LBL-12528
Reprint c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA, BERKELEY

EARTH SCIENCES DIVISION

Published in Geochimica et Cosmochimica Acta,
Vol. 44, No. 11, 1980, pp. 1753-1766

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUN 11 1981

LIBRARY AND
DOCUMENTS SECTION

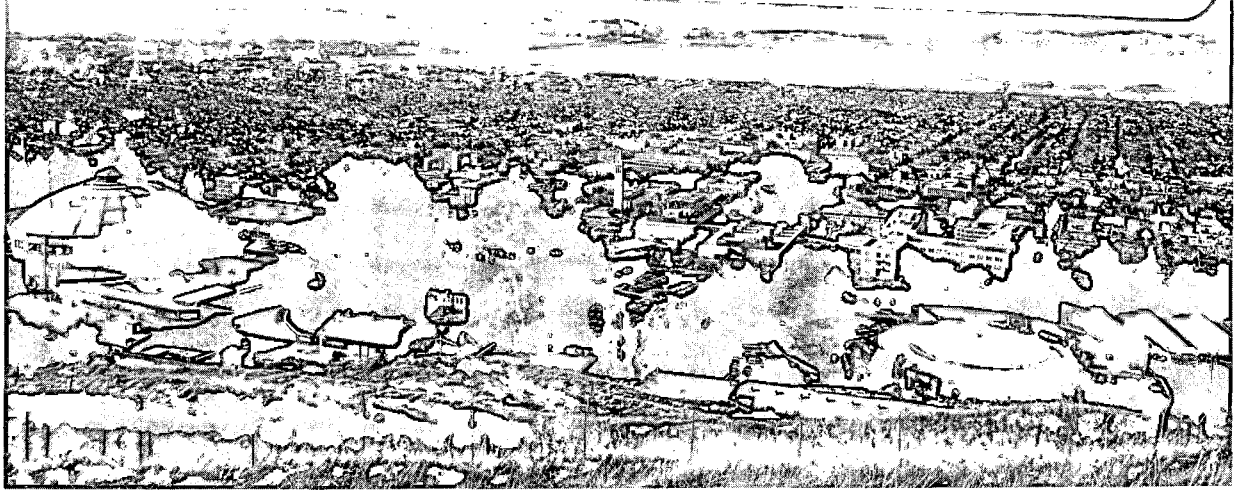
THE MOBILITY OF THORIUM IN NATURAL WATERS AT LOW TEMPERATURES

Donald Langmuir and Janet S. Herman

July 1980

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782



LBL-12528 c.2

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Geochimica et Cosmochimica Acta Vol. 44, pp. 1753 to 1766
0016-7037/80/1101-1753$02.00/0
© Pergamon Press Ltd 1980. Printed in Great Britain

Reproduced with permission from
Pergamon Press, Oxford, England

The mobility of thorium in natural waters at low temperatures

DONALD LANGMUIR
Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401, U.S.A.

and

JANET S. HERMAN
Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, U.S.A.

(*Received* 13 *December* 1979; *accepted in revised form* 7 *July* 1980)

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 ($\Sigma Cl = 10$ ppm, $\Sigma F = 0.3$ ppm, $\Sigma SO_4 = 100$ ppm, and $\Sigma PO_4 = 0.1$ ppm), the predominant thorium species are $Th(SO_4)_2^0$, ThF_2^{2+}, and $Th(HPO_4)_2^0$ below pH ≈ 4.5; $Th(HPO_4)_3^{2-}$ from about pH 4.5 to 7.5; and $Th(OH)_4^0$ above 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 $Th(OH)_4^0$. The tendency for thorium to form strong complexes enhances its potential for transport in natural waters by many orders of magnitude below pH 7 in the case of inorganic complexing, and below about 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 (pH values generally 5–8) usually ranges from about 0.01 to 1 ppb and in surface seawater (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 $Th(OH)_4^0$ above pH 5. Although complexing increases the solubility of thorium-bearing heavy minerals below 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; BONDIETTI, 1974). It occurs as a major species only in a few rare minerals such as thorianite (ThO_2), and thorite ($ThSiO_4$). 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 (Ce, La, Y, Th) PO_4 which usually contains 3–9% and up to 20% ThO_2. Along with zircon, monazite is concentrated with other resistant heavy minerals in stream and beach sands (RANKAMA and SAHAMA, 1958). Igneous UO_2 can form a complete solid solution with 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 ± 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 μm filter before chemical analysis. MIYAKE *et al.* (1964) found 0.0087–0.045 ppb Th in ten Japanese river waters. Samples were passed through a 5 μm filter before analysis. Based on a sampling of (filtered?) waters from five lakes and eleven streams in California, Nevada and Utah, THURBER (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 μm 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 TELLIER, 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 $Th(OH)_4^0$ 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, $Th(OH)_4$, ThF_4 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 $H_2PO_4^-$ activity, while $H_3PO_4^0$, HPO_4^{2-} and 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 ($C_6H_5O_7^{3-}$), oxalate ($C_2O_4^{2-}$) and EDTA ($C_{10}H_{12}O_8N_2^{4-}$) 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). LIND 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

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 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}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 ABAKIROV, 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 $Th(OH)_4^0$ complex which will have little tendency to associate with carbonate ion.

