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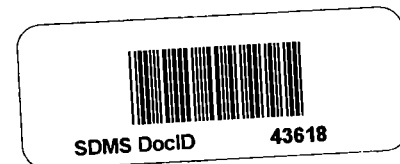
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June 28, 1989

Mr. Randy Sturgeon  
U. S. Environmental Protection Agency  
841 Chestnut Building  
Philadelphia, Pennsylvania 19107



RE: Telephone Conference, Review of Radiological  
Investigation Data, Thorium Mobility, Dupont  
Newport Site, WA No. 877 (Co3001).

Dear Mr. Sturgeon:

Per the telephone conference held on Friday, June 23, 1989, at 1100 hours, enclosed is information provided by Dr. D. Gonzales on the Mobility of Thorium in natural water at low temperatures.

I have sent five (5) copies for your distribution to ensure legibility of reproduced copies.

I trust this meets your requirements.

If you have any questions, please call me at (713) 669-2245.

Very truly yours,

*Paul Fikac /smo*

Paul Fikac  
Work Assignment Manager

PJF:smo

cc: S. Loftus  
D. Gonzales  
File

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## The mobility of thorium in natural waters at low temperatures

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**Abstract**—Thermodynamic properties of 32 dissolved thorium species and 9 thorium-bearing solid phases have been collected from the literature, critically evaluated and estimated where necessary for 25°C and 1 atm pressure. Although the data are incomplete, especially for thorium minerals and organic complexes, some tentative conclusions can be drawn. Dissolved thorium is almost invariably complexed in natural waters. For example, based on ligand concentrations typical of ground water ( $\text{Cl}^- = 10$  ppm,  $\text{F}^- = 0.3$  ppm,  $\text{SO}_4^{2-} = 100$  ppm, and  $\text{PO}_4^{3-} = 0.1$  ppm), the predominant thorium species are  $\text{Th}(\text{SO}_4)_2$ ,  $\text{ThF}_3^+$ , and  $\text{Th}(\text{HPO}_4)_2^+$  below  $\text{pH} \approx 4.5$ ;  $\text{Th}(\text{HPO}_4)_2^+$  from about  $\text{pH} 4.5$  to 7.5; and  $\text{Th}(\text{OH})_2^2+$  above  $\text{pH} 7.5$ . Based on stability constants for thorium citrate, oxalate and EDTA complexes, it seems likely that organic complexes predominate over inorganic complexes of thorium in organic-rich stream waters, swamp waters, soil horizons, and waterlogged recent sediments. The thorium dissolved in seawater is probably present in organic complexes and as  $\text{Th}(\text{OH})_2^2+$ . The tendency for thorium to form strong complexes enhances its potential for transport in natural waters by many orders of magnitude below  $\text{pH} 7$  in the case of inorganic complexing, and below about  $\text{pH} 8$  when organic complexing is important. The existence of complexes in addition to those formed with hydroxyl, is apparent from the fact that measured dissolved thorium in fresh surface waters ( $\text{pH}$  values generally 5–8) usually ranges from about 0.01 to 1 ppb and in surface seawater ( $\text{pH} = 8.1$ ) is about 0.00064 ppb. This may be contrasted with the computed solubility of thorianite in pure water which is only 0.00001 ppb Th as  $\text{Th}(\text{OH})_2^2+$  above  $\text{pH} 5$ . Although complexing increases the solubility of thorium-bearing heavy minerals below  $\text{pH} 8$ , maximum thorium concentrations in natural waters are probably limited in general by the paucity and slow solution rate of these minerals and by sorption processes, rather than by mineral-solution equilibria.

### INTRODUCTION

THE THERMODYNAMIC properties of dissolved thorium species and thorium minerals can be used to compute solution-mineral equilibria relations. These theoretical calculations tell much about the possible conditions for and extent of thorium mobility. Such information helps us to understand controls on thorium concentrations in ground water, and to predict the risk of thorium release in leachates from mining activity and radioactive wastes.

Thorium is found in nature only as a tetravalent cation. The element usually occurs in geologic materials as a trace constituent in solid solution in phosphate, oxide and silicate minerals, and sorbed onto clays and other soil colloids (HANSEN, 1970; BONDIETTL, 1974). It occurs as a major species only in a few rare minerals such as thorianite ( $\text{ThO}_2$ ), and thorite ( $\text{ThSiO}_4$ ). The former mineral is isomorphous with uraninite, the latter with zircon. For this reason a large part of naturally occurring thorium is found incorporated in the zircon structure. The chief source of thorium is monazite ( $\text{Ce, La, Y, Th} \text{ PO}_4$ ), which usually contains 3–9% and up to 20%  $\text{ThO}_2$ . Along

with zircon, monazite is concentrated with other resistant heavy minerals in stream and beach sands (RANKAMA and SAHAMA, 1958). Igneous  $\text{UO}_2$  can form a complete solid solution with  $\text{ThO}_2$  (ROGERS and ADAMS, 1969). Most Th host minerals are highly refractory to weathering and thorium has long been considered a very insoluble and immobile element in natural waters.

Data on dissolved thorium concentrations in natural waters is generally of poor quality or nonexistent. Few researchers have distinguished carefully or at all between the thorium in true solution, and that associated with suspended matter. For this reason it must usually be assumed that reported thorium concentrations are the maximum possible amounts dissolved.

MOORE and SACKETT (1964) measured  $0.00064 \pm 0.0002$  ppb Th in two centrifuged Atlantic Ocean surface water samples. Because this is among the lowest seawater values reported (see ROGERS and ADAMS, 1969), and because the salinity and cations present in seawater tend to flocculate colloidal materials, this value should closely approximate the dissolved thorium present. SOMAYAJULU and GOLDBERG (1966)

found 0.00033 ppb Th in one Pacific Ocean surface water sample. They did not filter or centrifuge their samples, and determined the thorium value indirectly, so that this value is approximate at best. Moore and Sackett, and Somayajulu and Goldberg reported Th concentrations in deep waters in the two oceans which were sometimes higher and sometimes lower than their surface ocean values.

KAMATH *et al.* (1964) obtained 1.1–2.7 ppb Th in five surface waters from non-uraniferous areas in India. The samples were passed through a 10  $\mu$ m filter before chemical analysis. MRYAKE *et al.* (1964) found 0.0087–0.045 ppb Th in ten Japanese river waters. Samples were passed through a 5  $\mu$ m filter before analysis. Based on a sampling of (filtered?) waters from five lakes and eleven streams in California, Nevada and Utah, THURMER (1965) reported 0.08–0.4 ppb Th with a few values <0.03 ppb.

DEMENTYEV and SYROMYATNIKOV (1965) measured Th in some spring and well waters in granite, weathered mantle and alluvium on granite. For 6, clear (unfiltered) ground waters, they obtained 0.2–0.9 ppb Th, whereas, 2 anomalous waters showed 7 and 40 ppb. Both OSMOND (1964) and KAMATH *et al.* (1964) studied thorium in ground waters of different temperatures. Osmond presumably analyzed unfiltered waters from carbonate rocks. Kamath and his coworkers passed their samples through a 10  $\mu$ m filter before analysis. Both studies reported Th concentrations increasing with ground water temperature. Osmond obtained 0.1 to 2 ppb Th in 4 waters having temperatures from about 25 to 91°C, respectively. KAMATH *et al.* noted that Th concentrations increased from 0.27 to 0.74 ppb in three spring waters with temperatures from 47 to 56°C, respectively.

In four surface and ground waters from areas near uranium mining, KAMATH *et al.* (1964) found 1.9–5.4 ppb Th. Based on the Russian literature, DROZDOVSKAYA and MEL'NIK (1968) concluded that as much as 0.1–10 ppb Th can occur in 'ground and mine waters'. Even higher Th concentrations (up to 38 ppm) have been recorded in seeps and ground waters associated with uranium mining and milling in the U.S.A. and Canada (see KAUFMAN *et al.*, 1976; MOFFETT and TELLER, 1978). These situations are described in detail later in this paper.

Admittedly, much or most of the thorium reported in the above studies must be in suspended matter, not in true solution. Nevertheless, even the surface seawater value measured by MOORE and SACKETT (1964) exceeds the solubility of thorianite which is 0.00001 ppb Th as  $\text{Th}(\text{OH})_3$  above pH 5. The available data therefore suggest that the concentration of Th in natural waters and therefore its mobility, is greatly increased by thorium complex formation.

The behavior of thorium in aqueous systems has been summarized by AMES and RAI (1978) and RAI and SERNE (1978). They have published solubility vs pH diagrams for thorianite,  $\text{Th}(\text{OH})_3$ ,  $\text{ThF}_3$ , and thorium phosphate solids. However, their diagrams are

computed considering only a few inorganic complexes of thorium, and for simplified conditions. For example, they fix  $\text{H}_2\text{PO}_4^-$  activity, while  $\text{H}_3\text{PO}_4$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  are assigned zero activity regardless of pH.

