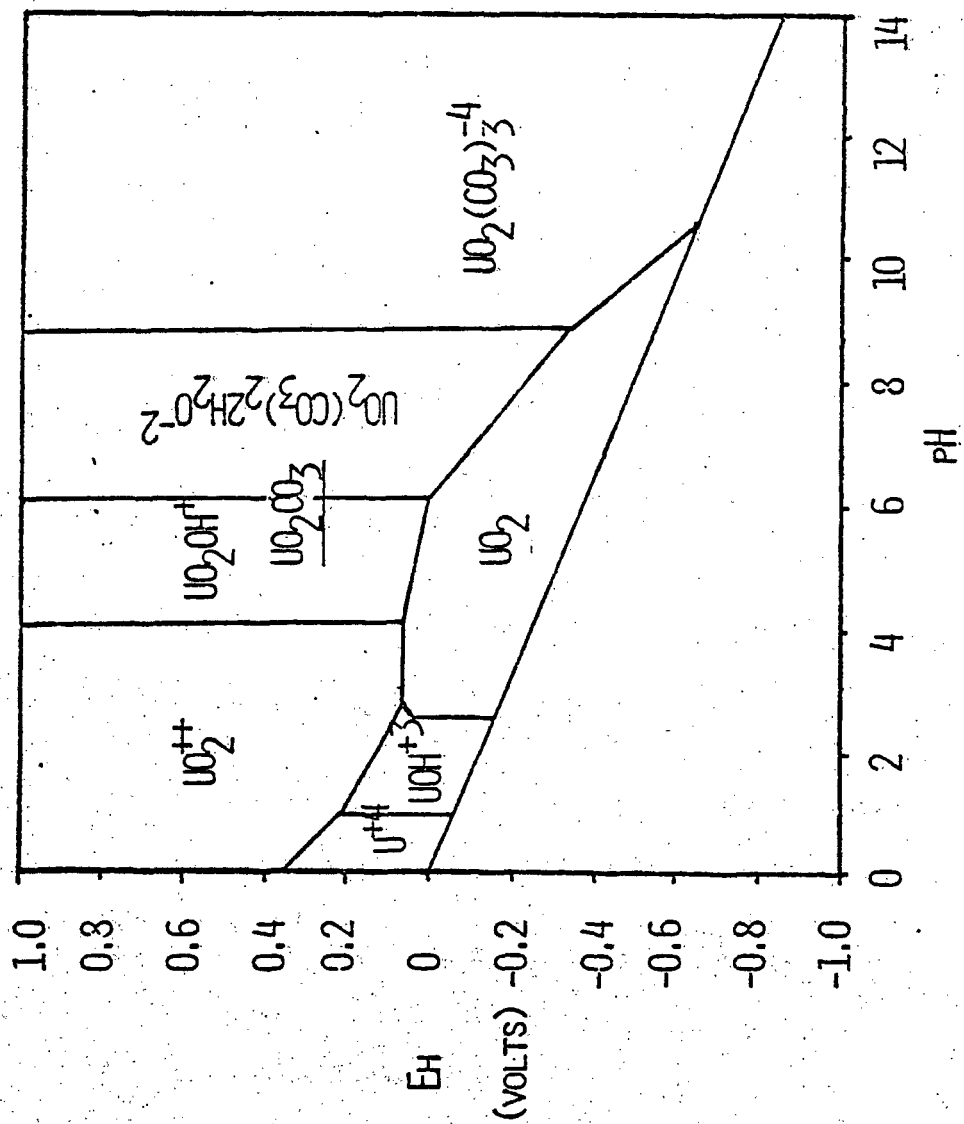
Figure 7. Aqueous equilibrium diagram of the $U-O_2-H_2O-CO_2$ system at $25^{\circ}C$ and 1 atm. and with P_{CO_2} constant at $10^{-3.4}$ atm.

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The soluble species are the uranyl anion complexes dicarbonato-uranylate ($UO_2(CO_3)_2 2H_2O^{2-}$) and tricarbonatouranylate ($UO_2(CO_3)_3^{4-}$). These are commonly referred to in geochemical literature as uranyl dicarbonate (UDC) and uranyl tricarbonate (UTC), respectively (fig. 7).

Subsurface waters that carry significant CO_2 and uranium (VI) and other metals may also contain significant sulfate, chloride, sodium, calcium, and magnesium. Sulfate and chloride anions do not produce any insoluble phases but SO_4^{-2} will complex with uranium below pH 3.5 to form $UO_2(SO_4)_4^{-6}$ and $UO_2(SO_4)_3^{-4}$ (Hostetler and Garrels, 1962).