In Fig. 1 are plotted entropies (S^0 values) of thorium

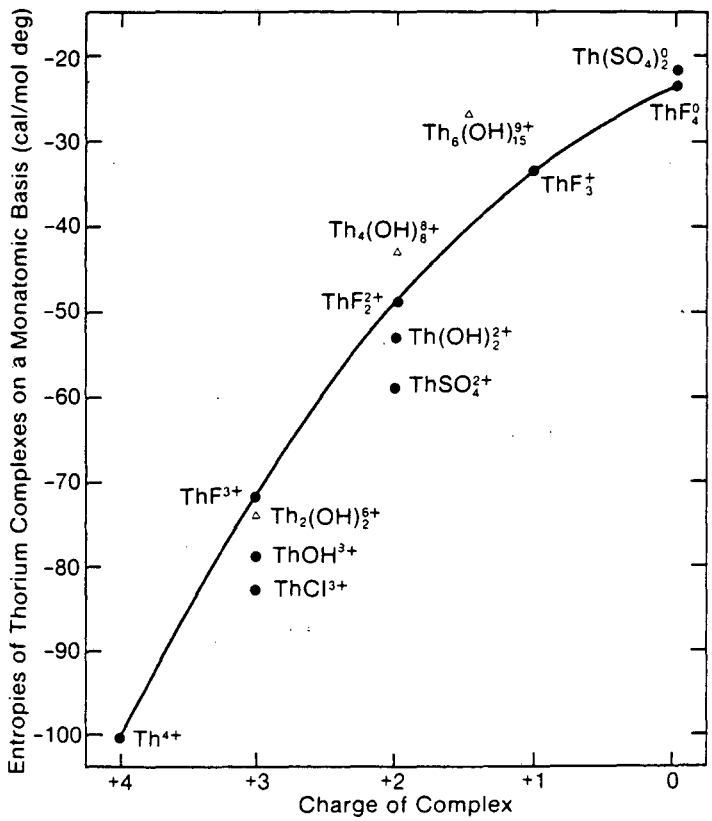


Fig. 1. Entropy vs valence for thorium ion and some thorium complexes on a monatomic basis.

Table 1. Thermochemical data for thorium minerals and aqueous species at 25°C and 1 atm total pressure. ΔH_f^0, ΔG_f^0 and S^0 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	ΔH_f^0 (kcal/mol)	ΔG_f^0 (kcal/mol)	S^0 (cal/mol deg)	Source
α-Th(c)	0	0	12.76	FUGER and OETTING (1976)
Th^{4+}	−183.8	−168.4	−101	FUGER and OETTING (1976)
$ThOH^{3+}$	(−246.2)	−220.7	−79*	FUGER and OETTING (1976)
$Th(OH)_2^{2+}$	(−306.5)	−272.3	−53*	FUGER and OETTING (1976)
$Th(OH)_3^+$	(−368.4)	(−322.5)	(−36)	See footnotes
$Th(OH)_4^0$	(−438.4)	−373.5	(−24)	See footnotes
$Th_2(OH)_2^{6+}$	(−489.4)	−441.8	−147*	BAES and MESMER (1976)
$Th_4(OH)_8^{8+}$	(−1224)	−1098.3	−173*	BAES and MESMER (1976)
$Th_6(OH)_{15}^{9+}$	(−2019)	−1810.6	−160*	BAES and MESMER (1976)
$Th(OH)_4$	(−449.5)	−408.0	(34)	See footnotes
ThO_2(c)	—	−273.2	—	See footnotes
ThO_2(c) thorianite	−293.12	−279.35	15.59	CODATA (1977), WAGMAN *et al.* (1977)
$ThSiO_4$(c) thorite (huttonite)	—	—	(25.5)	See footnotes
ThF^{3+}	−265.15	−246.70	−72	WAGMAN *et al.* (1977)
ThF_2^{2+}	−346.1	−322.52	−49	WAGMAN *et al.* (1977)
ThF_3^+	−427.1	−396.2	−34	WAGMAN *et al.* (1977)
ThF_4^0	−508.1	−468.2	−24	WAGMAN *et al.* (1977)
ThF_4(c)	−501.4	−478.9	33.95	WAGMAN *et al.* (1977)
$ThF_4 \cdot 2.5H_2O$(c)	(−682.2)	(−624.7)	(56.0)	WAGMAN *et al.* (1977)
$ThCl^{3+}$	−223.7	−201.3	−83	WAGMAN *et al.* (1977)
$ThCl_2^{2+}$	—	−232.3	—	WAGMAN *et al.* (1977)
$ThCl_3^+$	—	−264.8	—	WAGMAN *et al.* (1977)
$ThCl_4^0$	—	−295.6	—	WAGMAN *et al.* (1977)
$ThCl_4$(c)	−283.6	−261.6	(45.5)	WAGMAN *et al.* (1977)
$ThSO_4^{2+}$	−397.2	−353.8	−59	WAGMAN *et al.* (1977)
$Th(SO_4)_2^0$	−611.0	−537.6	−22	WAGMAN *et al.* (1977)
$Th(SO_4)_3^{2-}$	—	−716.6	—	WAGMAN *et al.* (1977)
$Th(SO_4)_4^{4-}$	—	−891.8	—	WAGMAN *et al.* (1977)
$ThH_3PO_4^{4+}$	—	−444.1*	—	See footnotes
$ThH_2PO_4^{3+}$	—	−444.9	—	WAGMAN *et al.* (1977)
$Th(H_2PO_4)_2^{2+}$	—	−720.9	—	WAGMAN *et al.* (1977)
$ThHPO_4^{2+}$	(−450.3)	−443.5*	(−60)	See footnotes
$Th(HPO_4)_2^0$	(−762.3)	−720.2*	(−24)	See footnotes
$Th(HPO_4)_3^{2-}$	—	−992.1*	—	See footnotes
$Th(HPO_4)_2 \cdot 4H_2O$(c)	(−1070)	−952.5*	(89)	See footnotes
$ThC_2O_4^{2+}$	—	−342.2	—	WAGMAN *et al.* (1977)
$Th(C_2O_4)_2^0$	—	−515.9	—	WAGMAN *et al.* (1977)
$Th(C_2O_4)_3^{2-}$	—	−686.8	—	WAGMAN *et al.* (1977)