This report contains a collection and critical evaluation of the thermodynamic data for 9 solid and 32 dissolved thorium species including organic complexes. These data are then used to evaluate the distribution of thorium aqueous species and the solubility of thorianite at various ligand concentrations chosen to simulate those found in natural waters. The importance of thorium complexes to thorium mobility, thus far a matter of relative ignorance, has been estimated from these calculations. The report also includes a brief discussion of the role of sorption in thorium mobility.

### THE CHOICE OF ORGANIC LIGANDS

The selection of inorganic ligands and corresponding thorium complexes for consideration was relatively straightforward in that thermodynamic data for these ligands and complexes was accessible. Also, typical concentrations of inorganic ligands in natural waters are well known. In contrast, both the identity and concentrations of organic ligands in such waters are poorly known.

The bulk of the organic material dissolved in natural waters has been described as humic substances. According to REUTER and PERDUE (1977) most of this material resembles the fulvic acids present in soils. A representative concentration of humic substances in surface waters may be about 10 mg/l (REUTER and PERDUE, *ibid.*), whereas the average concentration of humic substances in shallow ground waters may be nearer to 1 mg/l. Higher amounts are likely in most soil waters (100 mg/l, cf. McKEAGUE *et al.*, 1976). The acidic functional groups present in natural fulvic acids (carboxyl and phenolic hydroxyl groups) vary in both strength and relative abundance (SCHNITZER and KHAN, 1978). Consequently, stabilities of metal fulvic complexes vary with solution composition and with pH. This makes the use of such stability data impractical in model calculations. For this reason we have selected citrate ( $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ), oxalate ( $\text{C}_2\text{O}_4^{2-}$ ) and EDTA ( $\text{C}_{10}\text{H}_{12}\text{O}_{16}\text{N}_8^{4-}$ ) to exemplify the probable role of thorium-organic complexes in natural waters.

The occurrence of oxalate and citrate in soils and some natural waters supports our choice of these ligands. Oxalate is present in many plants and is released upon organic decomposition (LEAVENS, 1960). LUND and HEM (1975) reported oxalic and citric acids as two of the principal organic acids in forest soils and litter. GRAUSTEIN *et al.* (1977) identified whewellite and weddellite, calcium salts of oxalic acid, as common phases in the litter layer of soils. The same observers measured 900 ppb of dissolved oxalate at

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20 cm depth in an Oregon forest soil, and concluded that oxalic acid was the chief low molecular weight organic acid in solution at the base of the humus layer. LAKIN (1979) noted that plant root exudates (as exemplified by those from wheat) contain oxalic and citric acids among others. He also showed that pine tree root exudates contain oxalic acid. It is likely, therefore, that citrate and oxalate are not uncommon in natural waters, although their concentrations will usually be much lower than those of humic substances.

EDTA was included in our study more as a 'type' ligand than as a specific constituent in natural waters. EDTA was chosen as an example of a multidentate organic chelating agent which forms an extremely strong complex with thorium. In fact, one EDTA group can completely satisfy the coordination requirements of the  $\text{Th}^{4+}$  ion. Communications with MALCOLM (1980) and WEBER (1980) suggest that EDTA may be equivalent in complexing ability to some aqueous humic species. Also, the present and proposed use of EDTA in cleansers and decontaminants in laboratory research and in large-scale decontamination operations involving radionuclides at nuclear facilities (cf. AYRES, 1970; MEANS *et al.*, 1978) makes its consideration here the more appropriate.

The wastes from clean-up operations at such facilities are treated and disposed of in a variety of ways, but quite often end up in near-surface tanks or trenches at radioactive burial sites (CERRE and MESTRE, 1970). There, agents including EDTA can

continue to hold metals such as thorium in solution and so enhance its mobility in leachates that escape the trenches. While oxalate and citrate are eventually destroyed in biochemical processes, EDTA can persist for long periods in solution. MEANS *et al.* (1978) observed migration of  $^{60}\text{Co}$  and other radionuclides, including thorium, from pits and trenches at the Oak Ridge National Laboratory burial site. The mobile species were identified as dissolved complexes of organic ligands, particularly EDTA. These authors found an EDTA concentration of about 98 ppb in well waters near disposal trenches at Oak Ridge.

### THE THERMOCHEMICAL DATA

The thermodynamic data for thorium minerals and solutes at 25°C and 1 atm total pressure are given in Table 1. Table 2 lists thermodynamic data for non-thorium minerals and solutes used to derive the data in Table 1. Footnotes to the tables explain the data sources and methods of calculation. Such data was unavailable for citric acid or EDTA, or for their thorium complexes. However, stability constants for these species were available and are given in Table 3. The data in the tables are considered internally consistent.

A number of Russian authors have proposed that thorium carbonate complexes are important in alkaline waters (cf. SHCHERBINA and ABRAKIROV, 1967). No thermodynamic data exist for such species, which in any case are unlikely to ever be significant. Thus, at alkaline pHs, thorium occurs chiefly as the strong neutral  $\text{Th}(\text{OH})_2$  complex which will have little tendency to associate with carbonate ion.

In Fig. 1 are plotted entropies ( $S^\circ$  values) of thorium

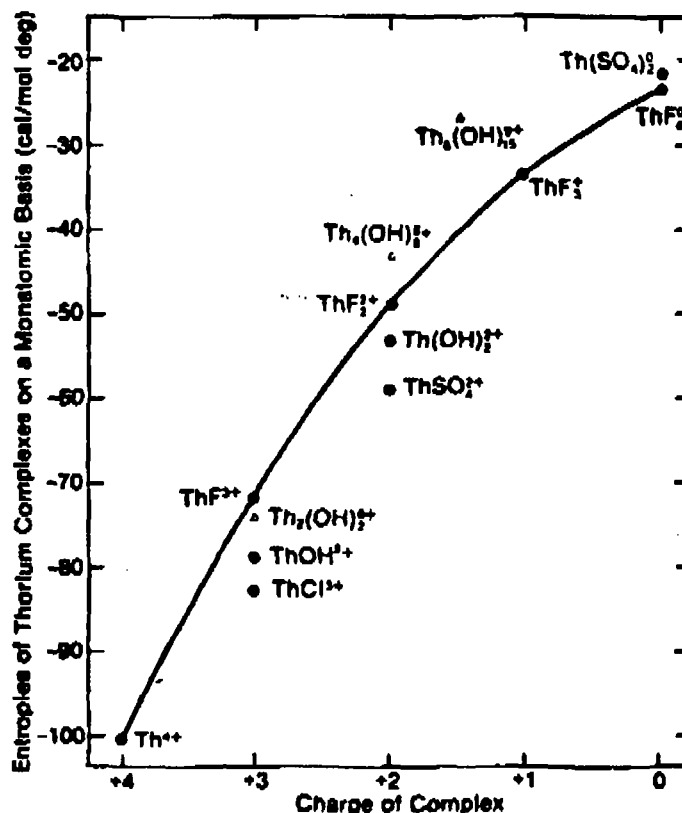


Fig. 1. Entropy vs valence for thorium ion and some thorium complexes on a monatomic basis.

Table 1. Thermochemical data for thorium minerals and aqueous species at 25°C and 1 atm total pressure.  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  and  $S^\circ$  are the free energy and enthalpy of formation from the elements and the entropy, respectively. Parentheses enclose approximate or estimated values, or values derived from them. An asterisk denotes a value derived from measurements in solution at an ionic strength greater than zero (see footnotes)