Thermodynamic data

Using the standard free energy of formation given in Hostetler and Garrels (1962) (table 4) the following equilibrium constants (K) can be calculated for reactions between predominant species in the Eh/pH diagram of figure 7. The authors' calculations are given in table 5. The K value was calculated in the following manner:

Example: $UO_2^{++} + OH^- \rightleftharpoons UO_2OH^+$
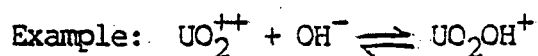
ΔG_r^O = standard free energy of reaction

= standard free energy of formation of products-

standard free energy of formation of reactants

$\Delta G_r^O = (-287.4) - (-236.4 + (-37.6)) = -13.4$ Kcal

$\Delta G_r^O = -RT \ln K$

where K is the equilibrium constant (p.39)

$\Delta G_r^O = -0.001987 \frac{Kcal}{deg.mol} (298^OK) \ln K$

$$\ln K = \frac{\Delta G_r^O}{-0.001987 \frac{Kcal}{deg.mole}(298^OK)} = \frac{-13.4 \ Kcal}{-0.001987 \frac{Kcal}{deg.mole}(298^OK)}$$

$\ln K = 22.63$

$K = 6.73 \times 10^9 = \frac{(UO_2OH^+)}{(UO_2)(OH-)}$

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Table 4.—Free-energy values (ΔG) from the elements at $25^{\circ}C$
and 1 atmosphere total pressure
(Data from Hostetler and Garrels, 1962)

Aqueous species	ΔG (Kcal)	Solid phases	ΔG (Kcal)
H_2O	-56.69	UO_2	-246.6
H^+	0.0	$UO_2(OH)_2 \cdot H_2O$	-398.8
OH^-	-37.6	UO_2CO_3	-385.0
$H_2CO_3^{\,o}$	-149.00	V_2O_3	-271.0
HCO_3^-	-140.31	V_2O_4	-381.0
CO_3^{-2}	-126.22	V_2O_5	-344.0
K^+	-67.46	$K_2(UO_2)_2V_2O_3 \cdot 3H_2O$	-1.294.0
$H_2VO_4^-$	-248.8		
UO_2^{++}	-236.4		
U^{+4}	-138.4		
$U(OH)^{+2}$	-193.5		
$UO_2(OH)^+$	-287.4		
HUO_4^-	-317.6		
$UO_2(CO_3)_2 \cdot 2H_2O^{-2}$	-630.0		
$UO_2(CO_3)_3^{-4}$	-648.0		

Table 5.—Calculated K values

[Equations are written so that products are the stable species. Underlined species are in the solid form]

Equation	K
1. $UO_2^{++} + OH^- \quad UO_2OH^+$	6.73×10^9
2. $UO_2OH^+ + CO_3^= \quad \underline{UO_2CO_3} + OH^-$	4.07×10^6
3. $\underline{UO_2CO_3} + CO_3^= + 2H_2O \quad UO_2)CO_3)_2 \cdot 2H_2O^{-2}$	9.41×10^3
4. $\underline{UO_2CO_3} + HCO_3^- + OH^- + H_2O \quad UO_2(CO_3)_2 \cdot 2H_2O^{-2}$	4.53×10^8
5. $UO_2(CO_3)_2 \cdot 2H_2O^{-2} + CO_3^= \quad UO_2(CO_3)_3^{-4} + 2H_2O$	6.30×10^3
6. $\underline{UO_2(OH)_2 \cdot H_2O} + 3CO_3^{-2} \quad UO_2(CO_3)_3^{-4} + 2OH^- + H_2O$	50
7. $HUO_4^- + 2H_2O \quad \underline{UO_2(OH)_2 \cdot H_2O}$	$9.9^\circ \times 10^3$
8. $UO_2^{++} + 4H^= \quad U^{+4} + 2H_2O$	$2.18 \times 10^{"}$
9. $UOH^{+3} + H^+ \quad U^{+4} + H_2O$	14.30
10. $UOH^{+3} + 1/2O_2 \quad UO_2^{++} + H^+$	3.79×10^{31}
11. $\underline{UO_2} + 3H^+ \quad UOH^{+3} + H_2O$	4.38×10^2
12. $\underline{UO_2} + 2H^+ 1/2O_2 \quad UO_2^{++} + H_2O$	1.66×10^{34}
13. $\underline{UO_2} + 1/2O_2 + H_2O \quad UO_2OH^+ + OH^-$	9.56×10^{15}
14. $\underline{UO_2} + H_2O + 1/2O_2 + CO_3^= \quad \underline{UO_2CO_3} + 2OH^-$	3.89×10^{22}
15. $\underline{UO_2} + 1/2O_2 + H_2CO_3 \quad \underline{UO_2CO_3} + H_2)$	8.44×10^{33}
16. $\underline{UO_2} + 1/2O_2 + H_2CO_3 + CO_3^= + 2H_2O \quad UO_2(CO_3)_2 \cdot 2H_2O^{-2} + H$	7.97×10^{37}
17. $\underline{UO_2} + H_2O + 1/2O_2 + 2CO_3^= + 2H_2 \quad UO_2(CO_3)_2 \cdot 2H_2O^{-2} + 2OH^-$	3.68×10^{26}
18. $\underline{UO_2} + 1/2O_2 + H_2CO_3 + 2CO^= \quad UO_2(CO_3)_3^{-4} + H_2O$	1.38×10^{41}
19. $\underline{UO_2} + H_2O + 1/2O_2 + 3CO_3^= \quad UO_2(CO_3)_3^{-4} + 2OH^-$	2.31×10^{30}
20. $\underline{UO_2(OH)_2 \cdot H_2O} \quad \underline{UO_2} + 1/2O_2 + 3H_2O$	1.43×10^{13}
21. $\underline{UO_2} + 1/2O_2 + OH^- \quad HUO_4^-$	3.85×10^{24}

IV. Metal-Organic Associations

Metal-organic bond

A simple, isolated ion exists only in the gaseous phase. When considering a metal ion (M) in aqueous solution, the reactions it participates in would be complex reactions, where one or several of the solvent molecules (H_2O) would be replaced by other groups.