α-Th(c): S^0 supported by RAND (1975), CODATA (1977), and WAGMAN *et al.* (1977). Th^{4+}: Properties determined by FUGER and OETTING (1976), adopted by WAGMAN *et al.* (1977). $ThOH^{3+}$ and $Th(OH)_2^{2+}$: S^0 values based on potentiometric measurements in 1 M $NaClO_4$ (BAES and MESMER, 1976). $Th(OH)_3^+$: ΔG_f^0 based on estimated K value (BAES and MESMER, 1976). S^0 estimated from Fig. 2. $Th(OH)_4^0$: ΔG_f^0 based on K from BAES and MESMER (1976). S^0 estimated from Fig. 2. $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$ and $Th_6(OH)_{15}^{9+}$: S^0 values based on potentiometric measurements in 1 M $NaClO_4$ (BAES and MESMER, 1976). $Th(OH)_4$: ΔG_f^0 based on solubility of 'active' or 'hydrous' ThO_2 given by BAES and MESMER (1976), assuming $\Delta G_f^0 = 0$ for: ThO_2 (active) + $2H_2O = Th(OH)_4$. S^0 estimated using Latimer's method with component entropies from NAUMOV *et al.* (1974). ThO_2(c): $\Delta G_f^0 = -273.2$ based on solubility given by BAES and MESMER (1976). $ThSiO_4$(c): Huttonite is apparently the stable polymorph at all temperatures (ROGERS and ADAMS, 1969). S^0 is estimated as the sum of values for ThO_2(c) and SiO_2(c) quartz. $ThH_3PO_4^{4+}$: ΔG_f^0 computed from $K = 10^{1.89}$ measured at $I = 2$ for: $Th^{4+} + H_3PO_4^0 = ThH_3PO_4^{4+}$ (KATZ and SEABORG, 1957). $ThHPO_4^{2+}$ through $Th(HPO_4)_3^{2-}$: ΔG_f^0 values based on stability constants measured at $I = 0.35$ (MOSKVIN *et al.*, 1967). S^0 values estimated from Fig. 2. $Th(HPO_4)_2 \cdot 4H_2O$(c): ΔG_f^0 based on solubility measured by MOSKVIN *et al.* (1967) at $I = 0.35$. S^0 estimated by Latimer's method with component entropies: S^0 (Th) = 15.9, S^0 (HPO_4) = 15 and S^0 (H_2O) = 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^0 values for the OH polymers are also plotted for comparison purposes in Fig. 1, where S^0 (plotted) = S^0 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

$$Th^{4+} + nL^{z-} = ThL_n^{4-nz}.$$

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	ΔH_f^0 (kcal/mol)	ΔG_f^0 (kcal/mol)	S^0 (cal/mol deg)	Source
$H_2(g)$	0	0	31.207	CODATA (1976)
$O_2(g)$	0	0	49.005	CODATA (1976)
$H_2O(l)$	−68.315	−56.687	16.71	CODATA (1976)
OH^-	−54.977	−37.604	−2.560	CODATA (1976)
HF^0	−76.97	−71.68	22.09	PARKER *et al.* (1976)
F^-	−80.15	−67.34	−3.15	PARKER *et al.* (1976)
Cl^-	−39.933	−31.379	13.56	CODATA (1976)
PO_4^{3-}	−305.3	−243.5	−53.	WAGMAN *et al.* (1968)
HPO_4^{2-}	−308.83	−260.34	−8.0	WAGMAN *et al.* (1968)
$H_2PO_4^-$	−309.82	−270.17	21.6	See footnotes
$H_3PO_4^0$	−307.92	−273.10	37.8	WAGMAN *et al.* (1968)
SiO_2(c) quartz	−217.66	−204.66	9.91	CODATA (1976)
SiO_2(am)	−215.33	−202.91	11.8	See footnotes
$H_4SiO_4^0$	−348.30	−312.58	45.1	See footnotes
$H_3SiO_4^-$	−342.18	−299.18	20.7	BUSEY and MESMER (1977)
$H_2SiO_4^{2-}$	—	−281.31	—	BAES and MESMER (1976)
SO_4^{2-}	−217.40	−177.95	4.50	CODATA (1977)
HSO_4^-	−212.16	−180.67	31.2	See footnotes
$H_2C_2O_4^0$	−194.7	−168.6	44.4	See footnotes
$HC_2O_4^-$	−195.6	−166.93	35.7	WAGMAN *et al.* (1968)
$C_2O_4^{2-}$	−197.2	−161.1	10.9	WAGMAN *et al.* (1968)