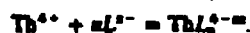
Mineral or aqueous species	$\Delta H_f^\circ$ (kcal/mol)	$\Delta G_f^\circ$ (kcal/mol)	$S^\circ$ (cal/mol deg)	Source
a-Th(c)	0	0	12.76	FUGER and OETTING (1976)
Th <sup>4+</sup>	-183.8	-168.4	-101	FUGER and OETTING (1976)
ThOH <sup>3+</sup>	(-246.2)	-220.7	-79*	FUGER and OETTING (1976)
Th(OH) <sub>2</sub> <sup>2+</sup>	(-306.5)	-272.3	-53*	FUGER and OETTING (1976)
Th(OH) <sub>3</sub> <sup>+</sup>	(-368.4)	(-322.5)	(-36)	See footnotes
Th(OH) <sub>4</sub>	(-438.4)	-373.5	(-24)	See footnotes
Th <sub>2</sub> (OH) <sub>7</sub> <sup>+</sup>	(-489.4)	-441.8	-147*	BAES and MESMER (1976)
Th <sub>3</sub> (OH) <sub>10</sub> <sup>+</sup>	(-1224)	-1098.3	-173*	BAES and MESMER (1976)
Th <sub>4</sub> (OH) <sub>13</sub> <sup>+</sup>	(-2019)	-1810.6	-160*	BAES and MESMER (1976)
Th(OH) <sub>4</sub>	(-449.5)	-408.0	(34)	See footnotes
ThO <sub>2</sub> (c)	—	-273.2	—	See footnotes
ThO <sub>2</sub> (c) thorite	-293.12	-279.35	15.59	CODATA (1977)
ThSiO <sub>4</sub> (c) thorite (huttonite)	—	—	(25.5)	WAGMAN <i>et al.</i> (1977)
ThF <sup>3+</sup>	-265.15	-246.70	-72	See footnotes
ThF <sub>2</sub> <sup>2+</sup>	-346.1	-322.52	-49	WAGMAN <i>et al.</i> (1977)
ThF <sub>3</sub> <sup>+</sup>	-427.1	-396.2	-34	WAGMAN <i>et al.</i> (1977)
ThF <sub>4</sub>	-508.1	-468.2	-24	WAGMAN <i>et al.</i> (1977)
ThF <sub>4</sub> (c)	-501.4	-478.9	33.95	WAGMAN <i>et al.</i> (1977)
ThF <sub>4</sub> ·2.5H <sub>2</sub> O(c)	(-682.2)	(-624.7)	(56.0)	WAGMAN <i>et al.</i> (1977)
ThCl <sup>3+</sup>	-223.7	-201.3	-83	WAGMAN <i>et al.</i> (1977)
ThCl <sub>2</sub> <sup>2+</sup>	—	-232.3	—	WAGMAN <i>et al.</i> (1977)
ThCl <sub>3</sub> <sup>+</sup>	—	-264.8	—	WAGMAN <i>et al.</i> (1977)
ThCl <sub>4</sub>	—	-295.6	—	WAGMAN <i>et al.</i> (1977)
ThCl <sub>4</sub> (c)	-283.6	-261.6	(45.5)	WAGMAN <i>et al.</i> (1977)
ThSO <sub>4</sub> <sup>2+</sup>	-397.2	-353.8	-59	WAGMAN <i>et al.</i> (1977)
Th(SO <sub>4</sub> ) <sub>2</sub> <sup>+</sup>	-611.0	-537.6	-22	WAGMAN <i>et al.</i> (1977)
Th(SO <sub>4</sub> ) <sub>3</sub>	—	-716.6	—	WAGMAN <i>et al.</i> (1977)
Th(SO <sub>4</sub> ) <sub>4</sub>	—	-891.8	—	WAGMAN <i>et al.</i> (1977)
ThH <sub>2</sub> PO <sub>4</sub> <sup>+</sup>	—	-444.1*	—	See footnotes
ThH <sub>2</sub> PO <sub>4</sub> <sup>+</sup>	—	-444.9	—	WAGMAN <i>et al.</i> (1977)
Th(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> <sup>+</sup>	—	-720.9	—	WAGMAN <i>et al.</i> (1977)
ThHPO <sub>4</sub> <sup>+</sup>	(-450.3)	-443.5*	(-60)	See footnotes
Th(HPO <sub>4</sub> ) <sub>2</sub> <sup>+</sup>	(-762.3)	-720.2*	(-24)	See footnotes
Th(HPO <sub>4</sub> ) <sub>3</sub>	—	-992.1*	—	See footnotes
Th(HPO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O(c)	(-1070)	-952.5*	(89)	See footnotes
ThC <sub>2</sub> O <sub>4</sub> <sup>2+</sup>	—	-342.2	—	WAGMAN <i>et al.</i> (1977)
Th(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> <sup>2-</sup>	—	-515.9	—	WAGMAN <i>et al.</i> (1977)
ThC <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	—	-686.8	—	WAGMAN <i>et al.</i> (1977)

a-Th(c):  $S^\circ$  supported by RAND (1975), CODATA (1977), and WAGMAN *et al.* (1977). Th<sup>4+</sup>: Properties determined by FUGER and OETTING (1976), adopted by WAGMAN *et al.* (1977). ThOH<sup>3+</sup> and Th(OH)<sub>2</sub><sup>2+</sup>:  $S^\circ$  values based on potentiometric measurements in 1 M NaClO<sub>4</sub> (BAES and MESMER, 1976). Th(OH)<sub>3</sub><sup>+</sup>:  $\Delta G_f^\circ$  based on estimated K value (BAES and MESMER, 1976).  $S^\circ$  estimated from Fig. 2. Th(OH)<sub>4</sub>:  $\Delta G_f^\circ$  based on K from BAES and MESMER (1976).  $S^\circ$  estimated from Fig. 2. Th<sub>2</sub>(OH)<sub>7</sub><sup>+</sup>, Th<sub>3</sub>(OH)<sub>10</sub><sup>+</sup> and Th<sub>4</sub>(OH)<sub>13</sub><sup>+</sup>:  $S^\circ$  values based on potentiometric measurements in 1 M NaClO<sub>4</sub> (BAES and MESMER, 1976). Th(OH)<sub>4</sub>:  $\Delta G_f^\circ$  based on solubility of 'active' or 'hydrous' ThO<sub>2</sub> given by BAES and MESMER (1976), assuming  $\Delta G_f^\circ = 0$  for: ThO<sub>2</sub> (active) + 2H<sub>2</sub>O = Th(OH)<sub>4</sub>.  $S^\circ$  estimated using Latimer's method with component entropies from NAUMOV *et al.* (1974). ThO<sub>2</sub>(c):  $\Delta G_f^\circ = -273.2$  based on solubility given by BAES and MESMER (1976). ThSiO<sub>4</sub>(c): Huttonite is apparently the stable polymorph at all temperatures (ROGERS and ADAMS, 1969).  $S^\circ$  is estimated as the sum of values for ThO<sub>2</sub>(c) and SiO<sub>2</sub>(c) quartz. ThH<sub>2</sub>PO<sub>4</sub><sup>+</sup>:  $\Delta G_f^\circ$  computed from  $K = 10^{1.89}$  measured at  $I = 2$  for: Th<sup>4+</sup> + H<sub>2</sub>PO<sub>4</sub><sup>-</sup> = ThH<sub>2</sub>PO<sub>4</sub><sup>+</sup> (KATZ and SEABORG, 1957). ThHPO<sub>4</sub><sup>+</sup> through Th(HPO<sub>4</sub>)<sub>2</sub><sup>+</sup>:  $\Delta G_f^\circ$  values based on stability constants measured at  $I = 0.35$  (MOSKVIN *et al.*, 1967).  $S^\circ$  values estimated from Fig. 2. Th(HPO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O(c):  $\Delta G_f^\circ$  based on solubility measured by MOSKVIN *et al.* (1967) at  $I = 0.35$ .  $S^\circ$  estimated by Latimer's method with component entropies:  $S^\circ$  (Th) = 15.9,  $S^\circ$  (HPO<sub>4</sub>) = 15 and  $S^\circ$  (H<sub>2</sub>O) = 10.7.

complexes vs their charge, where the entropy values are reasonably well known based on calorimetric or potentiometric measurements. This plot was used to estimate entropies of other monomeric complexes of the same valence.  $S^\circ$  values for the OH polymers are also plotted for comparison purposes in Fig. 1, where  $S^\circ$  (plotted) =  $S^\circ$  polymer/x;

[x is the number of thorium atoms in the polymer, and the charge of complex (plotted) = charge of polymer/x].

Table 3 lists the cumulative formation constants of thorium complexes with their formation reactions written



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Table 2. Thermochemical data for non-thorium minerals and aqueous species at 25°C and 1 atm total pressure. Values in parentheses are estimates or have been computed using estimated values (see footnotes)

Mineral or aqueous species	$\Delta H_f^\circ$ (kcal/mol)	$\Delta G_f^\circ$ (kcal/mol)	$S^\circ$ (cal/mol deg)	Source
H <sub>2</sub> (g)	0	0	31.207	CODATA (1976)
O <sub>2</sub> (g)	0	0	49.005	CODATA (1976)
H <sub>2</sub> O(l)	-68.315	-56.687	16.71	CODATA (1976)
OH <sup>-</sup>	-54.977	-37.604	-2.560	CODATA (1976)
HF <sup>0</sup>	-76.97	-71.68	22.09	PARKER <i>et al.</i> (1976)
F <sup>-</sup>	-80.15	-67.34	-3.15	PARKER <i>et al.</i> (1976)
Cl <sup>-</sup>	-39.933	-31.379	13.56	CODATA (1976)
PO <sub>4</sub> <sup>3-</sup>	-305.3	-243.5	-53	WAGMAN <i>et al.</i> (1968)
HPO <sub>4</sub> <sup>2-</sup>	-308.83	-260.34	-8.0	WAGMAN <i>et al.</i> (1968)
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-309.82	-270.17	21.6	See footnotes
H <sub>3</sub> PO <sub>4</sub> <sup>0</sup>	-307.92	-273.10	37.8	WAGMAN <i>et al.</i> (1968)
SiO <sub>2</sub> (c) quartz	-217.66	-204.66	9.91	CODATA (1976)
SiO <sub>2</sub> (am)	-215.33	-202.91	11.8	See footnotes
H <sub>4</sub> SiO <sub>4</sub> <sup>0</sup>	-348.30	-312.58	45.1	See footnotes
H <sub>3</sub> SiO <sub>3</sub> <sup>-</sup>	-342.18	-299.18	20.7	BUESY and MERMER (1977)
H <sub>2</sub> SiO <sub>2</sub> <sup>2-</sup>	—	-281.31	—	BAES and MERMER (1976)
SO <sub>4</sub> <sup>2-</sup>	-217.40	-177.95	4.50	CODATA (1977)
HSO <sub>4</sub> <sup>-</sup>	-212.16	-180.67	31.2	See footnotes
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-194.7	-168.6	44.4	See footnotes
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	-195.6	-166.93	35.7	WAGMAN <i>et al.</i> (1968)
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	-197.2	-161.1	10.9	WAGMAN <i>et al.</i> (1968)