$$M(H_2O)_n + L \rightleftharpoons M(H_2O)_{n-1}L + H_2O \qquad (1)$$
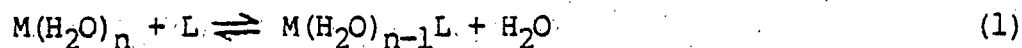
The ligand (L) is the electron donor group bound to the central ion and can be either an uncharged molecule or a charged ion. This relationship can be shown more simply in the following schematic form for a metal complex forming four coordinate bonds:

$$M(H_2O)_4 + 4L \rightleftharpoons \begin{matrix} L \\ L-M-L \\ L \end{matrix} + 4H_2O \qquad (2)$$
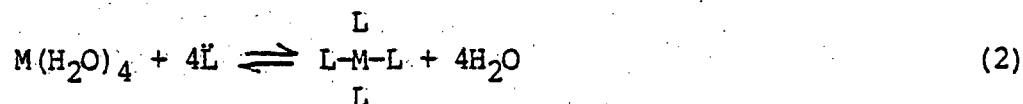
If the ligand combining with the metal has two or more donor groups, so that one or more rings are formed, the structure is then termed a chelate (Greek derivation meaning "claw") and the donor group is the chelating agent (Martell and Calvin, 1952).

$$M + 2L-L \rightleftharpoons \begin{matrix} L \\ L-M-L \\ L \end{matrix} \qquad (3)$$

Polynuclear complexes contain two or more central ions.

Electrostatic attraction is not an adequate explanation for the stability of the complex. Chelate complexes, where the ligand is attached to the metal through more than one bond, have exceptionally high stabilities.

The Lewis acid-base concept of electron donor-acceptor can be applied to complex reactions between metal ions and ligands. A complexation reaction could then be considered a neutralization reaction. The ligand acts as a base since it is an electron-pair donor. The metal ion is an electron-pair acceptor and functions as an acid. It is important to note that carbon (the major element in organic material) does not usually participate in these complexes. Carbon is not a Lewis base and therefore has no electrons to donate.

Nearly all metals form complexes and chelates. Although there is a large number of chelating agents, the donor atoms are limited to the strongly non-metallic elements of groups V and VI. Within these groups only nitrogen, oxygen, and sulfur are commonly found in complexes as electron donor atoms.

Manganese and iron in natural waters

A series of U.S. Geological Survey Water-Supply Papers by Hem (1960A and B, 1963, 1965) and Hem and Cropper (1959) report on studies of natural waters and various characteristics of manganese and iron in these waters. The most common form of ferric iron found in natural waters is $Fe(OH)_3$. In the range pH 5-8 ferric hydroxide is a stable solid that commonly forms colloidal suspensions. The most common form of manganese is the soluble Mn^{+2} ion.

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The physical nature of the ferric hydroxide precipitate depends on pH, concentration of iron and other ions in solution, temperature, and other factors. Under certain conditions the precipitate may be a rapidly settling floc that can remove other small suspended particles and dissolved ions from solution. This precipitate can also remove organic colloids and microorganism.

Several simple acids that are found in natural aqueous organic solutions were used to study various complexes of manganese and iron. One of the acids used was metadigallic acid which has been found in IR studies of colored material from waters (Lamar and Goerlitz, 1963). Natural water in contact with plant debris commonly contains tannic acid or chemically similar material in solution. Tannic acid is formed by hydrolysis of tannins, which are commonly present in vegetation as are oxalic and tartaric acid.

Oxalic acid forms the anion $Fe(C_2O_4)^{-2}$ as its most stable complex and tartaric acid forms a similar ferrous complex. Ferric complexes formed with oxalic and tartaric acid are stronger than the ferrous complexes.

When excess tannic acid was added to complex iron solutions the rate of oxidation of iron was a function of the rate of oxidation of the tannic acid. Hem (1960A) demonstrated the ability of tannic acid to form complexes with ferrous iron and retard its oxidation in water.

In a study of Mn^{+2} and tannic acid (Hem, 1965), the measured Eh values of several solutions exceeded calculated values which indicated supersaturation with Mn^{+2}. The difference between the

calculated activity of manganese and the total dissolved manganese concentration is attributed to complex formation. Using this approach it was determined that from 77 to 99 percent of the manganese was complexed.

Complexes formed between manganous ion and digallic acid were also studied. A 1:1 mole ratio complex of manganese and digallic acid was indicated at a pH near or slightly above neutrality.

In general, stability constants determined for ferrous and manganous complexes with the same organic ligand show ferrous complexes to be more stable.

Accumulation of uranium

Laboratory experiments by Szalay (1964) showed lignite, peat, and other decayed fossil plant debris absorb uranium from dilute aqueous solution in pH range of 3 to 7. He obtained absorption isotherms with a steep rise at low uranium concentrations and determined an "enrichment" factor of 10^4 for peat, that is, in a mixture of peat and water the uranium will be 10,000 times more concentrated on the peat than in the water on a meg/g basis. He found that peat could "fix" as much as 10 percent (by dry weight) of uranium. This fixation or "absorption" is reversible, and was similar to that of other cations. In order to determine what component of the peat was responsible for the adsorption, the peat was extracted with dilute NaOH solutions which removes the humic acid. After this treatment the peat had lost the major portion of its ability to fix uranium, and he concluded that the humic acid was responsible for fixing the uranium. Szalay (1969) also comments that

the fixation of uranium in coals is not reversible, and he concludes that secondary processes have changed the original association.