$H_2PO_4^-$: WAGMAN *et al.* (1968) give $\Delta G_f^0 = -260.17$ kcal/mol, which is apparently a misprint. The tabulated value is consistent with well established stability constant data and with the tabulated ΔH_f^0 and S^0 values. SiO_2(am): ΔG_f^0 based on the stability of amorphous silica from 0–250°C, written $SiO_2(am) + 2H_2O = H_4SiO_4^0$, for which log $[H_4SiO_4^0]$ molar $= -0.259-731/T(K)$ (FOURNIER, 1976). KILDAY and PROSEN (1973) measured $\Delta H_r^0 = 2.22 \pm 0.07$ kcal/mol for SiO_2(quartz) = SiO_2(am) from which $\Delta H_f^0 = -215.33$ and combined with ΔG_f^0 from FOURNIER (1976), $S^0 = 11.8$ cal/mol deg. The temperature function of FOURNIER (1976) leads to $S^0 = 10.5$ cal/mol deg. $H_4SiO_4^0$: Data based on log$[H_4SiO_4^0]$ molar $= 0.394-1310/T(K)$ from 25–250°C for quartz solubility written $SiO_2(quartz) + 2H_2O = H_4SiO_4^0$ (MOREY *et al.*, 1962). HSO_4^-: ΔH_f^0, ΔG_f^0 and S^0 adjusted relative to values for SO_4^{2-} assuming properties for the reaction $H^+ + SO_4^{2-} = HSO_4^-$ unchanged from properties computed using values given by WAGMAN *et al.* (1968). $H_2C_2O_4^0$: MARTELL and SMITH (1977) list log $K = 1.252$ and $\Delta H_r^0 = 0.9 \pm 0.1$ kcal/mol for $H^+ + HC_2O_4^- = H_2C_2O_4^0$. The data for $H_2C_2O_4^0$ are computed from this information and tabulated results for $HC_2O_4^-$ and $C_2O_4^{2-}$. The properties of $H_2C_2O_4^0$ 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 MESMER (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 $ThOH^{3+}$, $Th(OH)_2^{2+}$ and the dimer $Th_2(OH)_2^{6+}$. Entropies of the first two fo 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^{4+} and $H_4SiO_4^0$ or $H_3SiO_4^-$; 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_2(thorianite) as

$$ThO_2 + 2H_2O = Th^{4+} + 4OH^-$$

permits us to compare the stabilities of ThO_2 and $Th(OH)_4$. Thus, K_{sp} $[Th(OH)_4] = 10^{-46.6}$; and K_{sp} $[ThO_2(c)] = 10^{-49.7}$ based on solubility measurements reported in BAES and MESMER (1976) and $10^{-54.2}$ computed from the CODATA (1977) ΔG_f^0 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 hydroxides is perfectly possible for a quadravalent cation such as Th^{4+}. Approximate solubilites of $Th(OH)_4$ and ThO_2(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^-, NO_3^-, and $H_3PO_4^0$ indicate that higher order complexes will also be unimportant. Strong complexes are formed with $H_2PO_4^-$, SO_4^{2-} and F^-. The strongest common inorganic complexes are formed with OH^- and HPO_4^{2-}. 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 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
$ThOH^{3+}$	10.8*	0	BAES and MESMER (1976)
	10.2	0	WAGMAN *et al.* (1977)
$Th(OH)_2^{2+}$	21.07*	0	BAES and MESMER (1976)
	21.23	0	WAGMAN *et al.* (1977)
$Th(OH)_3^{+}$	(30.3)	0	BAES and MESMER (1976)
$Th(OH)_4^{0}$	40.1	0	BAES and MESMER (1976)
ThF^{3+}	8.44	0	BAUMAN (1970)
	8.03*	0	WAGMAN *et al.* (1977)
ThF_2^{2+}	15.06	0	BAUMAN (1970)
	14.25*	0	WAGMAN *et al.* (1977)
ThF_3^{+}	19.81	0	BAUMAN (1970)
	18.93*	0	WAGMAN *et al.* (1977)
ThF_4^{0}	23.17	0	BAUMAN (1970)
	22.31*	0	WAGMAN *et al.* (1977)
$ThCl^{3+}$	1.35	0	See footnotes
	1.09*	0	WAGMAN *et al.* (1977)
$ThCl_2^{2+}$	0.80	0	WAGMAN *et al.* (1977)
$ThCl_3^{+}$	1.65	0	WAGMAN *et al.* (1977)
$ThCl_4^{0}$	1.26	0	WAGMAN *et al.* (1977)
$ThHPO_4^{2+}$	10.8	0.35	MOSKVIN *et al.* (1967)
$Th(HPO_4)_2^{0}$	22.8	0.35	MOSKVIN *et al.* (1967)
$Th(HPO_4)_3^{2-}$	31.3	0.35	MOSKVIN *et al.* (1967)
$ThH_2PO_4^{3+}$	4.52	0	WAGMAN *et al.* (1977)
$Th(H_2PO_4)_2^{2+}$	8.88	0	WAGMAN *et al.* (1977)
$ThH_3PO_4^{4+}$	1.91	2	KATZ and SEABORG (1957)
$ThSO_4^{2+}$	(6.17)	0	See footnotes
	5.45*	0	WAGMAN *et al.* (1977)
$Th(SO_4)_2^{0}$	(9.59)	0	See footnotes
	9.73*	0	WAGMAN *et al.* (1977)
$Th(SO_4)_3^{2-}$	(10.34)	0	See footnotes
	10.50*	0	WAGMAN *et al.* (1977)
$Th(SO_4)_4^{4-}$	(8.27)	0	See footnotes
	8.48*	0	WAGMAN *et al.* (1977)
$ThNO_3^{3+}$	0.94	0	WAGMAN *et al.* (1977)
$Th(NO_3)_2^{2+}$	1.97	0	WAGMAN *et al.* (1977)
$ThC_2O_4^{2+}$	9.30	0	WAGMAN *et al.* (1977)
$Th(C_2O_4)_2^{0}$	18.54	0	WAGMAN *et al.* (1977)
$Th(C_2O_4)_3^{2-}$	25.73	0	WAGMAN *et al.* (1977)
$ThC_6H_5O_7^{+}$	13.00	0.5	See footnotes
$Th(C_6H_5O_7)_2^{2-}$	20.97	0.5	See footnotes
$ThEDTA^{0}$	25.30	0.1	See footnotes
$ThHEDTA^{+}$	17.02	0.1	See footnotes