H<sub>2</sub>PO<sub>4</sub><sup>-</sup>: WAGMAN *et al.* (1968) give  $\Delta G_f^\circ = -260.17$  kcal/mol, which is apparently a misprint. The tabulated value is consistent with well established stability constant data and with the tabulated  $\Delta H_f^\circ$  and  $S^\circ$  values. SiO<sub>2</sub>(am):  $\Delta G_f^\circ$  based on the stability of amorphous silica from 0-250°C, written SiO<sub>2</sub>(am) + 2H<sub>2</sub>O = H<sub>4</sub>SiO<sub>4</sub><sup>0</sup>, for which log [H<sub>4</sub>SiO<sub>4</sub><sup>0</sup>] molar = -0.259-731/T(K) (FOURNIER, 1976). KILDAY and PROSEN (1973) measured  $\Delta H_f^\circ = 2.22 \pm 0.07$  kcal/mol for SiO<sub>2</sub>(quartz) = SiO<sub>2</sub>(am) from which  $\Delta H_f^\circ = -215.33$  and combined with  $\Delta G_f^\circ$  from FOURNIER (1976),  $S^\circ = 11.8$  cal/mol deg. The temperature function of FOURNIER (1976) leads to  $S^\circ = 10.5$  cal/mol deg. H<sub>4</sub>SiO<sub>4</sub><sup>0</sup>: Data based on log[H<sub>4</sub>SiO<sub>4</sub><sup>0</sup>] molar = 0.394-1310/T(K) from 25-250°C for quartz solubility written SiO<sub>2</sub>(quartz) + 2H<sub>2</sub>O = H<sub>4</sub>SiO<sub>4</sub><sup>0</sup> (MOREY *et al.*, 1962). HSO<sub>4</sub><sup>-</sup>:  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  and  $S^\circ$  adjusted relative to values for SO<sub>4</sub><sup>2-</sup> assuming properties for the reaction H<sup>+</sup> + SO<sub>4</sub><sup>2-</sup> = HSO<sub>4</sub><sup>-</sup> unchanged from properties computed using values given by WAGMAN *et al.* (1968). H<sub>2</sub>C<sub>2</sub>O<sub>4</sub><sup>2-</sup>: MARTELL and SMITH (1977) list log K = 1.252 and  $\Delta H_f^\circ = 0.9 \pm 0.1$  kcal/mol for H<sup>+</sup> + HC<sub>2</sub>O<sub>4</sub><sup>-</sup> = H<sub>2</sub>C<sub>2</sub>O<sub>4</sub><sup>2-</sup>. The data for H<sub>2</sub>C<sub>2</sub>O<sub>4</sub><sup>2-</sup> are computed from this information and tabulated results for HC<sub>2</sub>O<sub>4</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup>. The properties of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub><sup>2-</sup> listed by Wagman *et al.* are in error.

In this expression  $L$  is the ligand of valence  $z$  and  $n$  is the number of ligand groups in the complex. In some cases, for comparison purposes, more than a single source and constant are listed in Table 3. Sources of the data chosen for inclusion in Table 1 are indicated in the 'Source' column of that table. The stability constants and entropies of the Th-OH complexes given by BAES and MERMER (1976) have been adapted here. These authors provide a more complete description of the Th-OH system than do WAGMAN *et al.* (1977), who give only data for ThOH<sup>3+</sup>, Th(OH)<sub>2</sub><sup>2+</sup> and the dimer Th<sub>2</sub>(OH)<sub>4</sub><sup>2+</sup>. Entropies of the first two for these species given by Wagman *et al.* are -82 and -52 cal/mol deg respectively, in good agreement with the tabulated values.

Data are unavailable for complexes between Th<sup>4+</sup> and H<sub>4</sub>SiO<sub>4</sub><sup>0</sup> or H<sub>3</sub>SiO<sub>3</sub><sup>-</sup>; however, such complexes are likely to be important in acid, silica-rich waters. No empirical thermodynamic values are available for thorite.

Writing the solubility of ThO<sub>2</sub>(thorianite) as



permits us to compare the stabilities of ThO<sub>2</sub> and Th(OH)<sub>4</sub>. Thus,  $K_{sp}$  [Th(OH)<sub>4</sub>] = 10<sup>-44.0</sup>; and  $K_{sp}$  [ThO<sub>2</sub>(c)] = 10<sup>-44.7</sup> based on solubility measurements reported in BAES and MERMER (1976) and 10<sup>-44.2</sup> computed from the CODATA (1977)  $\Delta G_f^\circ$  value for thorianite. The disparity between these last 2 values is disturbing. However, the full range of  $K_{sp}$  values of 7.6 log units separating the amorphous and crystalline Th oxides and hy-

droxides is perfectly possible for a quadrivalent cation such as Th<sup>4+</sup>. Approximate solubilities of Th(OH)<sub>4</sub> and ThO<sub>2</sub>(c) as a function of temperature to near 300°C are reported by ROBINS (1967).

#### DISSOLVED THORIUM SPECIES

Cumulative formation constants of the complexes vs ligand number are plotted in Fig. 2. In general, the stronger the 1:1 complex, the more likely that an important 1:2 and 1:3 complex will also exist. Weak 1:1 complexes as are formed with Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>0</sup> indicate that higher order complexes will also be unimportant. Strong complexes are formed with H<sub>2</sub>PO<sub>4</sub><sup>0</sup>, SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>. The strongest common inorganic complexes are formed with OH<sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>. The organic species, oxalate, citrate and especially EDTA, form strong complexes with thorium.

Application of the stability constant data shows that thorium in natural waters is usually complexed with sulfate, fluoride, phosphate, hydroxide and organic anions. These complexes greatly increase the solubility of thorium minerals and the mobility of thorium in surface, soil and ground waters. To

Table 3. Cumulative formation constants of  $\text{Th}^{4+}$  complexes at 25°C. Parentheses denote estimated values. Where more than one value for a complex is shown, an asterisk indicates the value chosen for inclusion in Table 1

Complex	Log K	I	Source
$\text{ThOH}^{3+}$	10.8*	0	BAES and MESMER (1976)
	10.2	0	WAGMAN <i>et al.</i> (1977)
$\text{Th(OH)}_2^{2+}$	21.07*	0	BAES and MESMER (1976)
	21.23	0	WAGMAN <i>et al.</i> (1977)
$\text{Th(OH)}_3^{+}$	(30.3)	0	BAES and MESMER (1976)
$\text{Th(OH)}_4^0$	40.1	0	BAES and MESMER (1976)
$\text{ThF}^{3+}$	8.44*	0	BAUMAN (1970)
	8.03*	0	WAGMAN <i>et al.</i> (1977)
$\text{ThF}_2^{2+}$	15.06	0	BAUMAN (1970)
	14.25*	0	WAGMAN <i>et al.</i> (1977)
$\text{ThF}_3^{+}$	19.81	0	BAUMAN (1970)
	18.93*	0	WAGMAN <i>et al.</i> (1977)
$\text{ThF}_4^0$	23.17	0	BAUMAN (1970)
	22.31*	0	WAGMAN <i>et al.</i> (1977)
$\text{ThCl}^{3+}$	1.35	0	See footnotes
	1.09*	0	WAGMAN <i>et al.</i> (1977)
$\text{ThCl}_2^{2+}$	0.80	0	WAGMAN <i>et al.</i> (1977)
$\text{ThCl}_3^{+}$	1.65	0	WAGMAN <i>et al.</i> (1977)
$\text{ThCl}_4^0$	1.26	0	WAGMAN <i>et al.</i> (1977)
$\text{ThHPO}_4^{3+}$	10.8	0.35	MOSKVIN <i>et al.</i> (1967)
$\text{Th(HPO}_4)_2^{2+}$	22.8	0.35	MOSKVIN <i>et al.</i> (1967)
$\text{Th(HPO}_4)_3^{+}$	31.3	0.35	MOSKVIN <i>et al.</i> (1967)
$\text{ThH}_2\text{PO}_4^{2+}$	4.52	0	WAGMAN <i>et al.</i> (1977)
$\text{Th(H}_2\text{PO}_4)_2^{+}$	8.88	0	WAGMAN <i>et al.</i> (1977)
$\text{ThH}_3\text{PO}_4^0$	1.91	2	KATZ and SEABORG (1957)
$\text{ThSO}_4^{2+}$	(6.17)	0	See footnotes
	5.45*	0	WAGMAN <i>et al.</i> (1977)
$\text{Th(SO}_4)_2^0$	(9.59)	0	See footnotes
	9.73*	0	WAGMAN <i>et al.</i> (1977)
$\text{Th(SO}_4)_3^{2-}$	(10.34)	0	See footnotes
	10.50*	0	WAGMAN <i>et al.</i> (1977)
$\text{Th(SO}_4)_4^{4-}$	(8.27)	0	See footnotes
	8.48*	0	WAGMAN <i>et al.</i> (1977)
$\text{ThNO}_3^{3+}$	0.94	0	WAGMAN <i>et al.</i> (1977)
$\text{Th(NO}_3)_2^{2+}$	1.97	0	WAGMAN <i>et al.</i> (1977)
$\text{ThC}_2\text{O}_4^{2+}$	9.30	0	WAGMAN <i>et al.</i> (1977)
$\text{ThC}_2\text{O}_6^{2+}$	18.54	0	WAGMAN <i>et al.</i> (1977)
$\text{ThC}_2\text{O}_6^{2+}$	25.73	0	WAGMAN <i>et al.</i> (1977)
$\text{ThC}_6\text{H}_5\text{O}_7^{+}$	13.00	0.5	See footnotes
$\text{ThC}_6\text{H}_5\text{O}_7^{+}$	20.97	0.5	See footnotes
$\text{ThEDTA}^0$	25.30	0.1	See footnotes
$\text{ThHEDTA}^+$	17.02	0.1	See footnotes