The "sorption" of uranium is finite, saturation can be obtained, and the sorption is reversible. Szalay cites that the lignin (from plants) component of humic acid, which has a polyaromatic skeleton, contains a number of attached polar groups, notably hydroxyl and carboxyl. The carboxyl dissociates at a pH of 5 or greater and thus could participate in cation exchange. The phenol hydroxyl does not dissociate until a pH of 9 or greater and would not be expected to participate at naturally occurring pH values.

Szalay's (1964), initial laboratory experiments were using levels of uranium much higher (100-1,000x) than natural concentrations of uranium. He measured uranium contents of natural waters in Hungary and found the maximum to be 0.1 ppm (100 mg/ton). Porous nylon bags containing peat were exposed to natural waters, and a several-thousand-fold enrichment of uranium in the peat was noted in field experiments.

Szalay (1969) dealt with the question of ion exchange versus chelation of uranium. Breger, Deul and Rubinstein (1955) investigated the La^{+3} exchange with uranium in a fossil uraniferous lignite from Dakota and observed that only a small part of the uranium was exchangeable. This led them to the conclusion that uranium is fixed in the form of an organic complex. However, Szalay (1969) reports that the ion-exchange fixation of uranyl ion is only the primary process, which is followed by secondary mineralization in the course of geological time.

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Formation constants of metal-organic complexes

Coleman and others (1956) calculated apparent formation constants of a complex between copper and acid-washed peat. An apparent formation constant (K_c) is calculated from concentration of species of interest and does not take into account side reaction or activity of species. The peat-Cu (II) reaction may be written in two ways, with P referring to the concentration of peat functional groups:

$$2P^- + Cu^{++} == CuP_2 \qquad : K_c = \frac{(CuP_2)}{(Cu^{++})(P^-)^2} \qquad\qquad (4)$$

$$2HP + Cu^{++} == CuP_2 + 2H^+ \quad : K_c = \frac{(CuP_2)(H^+)^2}{(Cu^{++})(HP)^2} \qquad\qquad (5)$$
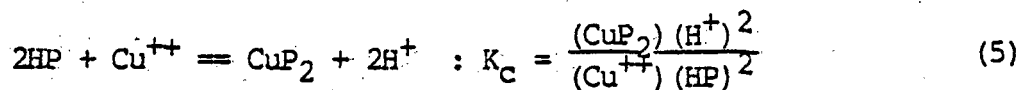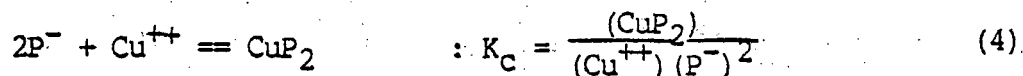
When calculating the apparent formation constant the condition is sought where $(CuP_2) = (Cu^{++})$ (that is, where the degree of formation is 0.5). Then $K_c = 1/(P^-)^2$ and K_c = products/reactant.

To evaluate equation (4) and (5) acid-washed peat was shaken with solutions containing varying amounts of $Cu(NO_3)_2$ and 0 to 0.35 milliequivalents of NaOH. The pH of each mixture was measured and the degree of neutralization calculated from the amount of base required to raise the pH to 7 in 1 N KNO_3. The points for each salt concentration were fitted to a straight line leading to the values of pKa (the negative logarithm of he acid ionization constant) and n listed in table 6.

To determine K_c, $\underline{n}$ (the average number of acid groups bound for each Cu(II) ion in the system) was plotted against pP (the negative logarithm of the concentration of ionized peat).

Two methods were used by Himes and Barber (1957) to determine the stability of a zinc-soil organic matter complex. They first assumed that only one type of adsorption site existed and that the chelation reaction followed a Langmuir-type of curve which could be extrapolated to give concentration of complexing sites. By this method they obtained a stability constant of log K = 3.4 to 5.6 for a zinc-organic matter complex. In the second method they equilibrated zinc between the soil and a soluble chelating agent. In this second method log K ranged from 1.9 to 10.4.

Miller and Ohlrogge (1958) were the first to apply Schubert's (1948) ion-exchange method to organic material. They used water extracts of barnyard manure, dried and ground alfalfa, and animal feces to complex zinc and remove it from soil. There were at least two complexing agents in the extract, one or more of which formed a

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Table 6.—Ionization constants of H-peat and formation constants

of Cu (II) -peat complexes

(Data from Coleman and others, 1956)

Cu (II) added (10^3 moles/liter)	KNO_3 (moles/liter)	pKa	n	K_c (x 10^{-6})
2	0.01	5.5	2.2	80.0
2	0.1	4.8	2.2	8.0
2	1.0	4.3	2.2	1.6
0.6	1.0	4.3	2.2	1.0
0.2	1.0	4.3	2.2	1.0

2:1 type complex and one or more of which formed a 1:1 complex. The "apparent" stability constants (which are given as log K values) of the combination of agents for zinc was found to be 7.8 at pH values that varied between 6.0 and 6.5. The ability of the extract to complex zinc increased as the pH of the extract was increased from 6.0 to 6.5.