$ThCl^{3+}$: At $I = 0.5$ KATZ and SEABORG (1957) give $K_1 = 2.24$ for $Th^{4+} + Cl^- = ThCl^{3+}$. Correction to $I = 0$, assuming the same activity coefficient behavior as observed for $ThOH^{3+}$ in perchlorate media (AHRLAND *et al.*, 1973), gives $K_1 = 10^{1.35}$. $ThSO_4^{2+}$ through $Th(SO_4)_4^{4-}$: ALLEN and MCDOWELL (1963) measured log $K_3 = 0.75$ and log $K_4 = -2.07$ for the successive stability constants of $Th(SO_4)_3^{2-}$ and $Th(SO_4)_4^{4-}$ respectively at $I = 0$. AHRLAND *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. Mathematical 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

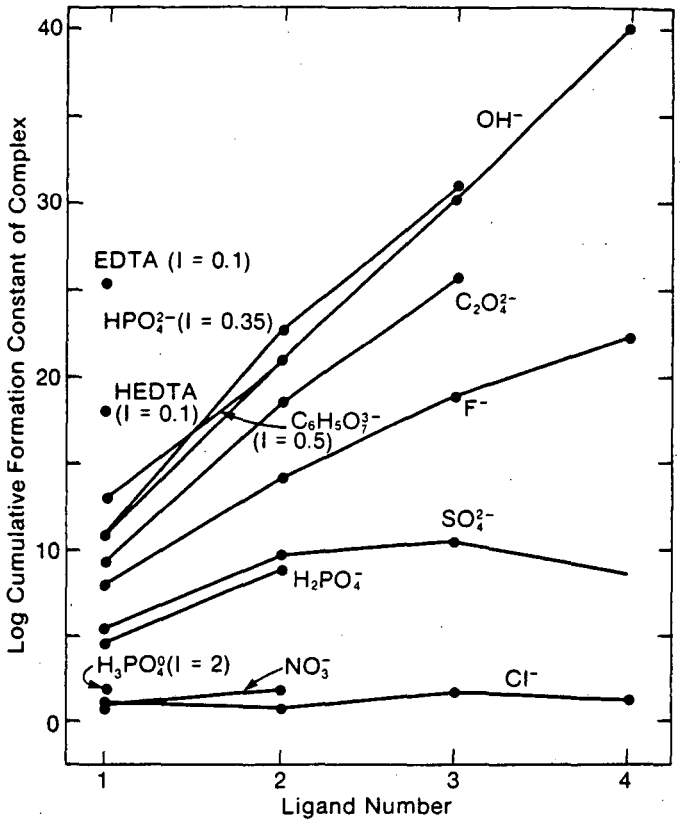


Fig. 2. Cumulative formation constants of monomeric Th^{4+} complexes at 25°C plotted against their ligand numbers. Constants are for zero ionic strength except where indicated.

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 Th^{4+} ion dominates at pH's below 3. From about pH 3 to 4.5,

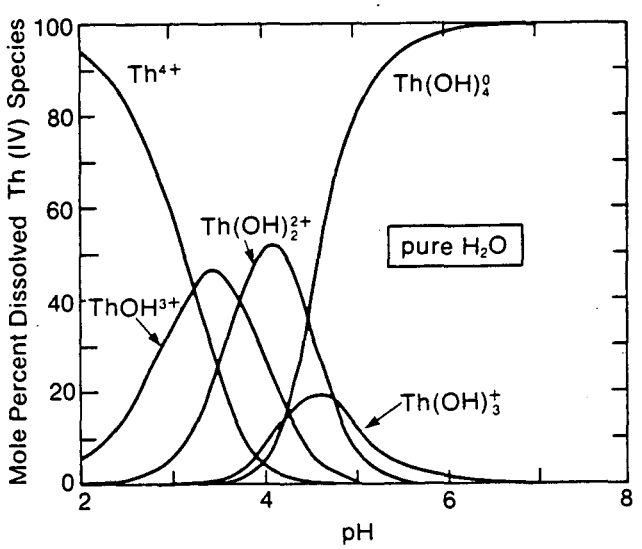


Fig. 3. Distribution of thorium–hydroxy complexes vs pH at 25°C with ΣTh = 0.01 ppb in pure water.

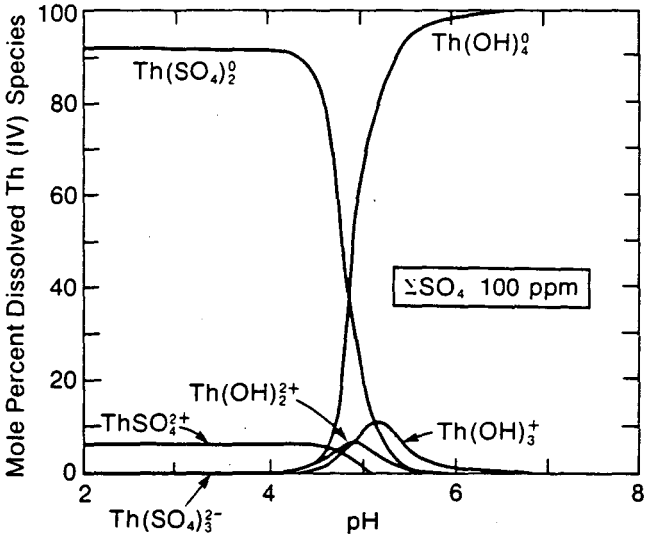


Fig. 4. Distribution of thorium–hydroxy and sulfate complexes vs pH at 25°C with $\Sigma Th = 0.01$ ppb and $\Sigma SO_4 = 100$ ppm.