$\text{ThCl}^{3+}$ : At  $I = 0.5$  KATZ and SEABORG (1957) give  $K_1 = 2.24$  for  $\text{Th}^{4+} + \text{Cl}^- = \text{ThCl}^{3+}$ . Correction to  $I = 0$ , assuming the same activity coefficient behavior as observed for  $\text{ThOH}^{3+}$  in perchlorate media (AHLAND *et al.*, 1973), gives  $K_1 = 10^{1.33}$ .  $\text{ThSO}_4^{2+}$  through  $\text{Th(SO}_4)_4^{4-}$ : ALLEN and McDOWELL (1963) measured  $\log K_3 = 0.75$  and  $\log K_4 = -2.07$  for the successive stability constants of  $\text{Th(SO}_4)_2^{2+}$  and  $\text{Th(SO}_4)_3^{2-}$  respectively at  $I = 0$ . AHLAND *et al.* (1973) give  $\log K_2 = 2.42$  for  $I = 2$ . Rough correction to  $I = 0$  gives  $\log K_2 = 3.42$ . These data lead to stepwise differences of  $\log (K_3/K_4) = 2.82$  and  $\log (K_2/K_3) = 2.67$ . Assuming the average of 2.75 applies to  $\log (K_1/K_2)$  leads to  $\log K_1 = 6.17$  at  $I = 0$ . Values based on these calculations are shown in parentheses in Table 3. Th-citrate: NEBEL and URBAN (1966) as reported in SILLEN and MARTELL (1971). Th-EDTA and Th-HEDTA: BOTTARI and ANDEREGG (1967), as reported in SILLEN and MARTELL (1971).

properly judge the relative importance of these complexes, we must compare their amounts in solutions that contain typical concentrations of the complexing ligands.

The thermochemical data in Tables 1-3 have been used to construct the diagrams in Figs 2-11. Math-

ematical methods needed to develop the percentage distribution of complexes in Figs 3-8 and the mineral solubility diagrams in Figs 9-11 are described by BUTLER (1964). Creation of the more complicated diagrams was accomplished by programming the calculations on an IBM 370/168 computer. The diagrams

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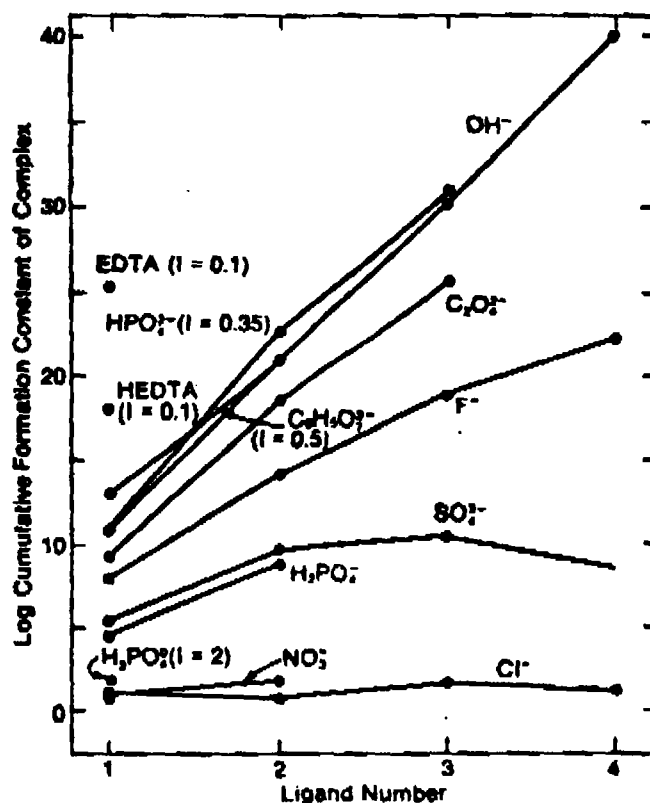
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Fig. 2. Cumulative formation constants of monomeric  $\text{Th}^{4+}$  complexes at 25°C plotted against their ligand numbers. Constants are for zero ionic strength except where indicated.

are presented in terms of Th species concentrations, assuming ionic strengths and activity coefficients defined by the total concentrations specified for each plot.

#### Distribution of aqueous species

The distribution of aqueous thorium species for different water compositions was calculated to establish the relative importance of the various complexes in typical natural waters. Since the degree of thorium

complexation is independent of its total concentration when a complexing ligand is in large excess over thorium, these distribution diagrams apply to a range of thorium concentrations depending upon which ligand is of interest. The calculations were made for 0.01 ppb total thorium, a concentration much smaller than that for any of the anions.

Figure 3 shows the range of predominance of dissolved thorium species in pure water. Free  $\text{Th}^{4+}$  ion dominates at pH's below 3. From about pH 3 to 4.5,

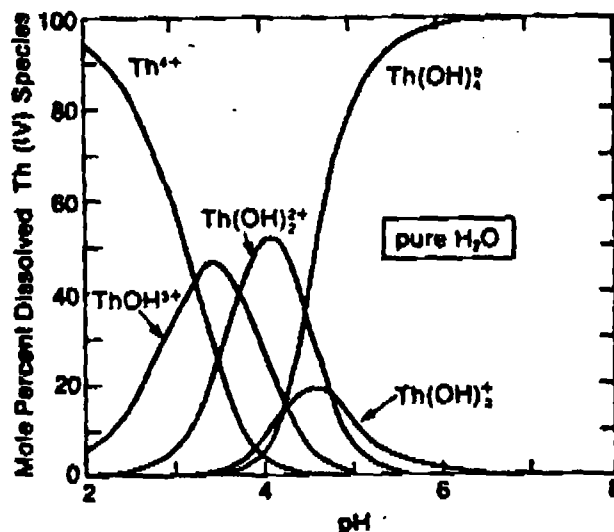


Fig. 3. Distribution of thorium-hydroxy complexes vs pH at 25°C with  $\Sigma\text{Th} = 0.01$  ppb in pure water.

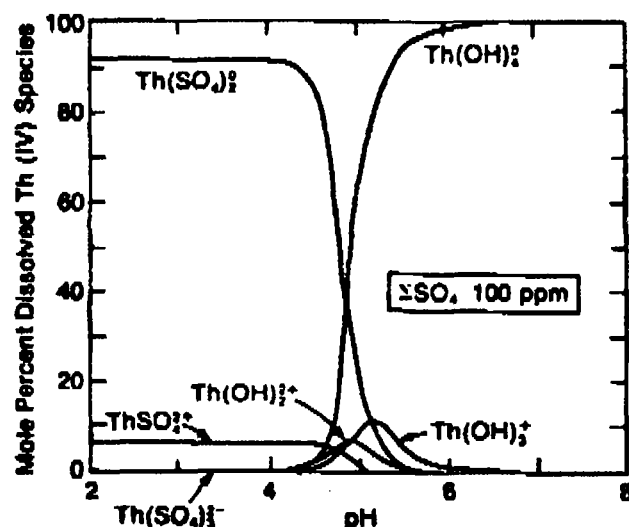


Fig. 4. Distribution of thorium-hydroxy and sulfate complexes vs pH at 25°C with  $\Sigma\text{Th} = 0.01$  ppb and  $\Sigma\text{SO}_4 = 100$  ppm.

the 1:1 and 1:2 hydroxy complexes predominate. Above pH 4.5,  $\text{Th}(\text{OH})_2^{2+}$  is the major species. Figures 4–6 show the distribution of species in solutions of common inorganic ligands, sulfate, fluoride and phosphate, respectively. The anion concentrations used in each case are typical of those in natural waters. In a solution of 100 ppm total sulfate,  $\text{Th}(\text{SO}_4)_3^{2-}$  is vastly more important than other sulfate complexes or free  $\text{Th}^{4+}$  ion. Above pH 5,  $\text{Th}(\text{OH})_2^{2+}$  is the most important aqueous species. Total fluoride equal to 0.3 ppm makes  $\text{ThF}_3^{+}$  the major fluoride complex, although the 1:3 and 1:1 complexes are also significant.  $\text{Th}(\text{OH})_2^{2+}$  dominates the pH region above about 5.5.  $\text{ThH}_2\text{PO}_4^{2+}$ ,  $\text{Th}(\text{HPO}_4)_2^{+}$ ,  $\text{Th}(\text{HPO}_4)_3^{-}$ , and  $\text{Th}(\text{OH})_2^{2+}$  each in turn predominate as pH increases in a 0.1 ppm total phosphate solution.