Stability constants of zinc-humic acid complexes were determined by Randhawa and Broadbent (1965) by equilibrating zinc between a cation-exchange resin and a humic acid preparation. The principle of ion exchange equilibrium was used to determine the ionic species of zinc capable of forming complexes with humic acid. The relationships developed by Schubert (1948) were then used to determine the apparent stability constants. At pH values of 3.6, 5.6, and 7.0 the apparent stability constants were 4.42, 6.18, and 6.80, respectively.

Schnitzer and Skinner (1966) determined the molecular weight of the fulvic acid preparation they used, thus they were able to express concentration of complexing agent in the classical manner of moles per liter. Schnitzer and Skinner investigated three metal ions to determine if their stabilities in fulvic acid complexes followed the Irving-Williams series. The stability constants of copper (II)-FA complexes were 5.8 (at pH 3.5) and 8.7 (at pH 5.0); Fe^{++}-FA complexes were 1.7 (at pH 3.5) and 2.3 (at pH 5.0). Schnitzer and Skinner determined from these data that the order of stabilities of the complexes was $Cu^{++} > Fe^{++} > Zn^{++}$ which does not follow the Irving-Williams series of Pb>Cu>Ni>Co>Zn>Cd>Fe>Mn>Mg (all as divalent cations).

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In 1967 Schnitzer and Skinner continued their 1966 work on six additional divalent metal ions, Pb, Ni, Mn, Co, Mg, and Ca. At pH 3.5, stability constants for the different metal-FA complexes were as follows: Ni-FA, 3.47; Pb-FA, 3.09; Co-FA, 2.20; Ca-Fa, 2.04; Mn-FA, 1.47; Mg-FA, 1.23. At pH 5.0, log K values were Pb-FA, 6.13; Ni-FA, 4.14; Mn-FA, 3.78; Co-FA, 3.69; Ca-FA, 2.92; and Mg-FA, 2.09.

These stability constants give the following order of stabilities at pH 3.5 for the divalent cations: Cu>Fe>Ni>Pb>Co>Ca>Zn>Mn>Mg. At pH 5.0 the order is: Cu>Pb>Fe>Ni>Mn Co>Ca>Zn>Mg. The order of stabilities of the metal-FA complex differs from the Irving-Williams series at both pH 3.5 and 5.0.

The ion exchange equilibrium method of determination of stability constants was compared with the method of continuous variations by Schnitzer and Hansen (1970). The method of continuous variations is based on variations of optical densities of solutions containing different ratios of metal ion and complexing agent, while simultaneously maintaining a constant total concentration of reactants. There was good agreement between these two methods as shown in the following table 7.

Malcolm and others (1970) also used Schubert's method to determine conditional stability constants for fulvic acid complexes. At pH 3.0, 4.5, and 6.0 conditional constants were 2.7, 4.0, and 6.6, respectively. Malcolm (1972) determined conditional stability constants for both the humic and fulvic acid fractions of soil and sediment organic matter. The constants for these complexes were determined at a constant ionic strength of 1.0 in KCl using

Table 7.—Stability constants of metal-FA complexes at μ—0.1
(CV—method) of continuous variations
IE—ion-exchange equilibrium method)
(Data from Schnitzer and Hanson, 1970)

| Metal | Log K | | | |
| | pH 3.0 | | pH 5.0 | |
	CV	IE	CV	IE
Cu^{++}	3.3	3.3	4.0	4.0
NI^{++}	3.1	3.2	4.2	4.2
Co^{++}	2.9	2.8	4.2	4.1
Pb^{++}	2.6	2.7	4.1	4.0
Ca^{++}	2.6	2.7	3.4	3.3
Zn^{++}	2.4	2.2	3.7	3.6
Mn^{++}	2.1	2.2	3.7	3.7
Mg^{++}	1.9	1.9	2.2	2.1
FE^{+++}	6.1*	—	—	—
Al^{+++}	3.7**	3.7*	—	—

*Determined at pH 1.70.
**Determined at pH 2.35.

radioisotopic tracer methods. The conditional stability constants were 4.0 (pH 4.5) and 6.6 (pH 6.0) for fulvic acid–Co(II) complexes, 6.0 (pH 4.5) and 8.3 (pH 6.0) for humic acid–Co(II) complexes; 5.4 (pH 4.5) and 5.6 (pH 6.0) for fulvic acid–Fe(III) complexes; and 6.8 (pH 4.5) and 7.2 (pH 6.0) for humic acid–Fe(III) complexes.

The correlation between stability constants of zinc-humic and zinc-fulvic complexes and the degree of humification was studied by Matsuda and Ito (1970). Schubert's (1948) ion exchange method was used to determine stability constants for zinc-humic and zinc-fulvic acid complexes, and a significant positive correlation was found with the humic acids. By applying the correlation concerning humic acids to soil humus, it was concluded that the adsorption strength of zinc for soil humus increased with the progress of humification.

V. Determination of Stability Constants

Conditional Stability Constants

A Conditional Stability Constant (CSC) is defined as $K = (\lambda_o/\lambda) - 1/(ORG)^x$

where: λ_o = distribution constant of metal between solution and ion-exchange resin when organic material (HAS or FAS) is absent,

λ = distribution constant in presence of organics,

(ORG) = concentration of organic material, Soluble Organic Material, Humic Acid Solid or Fulvic Acid Solution, in moles/liter, and,

x = number moles organics/one mole metal complexed.

A conditional stability constant is a measure of the equilibrium

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constant for the reaction of interest, uncorrected for competing side reactions.