the 1:1 and 1:2 hydroxy complexes predominate. Above pH 4.5, $Th(OH)_4^0$ 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, $Th(SO_4)_2^0$ is vastly more important than other sulfate complexes or free Th^{4+} ion. Above pH 5, $Th(OH)_4^0$ is the most important aqueous species. Total fluoride equal to 0.3 ppm makes ThF_2^{2+} the major fluoride complex, although the 1:3 and 1:1 complexes are also significant. $Th(OH)_4^0$ dominates the pH region above about 5.5. $ThH_2PO_4^{2+}$, $Th(HPO_4)_2^0$, $Th(HPO_4)_3^{2-}$, and $Th(OH)_4^0$ 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 corresponding distribution of thorium species in such a solution results in Fig. 7. $Th(SO_4)_2^0$, ThF_2^{2+}, $Th(HPO_4)_2^0$, $Th(HPO_4)_3^{2-}$, and $Th(OH)_4^0$ 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 $ThEDTA^0$ 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,

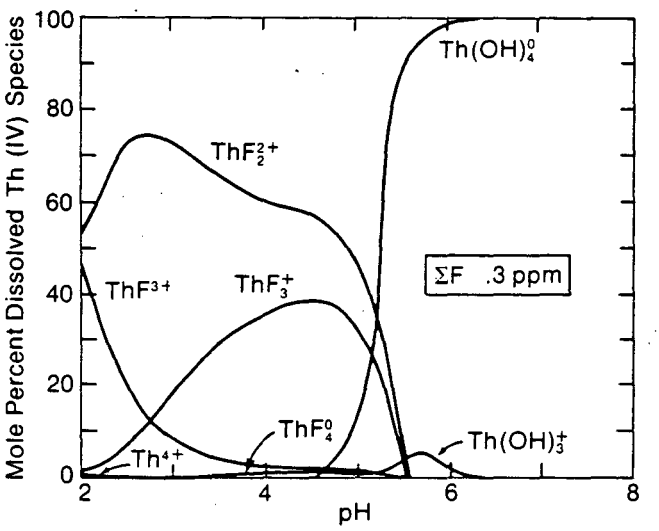


Fig. 5. Distribution of thorium–hydroxy and fluoride complexes vs pH at 25°C with $\Sigma Th = 0.01$ ppb and $\Sigma F = 0.3$ ppm.

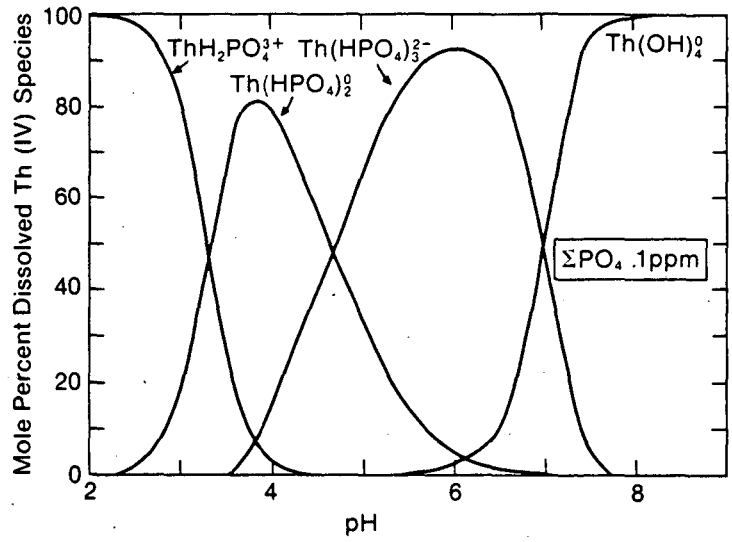


Fig. 6. Distribution of thorium–hydroxy and phosphate complexes vs pH at 25°C with ΣTh = 0.01 ppb and ΣPO_4 = 0.1 ppm.

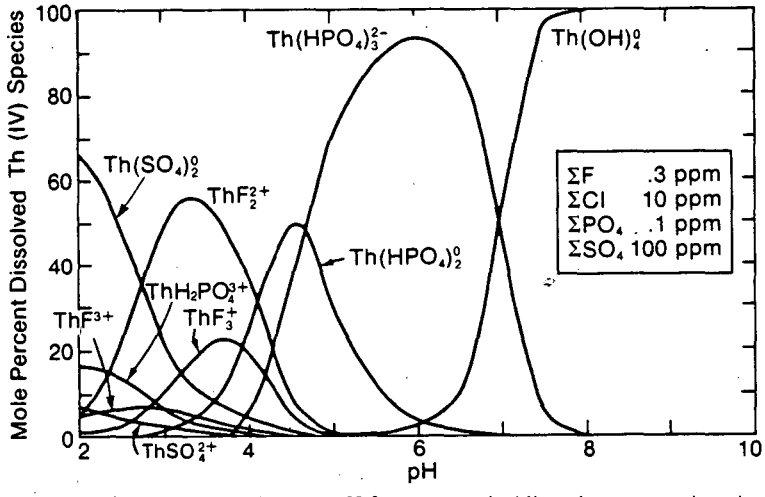


Fig. 7. Distribution of thorium complexes vs pH for some typical ligand concentrations in ground water at 25°C with ΣTh = 0.01 ppb.