Combining these anion concentrations to create a typical groundwater and calculating the correspond-

ing distribution of thorium species in such a solution results in Fig. 7.  $\text{Th}(\text{SO}_4)_3^{2-}$ ,  $\text{ThF}_3^{+}$ ,  $\text{Th}(\text{HPO}_4)_3^{-}$ ,  $\text{Th}(\text{HPO}_4)_2^{+}$ , and  $\text{Th}(\text{OH})_2^{2+}$  are each in turn the most abundant aqueous species as pH increases.

Similar distribution calculations made for each of the organic ligands considered individually showed generally that the thorium-organic complexes predominate over Th-OH complexes below about pH 7. Figure 8 is a percent dissolved total thorium vs pH diagram calculated for a water with all the anions previously considered as present. The  $\text{ThEDTA}^0$  complex clearly dominates among the aqueous species up to approximately pH 8.

#### Solubility of thorianite

Solubility diagrams were generated assuming equilibrium with thorianite. A more abundant mineral such as monazite, with thorium in solid solution,

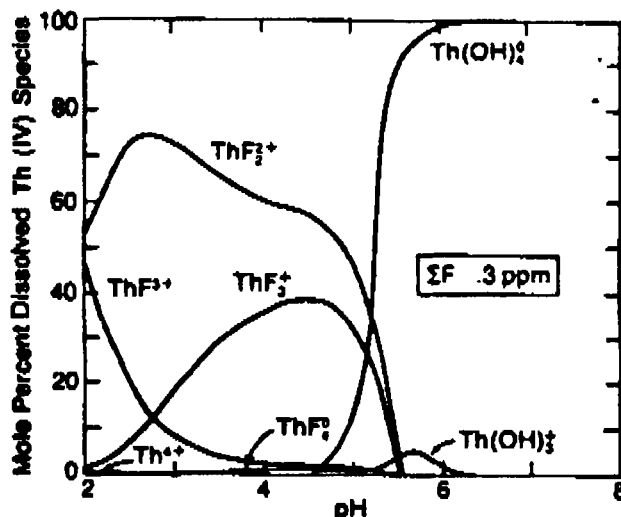


Fig. 5. Distribution of thorium-hydroxy and fluoride complexes vs pH at 25°C with  $\Sigma\text{Th} = 0.01$  ppb and  $\Sigma\text{F} = 0.3$  ppm.

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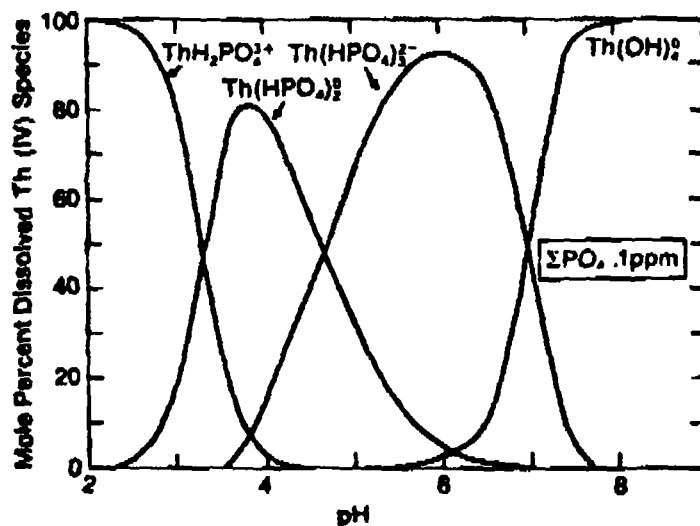


Fig. 6. Distribution of thorium-hydroxy and phosphate complexes vs pH at 25°C with  $\Sigma\text{Th} = 0.01$  ppb and  $\Sigma\text{PO}_4 = 0.1$  ppm.

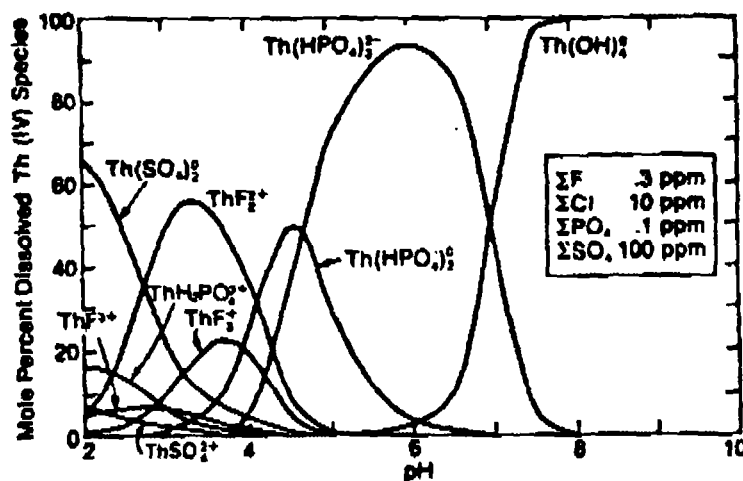


Fig. 7. Distribution of thorium complexes vs pH for some typical ligand concentrations in ground water at 25°C with  $\Sigma\text{Th} = 0.01$  ppb.

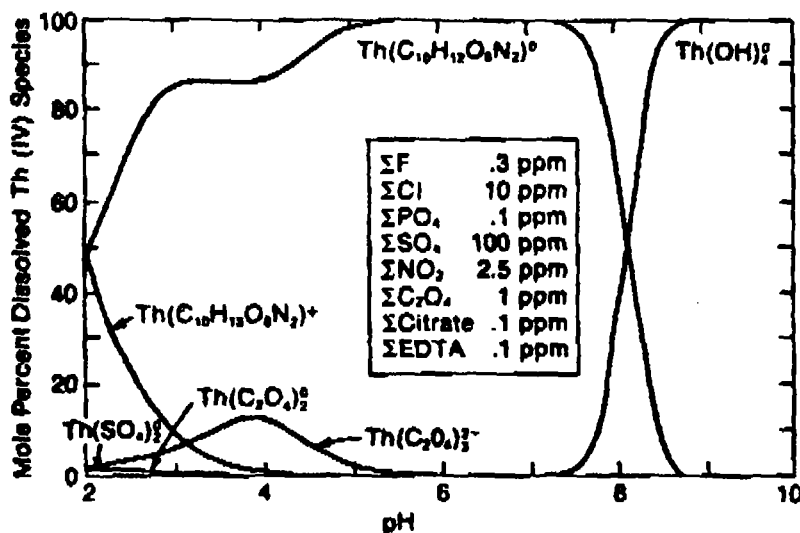


Fig. 8. Distribution of thorium complexes vs pH in a solution containing inorganic and organic species at the concentrations indicated and 25°C with  $\Sigma\text{Th} = 0.01$  ppb.

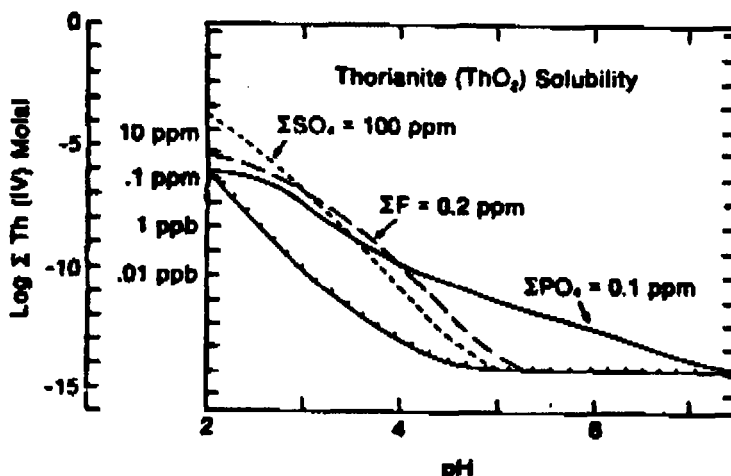


Fig. 9. The effect of thorium-sulfate, fluoride and phosphate complexing on the solubility of thorianite,  $\text{ThO}_2(\text{c})$ , as a function of pH at 25°C. The cross-hatched curve denotes the solubility of thorianite in pure water. The curves indicating thorianite solubility as affected by complexing have been constructed assuming each ligand present in the absence of the others.

could not be considered because of a lack of thermodynamic data.