Early work that quantified the metal-organic interaction used various names for this quantification number. In the following review the names used for these "constants" will be the same as used by the different authors. The definitions of these different constants are given in the respective referenced papers.

Stability constants have been used by several workers to quantify the association between organic material and various metal ions. Coleman and others (1956) determined "formation" constants for copper-peat complexes. Himes and Barber (1957), Randhawa and Broadbent (1965), and Miller and Ohlrogge (1958) determined constants for the chelating ability of organic material (SOM) with various metals. Irving and Williams (1948) postulated that within the divalent metal series Mn, Fe, Co, Ni, Cu, and Zn, as the ionic radius decreases and the ionization potential increases, the stability increases, reaching a maximum with copper. This has come to be known as the Irving-Williams series. The results of Schnitzer and Skinner indicated that the stability of some FA divalent metal complexes do not follow the Irving-Williams series, which would predict $Cu^{2+}>Zn^{2+}>Fe^{3+}$, but instead are of the order $Cu^{2+}>Fe^{3+}>Zn^{2+}$. Further work done by them (1967) on additional divalent metal ions at pH 3.5 and 5.0 also demonstrated deviation from the Irving-Williams series.

Malcolm and others (1970) demonstrated that the Conditional Stability Constant (CSC) of Fe^{3+}-FA complexes showed little dependence on pH. The Fe^{3+}-FA molar ratio also shows negligible

change across the pH range. Increasing the pH of the solution should increase the negative charge of the FA by deprotonating the functional groups. The overall effect is an increase in the negative sites available to complex the metal ions. More moles of metal will be complexed per mole FA and a lower FA-metal ratio will result. An opposing effect is found among metal ions that form hydroxo complexes at higher pH values. If the metal ion forms hydroxo complexes in the alkaline pH range, the number of moles of metal complexed per mole of FA would decrease, thus increasing the FA-metal molar ratio. These two opposing tendencies can give rise to increasing, constant, or decreasing molar ratios depending on the ability of the metal ion to form hydroxo complexes.

The Conditional Stability Constant is based on concentration of species rather than on activities as is a thermodynamic stability constant. A CSC is dependent on the ionic strength of the medium and includes no corrections for competing reactions in which the species of interest may be involved. Although a CSC is not as precise as a thermodynamic stability constant, it is very useful, as shown below.

One prerequisite necessary for determination of a CSC (Schubert, 1948) is that the complex be of the type MKe_x, where M = metal, Ke = ligand, and x = number of moles Ke (an integer greater than or equal to one). But from results by Schnitzer and Skinner (1966 and 1967), Miller and Ohlrogge (1958), and Randhawa and Broadbent (1965), the value for x (FA = metal molar ratio) has varied from 0.53 to 2.00.

The method commonly used to determine CSC is the ion exchange

equilibrium method developed by Schubert (1948). Schnitzer and Hansen (1970) checked values obtained from the ion-exchange method by determining CSC for the same complexes by the method of continuous variation (Rossotti and Rossotti, 1961). Discrepancies that occurred between results from the two methods were traced to the extreme sensitivity of the ion-exchange method to slight analytical variance. Once precautions were taken to maintain precision, the CSC calculated by the two methods were in agreement, and it was determined that 1:1 molar (mononuclear) complexes do exist between FA and 10 divalent metals.

Ion-exchange-Conditional Stability Constant

Schubert (1948) first used the ion-exchange technique to measure stability constants for reactions between strontium ions and citrates and tartrates. This technique incorporates an ion-exchange resin in the solution containing the metal and the chelating organic material. The ion-exchange method is dependent on the fact that at equilibrium the amount of ion held by a given amount of ion-exchange resin is proportional to the concentration of free metal ions in solution.

The equilibrium reaction for mononuclear chelate or complex formation can be written

$$M + nL \rightleftharpoons ML_n. \tag{6}$$

The equilibrium constant is then defined as

$$K = (ML_n)/ (M)(L)^n . \tag{7}$$

The relationship for the metal ion in the presence of the ion-exchange resin is shown in Martell and Calvin (1952):

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$$\frac{MR}{(M)} = \lambda_o = \frac{a_o V}{(100-a_o)g} \tag{8}$$

where: λ_o = a constant (for exchange in absence of chelating agent),

   MR = moles of metal bound by a unit weight of cation exchanger,

   (M) = concentration of all forms of the metal ion in solution except that found complexed,

   a_o = percent of the total metal used which is bound to exchanger,

   $100-a_o$ = percent of total metal used which remains in solution,

   V = volume of solution, and

   g = weight of cation exchange resin.

Without making any suppositions concerning mechanisms of reaction or bond types, a stability constant can be determined by measuring the concentration of metal in solution at two concentrations of the complexing agent. The temperature, pH, volume of solution, ionic strength, and weight of resin must all remain constant. The concentration of metal ion in solution should be negligible compared to that of the complexing agent. It is also necessary that the resin not bind the complexing agent. When working with fulvic and humic acids there is a problem with adsorption of the organics onto the resin at certain pH values and this effect has to be taken into consideration when data are evaluated.