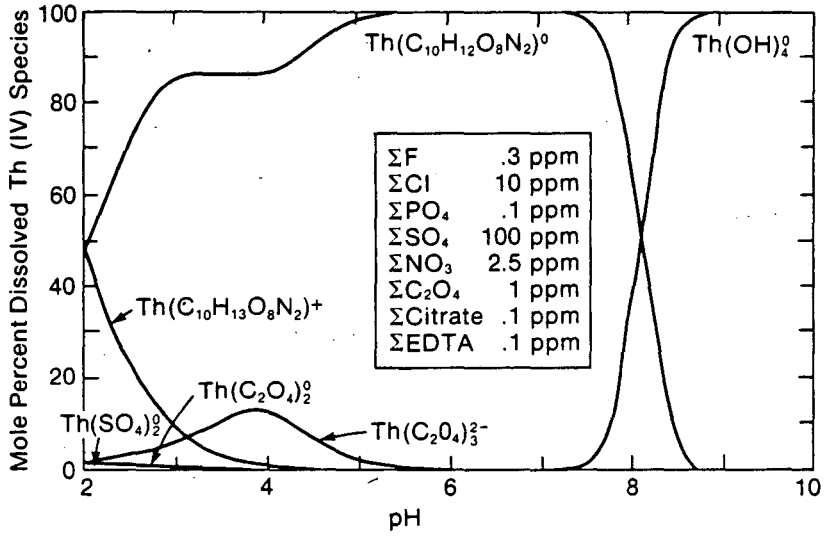


Fig. 8. Distribution of thorium complexes vs pH in a solution containing inorganic and organic species at the concentrations indicated and 25°C with ΣTh = 0.01 ppb.

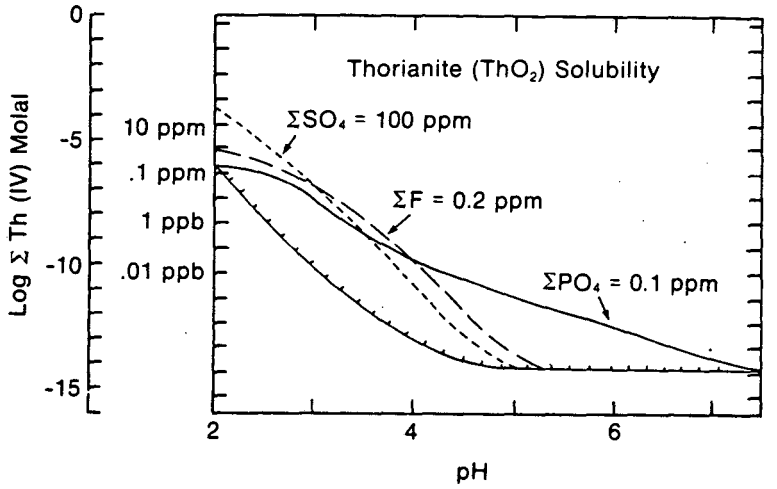


Fig. 9. The effect of thorium–sulfate, fluoride and phosphate complexing on the solubility of thorianite, ThO_2(c), as a function of pH at 25°C. The cross-hatched curve denotes the solubility of thorianite in pure water. The curves indicating thorianite solubility as affected by complexing have been 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 Cl^- and NO_3^- ions on thorianite solubility are negligible. Even in sea water (pH 8.1) with Cl = 19,000 ppm, Th–Cl^- complexing is insignificant relative to hydroxyl complexing. For nitrate concentrations up to 1000 ppm, Th–NO_3^- complexes never approach 1% of total 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 H_2SO_4 leachates from hydrothermal uranium ores, increases in ThO_2 solubility due to sulfate complexing would generally be unimportant. Even in seawater with SO_4 = 2650 ppm, sulphate complexes are insignificant relative to hydroxyl complexes. Fluoride also increases 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 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 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 despicts the effect of the combined

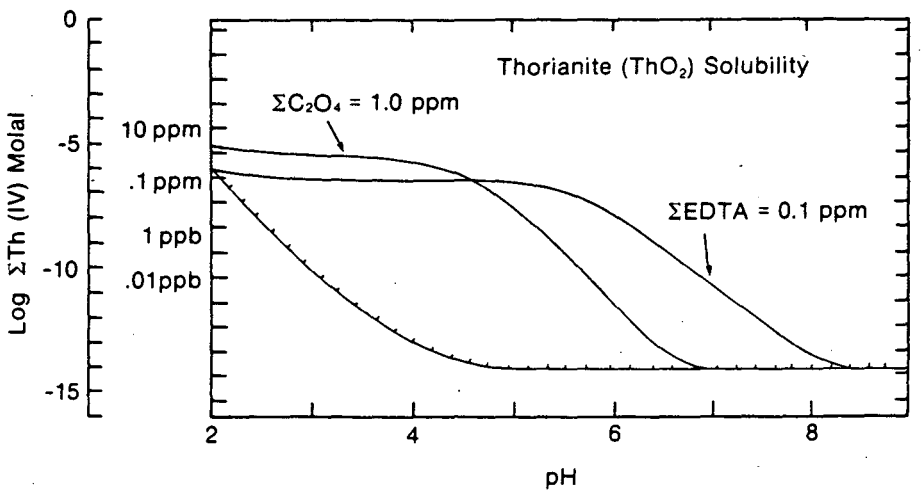


Fig. 10. The effect of thorium–oxalate vs thorium–EDTA complexing on the solubility of thorianite, ThO_2(c), as a function of pH at 25°C. The cross-hatched curve denotes the solubility of thorianite in pure water. The curves indicating thorianite solubility as affected by complexing have been constructed assuming each ligand present in the absence of the other.