The individual effects of  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions on thorianite solubility are negligible. Even in sea water (pH 8.1) with  $\text{Cl}^- = 19,000$  ppm,  $\text{Th-Cl}^-$  complexing is insignificant relative to hydroxyl complexing. For nitrate concentrations up to 1000 ppm,  $\text{Th-NO}_3^-$  complexes never approach 1% of total  $\text{Th-OH}^-$  complexes. Sulfate increases thorianite solubility below pH 5, as shown in Fig. 9. Dissolved thorium is increased by three orders of magnitude at pH 3 in the presence of 100 ppm total sulfate alone in solution. However, except in acid mine water and raffinates, and acid sulfate soils and  $\text{H}_2\text{SO}_4$  leachates from hydrothermal uranium ores, increases in  $\text{ThO}_2$  solubility due to sulfate complexing would generally be unimportant. Even in seawater with  $\text{SO}_4 = 2650$  ppm, sulphate complexes are insignificant relative to

hydroxyl complexes. Fluoride also increases  $\text{ThO}_2$  solubility in the low pH range (Fig. 9) and does so significantly more than does sulfate alone at the same concentration. Thus, 2 ppm total fluoride can increase dissolved thorium from  $10^{-4}$  ppb to 10 ppb at pH 4. Phosphate can increase thorianite solubility up to pH 7 (Fig. 9). For example, at pH 4, 0.1 ppm total phosphate increases  $\text{ThO}_2$  solubility by a thousand-fold.

In general, organic ligands greatly enhance the solubility of thorianite at pH's below 7. As shown in Fig. 10, 1 ppm total oxalate increases  $\text{ThO}_2$  solubility by  $10^7$  times at pH 4. Only 1 ppb total EDTA (not shown in Fig. 10) similarly increases thorianite solubility by nearly  $10^6$  times at pH 5. Corresponding calculations for citrate show it to be a less important complexer than oxalate or EDTA. The final solubility diagram in Fig. 11 depicts the effect of the combined

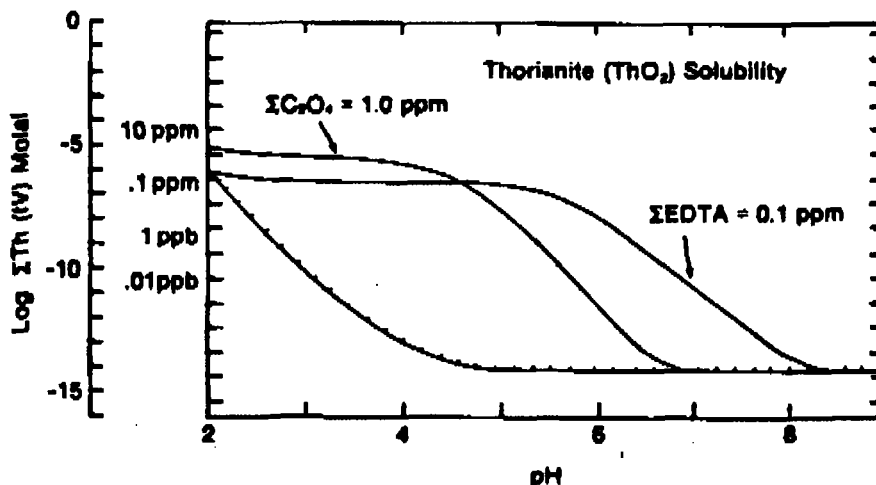


Fig. 10. The effect of thorium-oxalate vs thorium-EDTA complexing on the solubility of thorianite,  $\text{ThO}_2(\text{c})$ , as a function of pH at 25°C. The cross-hatched curve denotes the solubility of thorianite in pure water. The curves indicating thorianite solubility as affected by complexing have been constructed assuming each ligand present in the absence of the other.

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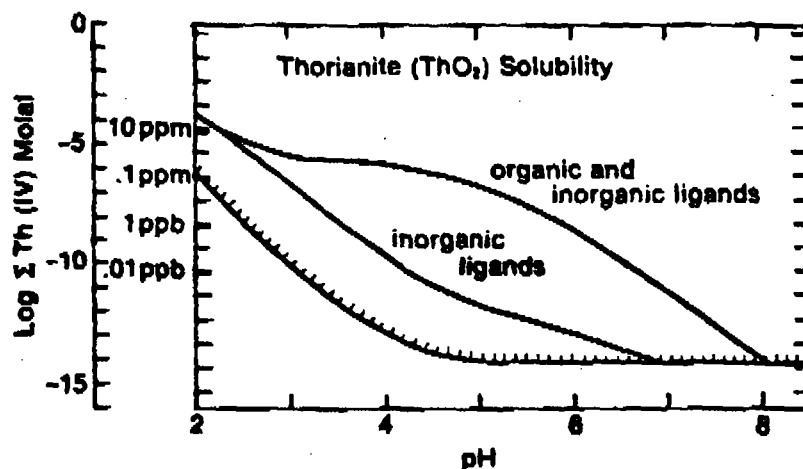
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Fig. 11. The effect of thorium complexing on the solubility of thorianite.  $\text{ThO}_2(\text{c})$  vs pH at  $25^\circ\text{C}$  in a solution of  $\text{ECI} = 10 \text{ ppm}$ ,  $\text{ZNO}_3 = 2.5 \text{ ppm}$ ,  $\text{ESO}_4 = 100 \text{ ppm}$ ,  $\text{ZF} = 0.3 \text{ ppm}$ ,  $\text{ZPO}_4 = 0.1 \text{ ppm}$ ,  $\text{Zoxalate} = 1 \text{ ppm}$ ,  $\text{Zcitrate} = 0.1 \text{ ppm}$  and  $\text{ZEDTA} = 0.1 \text{ ppm}$ .

solution compositions.  $\text{ThO}_2$  solubility with the organic ligands present is increased five orders of magnitude above the purely inorganic solubility at pH 5. The range of increased solubility extends up to pH 8, whereas inorganic ligands alone significantly effect solubility only below pH 7.

Qualitative calculations by AMES and RAI (1978) suggest that in the presence of calcium phosphates, thorium phosphate solids may be even less soluble than thorianite above pH 6. However, because their results were obtained without considering complexes such a conclusion is tenuous.

#### SORPTION OF THORIUM

Most studies of thorium-sorption onto natural materials have at best led to qualitative results. The bulk of such work has involved measurement of a distribution coefficient,  $K_d$ , defined as the radionuclide concentration on the solid/weight of solid, divided by the radionuclide concentration in solution/solution volume. Such values have rarely been determined with adequate consideration of the detailed mineralogy and surface chemistry of sorbent phases, or of the solution, including its speciation and reaction chemistry (cf. DAHLMAN *et al.*, 1976). AMES and RAI (1979, pp. 2-30) summarize some of the common deficiencies in such work. Nevertheless, some useful information on the sorption behavior of thorium has been obtained.

The adsorption of thorium onto clays, oxides and organic matter increases with increasing pH and is practically complete at pH 6.5 (BONDIETTI, 1974). Inhibition of adsorption and a tendency towards desorption is favored when strongly complexing organic ligands such as fulvic or citric acids, or EDTA are present (BONDIETTI, *ibid.*). In neutral to acid waters, thorium adsorption is less complete onto clays than onto solid humic substances. Conversely, the formation of thorium-organic complexes leads to more

complete desorption of thorium from clay than from organic matter.

Because thorium ion is largely hydrolyzed at pHs above 3.2, it is evident that the hydroxy complexes are involved in the sorption process and that aquothorium ion ( $\text{Th}^{4+}$ ) is not as readily adsorbed. This will in part reflect the fact that  $\text{Th}^{4+}$  must compete with protons for exchange sites (cf. DAVIS and LECKIE, 1979). VYDRA and GALBA (1967) found that only minor sorption of thorium onto silica gel occurred at pHs below 2, but that sorption increased with pH to maximum values at about pH 5.5. Employing a mixed quartz-illite soil as sorbent, RANCON (1973) measured a  $K_d$  value of 5 ml/g at pH 2, but  $K_d$  rose to  $5 \times 10^5 \text{ ml/g}$  at pH 6. With a quartz-illite-calcite-organic matter soil, RANCON found that  $K_d$  decreased from  $10^6 \text{ ml/g}$  at pH 8 to  $100 \text{ ml/g}$  at pH 10. This reduction in sorption with increased pH was attributed to dissolution of soil humic acids and the formation of thorium-organic complexes.

Unfortunately, the published research on thorium adsorption to date has been insufficiently detailed to allow more than qualitative application of such results to complex natural systems. Distribution coefficients have no accurate predictive value outside the laboratory systems employed for their measurement. Future research should instead be directed towards measurement of thermodynamically meaningful adsorption constants, which require a relatively complete knowledge of the activities of dissolved species including complexes, and of the surface properties of sorbent phases (cf. DAVIS and LECKIE, 1979; LANGMUIR and OZSVATH, 1980).