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The distribution constant is measured in the absence of the chelating agent (λ_0) and in the presence of the chelating agent (λ). Since measurements are made under fixed conditions, the equilibrium relation between free metal ion and the resin is maintained even in the presence of the chelating agent (humic acid). When the chelating agent is absent

$$(M) = MR/\lambda_0 \tag{9}$$

Because λ expresses the relationship between total metal species in solution, $(M) + (ML_n)$, and on the resin

$$(M) + (ML_n) = MR/\lambda \tag{10}$$

Combining the above two equations yields

$$(ML_n) = \frac{MR}{\lambda} - \frac{MR}{\lambda_0} \tag{11}$$

The equilibrium constant can then be rewritten in the form

$$K = \left(\frac{\lambda_0}{\lambda} - 1\right) / (L)^n \tag{12}$$

or

$$\log\left(\frac{\lambda_0}{\lambda} - 1\right) = \log K + n\log(L). \tag{13}$$

Thus $\log K$ and n may be obtained directly from the intercept and slope of a plot of $\log [(\lambda_0/\lambda) -1]$ versus $\log (L)$ is equal to the concentration of all forms of the ligand in solution.

According to Ringbom (1963), when complexation reactions are involved in the ion exchange equilibrium the term "conditional constant" is most fitting. Complexation and chelation reactions may cause tremendous changes in concentration of reacting species.

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Activity coefficients are often difficult to determine due to high charge of ions. Because the evaluation of concentration change is often within orders of magnitude, the effect of the activity coefficient is usually negligible.

To include the effects of all side reactions and interfering factors in the mass-action equation defining the system would be very difficult. The Conditional Stability Constant, therefore, quantifies the reaction of interest at the exclusion of these effects. However, the analyst must be aware of the variables that affect the CSC and make all attempts to maintain them at constant values for the calculation of λ_0 and λ. A major use of CSC's has been comparison of binding of different metal ions to fulvic or humic acids, which under identical and controlled conditions can give meaningful data.

VI. Summary

Much is known about natural soluble organic materials and also about inorganic uranium geochemistry; however, the interaction of uranium and organics is not quantified. Work on other elements, such as transition metal cations and their interaction with soluble organic species, has been well quantified using Conditional Stability Constant determination. This has led to a better understanding of metal-organic interactions in soil and water systems.

The technique of Conditional Stability Constant determination should be applied to uranium and soluble organic matter to quantify the relationship of uranium and organic matter. These experiments can give insight to the pH of association as well as the mechanism involved.

VII. References

Baker, W. E., 1973, The role of humic acids from Tasmanian podzolic

    soils in mineral degradation and metal mobilization: Geochem. et

    Cosmochem. Acta, v. 37, p. 269-281.

Bloomfield, C., and Kelso, W. I., 1973, Mobilization and fixation of

    molybdenum, vanadium and uranium by decomposing plant matter:

    Jour. Soil Sci., v. 24, no. 3, p. 368-379.

Breger, I. A., 1963, Origin and classification of naturally occurring

    carbonaceous substances, in I. A. Breger, ed. Organic

    geochemistry: New York, Pergamon Press, p. 50-86.

Breger, I. A., Duel, M., and Rubinstein, S., 1955, Geochemistry and

    mineralogy of a uraniferous lignite: Econ. Geology, v. 50, p.

    206-226.

Coleman, N. T., McClung, A. C., and Moore, D. P., 1956, Formation

    constants for copper-peat complexes: Science, v. 123, p. 330-331.

Gjessing, E. T., 1965, Use of Sephadex gel for estimation of molecular

    weight of humic substances in natural water: Nature, v. 208, p.

    1091-1092.

Haworth, R. D., 1971, The chemical nature of humic acid: Soil Sci.,

    v. 111, p. 71-79.

Hem, J. D., 1960A, Complexes of ferrous iron with tannic acid: U.S.

    Geol. Survey Water-Supply Paper 1459-D.

_____1960B, Restraints on dissolved ferrous iron imposed by

    bicarbonate redox potential, and pH: U.S. Geol. Survey Water-

    Supply Paper 1459-B.

_____1963, Chemical equilibria and rates of manganese oxidation: U.S. Geol. Survey Water-Supply Paper 1667-A.

_____1965, Reduction and complexing of manganese by gallic acids: U.S. Geol. Survey Water-Supply Paper 1667-D.

Hem, J. D., and Cropper, W. H., 1959, Survey of ferrous-ferric chemical equilibrium and redox potentials: U.S. Geol. Survey Water-Supply Paper 1459-A.

Himes, F. L., and Barber, L. S., 1957, Chelating ability of soil organic matter: Soil Sci. Soc. America Proc., v. 21, no. 10, p. 268-373.

Hostetler, P. B., and Garrels, R. M., 1962, Transportation and precipitation of uranium and vanadium at low temperature with special reference to sandstone-type uranium deposits: Econ. Geology, v. 57, no. 2, p. 137-167.

Irving, H., and Williams, R. J. P., 1948, Order of stability of metal complexes: Nature, v. 162, p. 746-747.

Khan, S. U., 1969, Interaction between the humic acid fraction of soils and certain metallic cations: Soil Sci. Soc. America Proc., v. 33, p. 851-854.

Khan, S. U., and Sowden, F. J., 1972, Distribution of nitrogen in fulvic acid fraction extracted from the Black Solonetzic and Black Chernozemic soils of Alberta: Canadian Jour. Soil Sci., v. 52(1), p. 116-118.

Kononova, M. M., 1961, Soil organic matter: New York, Pergamon Press, 453 p.

Lamar, W. L., and Goerlitz, D. F., 1963, Characterization of carboxylic acids in unpolluted streams by gas chromotography: Am. Water Works Assoc. Jour., v. 55, p. 797-802.

Malcolm, R. L., 1972, Comparison of conditional stability constants of North Carolina humic and fulvic acids with Co(II) and Fe(III): Geol. Soc. America Mem. 133, p. 79-83.

Malcolm, R. L., Jenne, E. A., and McKinley, P. W., 1970, Conditional stability constants of a North Carolina soil fulvic acid with Co^{+2} and Fe^{+3}: Alaska Univ. Inst. Mar. Sci., Occasional Pub. no. 1, p. 479-484.

Martell, E. A., and Calvin, M., 1952, Chemistry of metal chelate compounds: New York, Prentice Hall, Inc., p. 613.

Matsudo, K., and Ito, S., 1970, Absorption strength of zinc for soil humus, III. Relationship between stability constants of zinc-humic and fulvic-acid complexes, and the degree of humification: Soil Sci. and Plant Nutrition, v. 16, no. 1, p. 1-10.

Miller, M. E., and Ohlrogge, A. J., 1958, Water-soluble chelating agents in organic materials: Soil Sci. Soc. America Proc., v. 22, p. 225-228.

Ogner, G., 1973, Oxidation of nonhydrolyzable humic residue and its relation to lignin: Soil Sci., v. 116, p. 93-99.

Ong, H., Ling, 1968, The effectiveness of natural organic matter in concentrating metals: Colorado School Mines Thesis T-1127, p. 119.

Ong, H. L., and Bisque, R., 1968, Coagulation of humic colloids by

metal ions: Soil Sci., v. 106, no. 3, p. 220-224.

Pauling, L., 1956, General chemistry: San Francisco, Freeman and Co.,
710 p.

Picard, G. L., and Felbeck, G. T., Jr., 1976, The complexation of iron
by marine humic acid: Geochem. et Cosmochem. Acta, v. 40, p.
1347-1350.

Randhawa, N. S., and Broadbent, F. E., 1965, Soil organic matter-metal
complexes: Soil Sci., v. 99, no. 6, p. 262-266.

Ringbom, A., 1963, Complexation in analytical chemistry: New York,
Interscience Publishers, p. 378.

Rossotti, F. J. C., and Rossotti, H., 1961, The determination of
stability constants: New York, McGraw Hill, 364 p.

Schalscha, E. B., Appelt, H., and Schatz, A., 1967, Chelation as a
weathering mechanism-I. Effect of complexing agents on the
solubilization of iron from minerals and granodiorite: Geochem.
et Cosmochem. Acta, v. 31, p. 587-596.

Schnitzer, M., 1969, Metal-organic matter interaction in soils and
waters, in S. D. Faust and J. V. Hunte, eds., Organic compounds in
aquatic environments, New York, Marcel-Dekker, Inc., p. 297-315.

Schnitzer, M., and Desjardins, J. G., 1962, Molecular and equivalent
weights of the organic matter of a podzol: Soil Sci. Soc. America
Proc., v. 26, p. 362-365.

Schnitzer, M., and Hansen, E. H., 1970, Organic-metallic interactions
in soils: 8. An evaluation of methods for the determination of
stability constants of metal-fulvic acid complexes: Soil Sci.,

v. 190, p. 333-340.

Schnitzer, M., and Khan, S. U., 1972, Humic substances in the environment: New York, Mercel Dekker, Inc., p. 327.

Schnitzer, M., and Skinner, S. I. M., 1963A, Organo-metalic interactions in soils: 1. Reactions between a number of metal ions and the organic matter of a podzol Bh horizon: Soil Sci., v. 96, p. 86-93.

_____1963B, Organo-metallic interactions in soils: 2. Reactions between different forms of iron and aluminum and the organic matter of a podzol B_h horizon: Soil Sci., v. 96, p. 181-185.

_____1966, Organo-metallic interactions in soils: 5. Stability constants of Cu^{2+}-, Fe^{2+}-, and Zn^{2+}-fulvic acid complexes: Soil Sci., v. 102, p. 361-365.

_____1967, Organo-metallic interactions in soils: 7. Stability constants of PB^{2+}-, Ni^{2+}-, Co^{2+}-, Ca^{2+}-, and Mg^{2+}-fulvic acid complexes: Soil Sci., v. 103, p. 247-252.

Schubert, J., 1948, Use of ion exchangers for the determination of physical-chemical properties of substances, particularly radiotracers: Jour. Phys. and Colloidal Chem., v. 52, p. 340-350.

Swanson, V. E., and Palacas, J. G., 1965, Humates in coastal sands of northwest Florida: U.S. Geol. Survey Bull. 1214-B, p. B1-B27.

Szalay, A., 1964, Cation exchange properties of humic acids and enrichment of UO_2^{++}: Geochem. et Cosmochem. Acta, v. 28, p. 1605-1614.

Szalay, S., 1969, Accumulation of uranium and other micrometals in

coal and organic shales and the role of humic acids in those geochemical enrichments: Arkiv Mineralogi och Geologi, band 5 hr 3, p. 23-36.

Szalay, S., and Samsoni, Z., 1969, Investigation of the leaching of uranium from crushed magmatic rock: Geol. Jour., v. 97, no. 1, p. 60-72 (trans. Foldtani Koslony).

Wershaw, R. L., and Pinckney, D. J., 1971, Association and dissociation of a humic acid fraction as a function of pH: U.S. Geol. Survey Prof. Paper 750-D, p. D216-D218.