#### RELATIONSHIP BETWEEN THE MOLAR CONCENTRATION OF THORIUM AND ITS RADIOACTIVITY /

The radioactive isotopic concentration of a given element in water is usually determined from the

water's radioactivity reported in pico-Curies ( $10^{-12}$  Ci) per liter. To convert the radioactivity measurement to molar concentration per liter, the pico-Curies value must first be converted to decays per second (dps), where  $1 \text{ pCi} = 0.037 \text{ dps}$ . From the radioactive decay law, the expression  $T = (\ln 2)/\lambda$  is derived, where  $T$  is the half-life of the radionuclide in seconds and  $\lambda$  is the probability that the nuclide will decay within a given time. By definition: Disintegration rate ( $D$ ) =  $\lambda N$ , where  $N$  is the number of radioactive atoms present. Then:  $N = D(\text{dps})/\lambda(\text{sec}^{-1})$ . Substituting  $(\ln 2)/T$  for  $\lambda$ , and dividing the preceding expression by Avogadro's number ( $6.022 \times 10^{23}$  atoms/mol) to convert atoms per liter to moles per liter (M), leads to a general equation relating radioactivity to concentration for any radionuclide:

$$M(\text{mol/l}) = 10^{-23.65} D(\text{pCi/l}) \times T(\text{sec})$$

The predominant thorium isotope (near 100% of total Th) is  $^{232}\text{Th}$ , with a half-life of  $4.4 \times 10^{10}$  sec. The isotope  $^{230}\text{Th}$  has a half-life of  $2.5 \times 10^4$  sec. Half-lives of the other thorium isotopes are given by ROSLER and LANGE (1972). The total thorium concentration based on a  $^{232}\text{Th}$  isotope analysis is given by

$$^{232}\text{Th}(\text{mol/l}) = 10^{-7.41} D(\text{pCi/l})$$

Similarly, the molar concentration of  $^{230}\text{Th}$  based on a  $^{230}\text{Th}$  isotope analysis is given by

$$^{230}\text{Th}(\text{mol/l}) = 10^{-12.65} D(\text{pCi/l})$$

In order to predict the reaction chemistry of thorium it is necessary to compute total dissolved thorium from an isotopic analysis of  $^{232}\text{Th}$ .  $^{230}\text{Th}$  is the most important thorium isotope in the decay series beginning with  $^{238}\text{U}$  and the most important thorium isotope in terms of its radioactivity in uranium mill tailings (ANON., 1976) and in many ground waters affected by uranium mining, milling and tailings disposal (KAUFMAN *et al.*, 1976; MOFFETT and TELLIER, 1978). The effect of reaction chemistry on  $^{230}\text{Th}$  mobility can be estimated from its molar concentration ratio relative to  $^{232}\text{Th}$ . Without a  $^{232}\text{Th}$  analysis, however, the solution-reaction chemistry of  $^{230}\text{Th}$  can only be qualitatively predicted.

MOORE and SWAMI (1972) suggest that the natural radioactivity ratio of  $^{230}\text{Th}$  to  $^{232}\text{Th}$  is about 0.8 in river waters and river sediments. This corresponds to a molar concentration ratio of about  $4.6 \times 10^{-6}$ . In ground waters, seepages and injection well waters from the uraniumiferous Grants Mineral Belt in New Mexico (KAUFMAN *et al.*, 1976) the  $^{230}\text{Th}/^{232}\text{Th}$  radioactivity ratio averaged 431 and ranged from 0.96 to 1607 in 6 waters for which analyses of both isotopes were above detection. Clearly the radioactivity due to  $^{230}\text{Th}$  usually predominates in such waters. In these same waters the concentration ratio of these isotopes averaged  $2.5 \times 10^{-3}$  and ranged from  $6.8 \times 10^{-6}$  to  $9.1 \times 10^{-3}$ , indicating the predominance of  $^{232}\text{Th}$  on a concentration basis. Unfortunately, chemical and isotopic analyses of ground

waters and related hydrologic, geologic and mineralogic data are not complete enough in this or in other published studies to allow quantitative prediction of the roles of thorium complexing, solution-mineral equilibria, or thorium adsorption on thorium mobility in these natural systems.

## CONCLUSIONS AND DISCUSSION

Theoretical calculations based on critically assessed thermodynamic data indicate that thorium complexing can increase the mobility of dissolved thorium by many orders of magnitude below pH 8 relative to the solubility of thorium-bearing minerals in pure water as exemplified by the solubility of thorianite ( $\text{ThO}_2$ ) above pH 5, which is only  $10^{-5}$  ppb Th as  $\text{Th}(\text{OH})_2$ . The important inorganic complexes of thorium with increasing pH are  $\text{Th}(\text{SO}_4)_2$ ,  $\text{ThF}_2^+$ ,  $\text{Th}(\text{HPO}_4)_2$ ,  $\text{Th}(\text{HPO}_4)_3^-$  and  $\text{Th}(\text{OH})_2$  respectively. Organic complexes as exemplified by those formed with citrate, oxalate and EDTA must greatly predominate over inorganic thorium complexes in organic-rich waters including many soil waters.

Studies by BONDIETTI (1974) and others show that adsorption of dissolved thorium increases markedly with pH above pH 2, with maximum amounts of thorium adsorption (95–100%) onto clays, oxyhydroxides and organic matter attained at pH values above 5.5–6.5. Adsorption is more complete onto humic organic solids than onto clays. Organic ligands such as citrate and EDTA that form strong thorium complexes, inhibit adsorption and can lead to partial desorption of thorium (RANCON, 1973; BONDIETTI, 1974).

Thorium is concentrated in natural sediments largely either in detrital resistate minerals such as monazite, rutile and thorianite, or adsorbed onto natural colloidal-sized materials. The tendency of thorium to be strongly adsorbed by clays and oxyhydroxides explains its anomalously high mean concentrations in bauxites (49 ppm), bentonites (24 ppm) and pelagic clays (30 ppm), and its range in marine manganese nodules (24–124 ppm). Thorium in bauxites is apparently both sorbed and in resistate minerals. These values may be compared to thorium concentrations generally less than 13 ppm in shales, and less than 5–7 ppm in arkoses and graywackes. (Proceeding data are from ROGERS and ADAMS, 1969.)

Although thorium complexing in natural waters increases the solubility of thorium-bearing minerals and can lead to desorption of thorium, thorium concentrations in natural waters (pH 5–9) rarely exceed 1 ppb. This is equivalent to a radioactivity of 0.1 pCi/l as  $^{232}\text{Th}$ , and assuming a natural activity ratio of 0.8 for  $^{230}\text{Th}/^{232}\text{Th}$  (MOORE and SWAMI, 1972) to 0.08 pCi/l as  $^{230}\text{Th}$ . This low total thorium concentration must reflect a combination of slow solution rates, paucity and insolubility of thorium-bearing minerals, and strong adsorption of thorium by natural materials in this pH range.

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Thorium adsorption and the insolubility of thorium minerals in so-called 'low acid class' ground waters beneath an abandoned uranium tailings area at Elliot Lake, Ontario, may explain the fact that  $^{232}\text{Th}$  and  $^{230}\text{Th}$  activities in the ground water were below detection (MOFFETT and TELLER, 1978). In 'high acid class' ground waters beneath the tailings, however,  $^{232}\text{Th}$  concentrations were as high as 38 mg/l (4200 pCi/l) and  $^{230}\text{Th}$  concentrations in the same ground water up to 0.0028 mg/l (52,000 pCi/l). Probably the thorium in these ground waters was present chiefly as sulfate complexes, released in the case of  $^{232}\text{Th}$  by acid leaching of thorium-bearing minerals. The U.S. Environmental Protection Agency (ANON., 1976) has reported that waste milling solutions (sulfuric acid leach, pH 1.5-2) from the Highland Uranium Mill in Wyoming contained 22,000 pCi/l of  $^{230}\text{Th}$  (1.1 ppb). These high  $^{230}\text{Th}$  values reflect the greater mobility under acid conditions of  $^{230}\text{Th}$  formed from the radioactive decay of  $^{238}\text{U}$ . This may be contrasted with a  $^{230}\text{Th}$  activity of 110 pCi/l (0.0057 ppb) in alkaline (pH = 10) leach solutions discharged from the Humecca Uranium Mill (ANON., 1976). The alkaline pH values employed in the milling process tend to minimize both complexing and the solubility of thorium minerals and favor thorium adsorption onto clays, oxyhydroxides and other fine-sized materials in tailings from the mill.

The thermochemical data and adsorption results considered in this paper help to explain the behavior of thorium and its isotopes in natural waters, sediments and wastes. However, published studies of natural systems have inevitably lacked sufficient geochemical, mineralogic, geologic and/or hydrologic data to permit an unambiguous explanation for, or prediction of, thorium behavior. Also needed for such prediction is solubility data for important thorium-bearing minerals such as monazite, thorite and uranothorite. Finally, more sophisticated adsorption studies should be performed in which thorium adsorption is measured as a function of pH, thorium complexation, activities of competing cations and their complexes, and other solution properties, and with an understanding of the detailed surface properties of the sorbent phases.

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