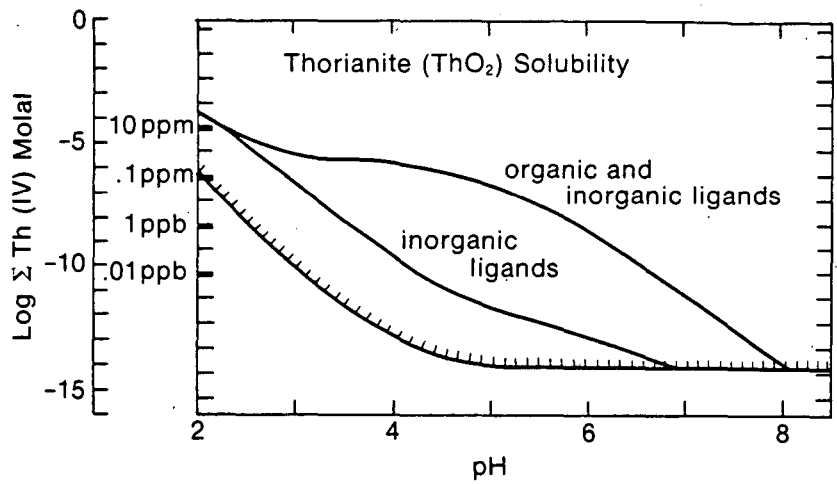


Fig. 11. The effect of thorium complexing on the solubility of thorianite. $ThO_2(c)$ vs pH at 25°C in a solution of ΣCl = 10 ppm, ΣNO_3 = 2.5 ppm, ΣSO_4 = 100 ppm, ΣF = 0.3 ppm, ΣPO_4 = 0.1 ppm, Σoxalate = 1 ppm, Σcitrate = 0.1 ppm and ΣEDTA = 0.1 ppm.

solution compositions. 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 (Th^{4+}) is not as readily adsorbed. This will in part reflect the fact that 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 pH's 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 5×10^5 ml/g at pH 6. With a quartz–illite–calcite–organic matter soil, Rancon found that K_d decreased from 10^6 ml/g at pH 8 to 100 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 reseach 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 pCi = 0.037 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 λ 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 λ, and dividing the preceding expression by Avogadro's number (6.022×10^{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:

$$\text{M(mol/l)} = 10^{-25.05}\, D(\text{pCi/l}) \times T(\text{sec})$$

The predominant thorium isotope (near 100% of total Th) is ^{232}Th, with a half-life of 4.4×10^{17} sec. The isotope ^{230}Th has a half-life of 2.5×10^{12} secs. Half-lives of the other thorium isotopes are given by ROSLER and LANGE (1972). The total thorium concentration based on a ^{232}Th isotope analysis is given by

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

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

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

In order to predict the reaction chemistry of thorium it is necessary to compute total dissolved thorium from an isotopic anslysis of ^{232}Th. ^{230}Th is the most important thorium isotope in the decay series beginning with ^{238}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}Th mobility can be estimated from its molar concentration ratio relative to ^{232}Th. Without a ^{232}Th analysis, however, the solution–reaction chemistry of ^{230}Th can only be qualitatively predicted.

MOORE and SWAMI (1972) suggest that the natural radioactivity ratio of ^{230}Th to ^{232}Th is about 0.8 in river waters and river sediments. This corresponds to a molar concentration ratio of about 4.6×10^{-6}/l. In ground waters, seepages and injection well waters from the uraniferous Grants Mineral Belt in New Mexico (KAUFMAN *et al.*, 1976) the ^{230}Th/^{232}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}Th usually predominantes in such waters. In these same waters the concentration ratio of these isotopes averaged 2.5×10^{-3} and ranged from 6.8×10^{-6} to 9.1×10^{-3}, indicating the predominance of ^{232}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 (ThO_2) above pH 5, which is only 10^{-5} ppb Th as $Th(OH)_4^0$. The important inorganic complexes of thorium with increasing pH are $Th(SO_4)_2^0$, ThF_2^{2+}, $Th(HPO_4)_2^0$, $Th(HPO_4)_3^{2-}$ and $Th(OH)_4^0$ 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 atttained 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. (Preceding 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}Th, and assuming a natural activity ratio of 0.8 for ^{230}Th/^{232}Th (MOORE and SWAMI, 1972) to 0.08 pCi/l as ^{230}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.

Thorium adsorption and the insolubility of thorium minerals in so-called 'low acid class' ground waters beneath an abandoned uranium tailings area at Eliot Lake, Ontario, may explain the fact that ^{232}Th and ^{230}Th activities in the ground water were below detection (MOFFETT and TELLIER, 1978). In 'high acid class' ground waters beneath the tailings, however, ^{232}Th concentrations were as high as 38 mg/l (4200 pCi/l) and ^{230}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}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}Th (1.1 ppb). These high ^{230}Th values reflect the greater mobility under acid conditions of ^{230}Th formed from the radioactive decay of ^{238}U. This may be contrasted with a ^{230}Th activity of 110 pCi/l (0.0057 ppb) in alkaline (pH = 10) leach solutions discharged from the Humeca 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.

Acknowledgements—Funding of the first author for the portion of this research devoted to thermodynamic data evaluation was provided by Lawrence Berkeley Laboratories, Berkeley, California under LBL Contract No. 45901AK, supported by the U.S. Department of Energy (Contract W-7405-ENG-48) through the sponsorship of the Office of Nuclear Waste Isolation, Battelle Memorial Institute. Additional support for the project was obtained through National Science Foundation Grant No. AER77-06551.

REFERENCES

AHRLAND S., LILJENZIN J. O. and RYDBERG J. (1973) Solution chemistry (of the actinides). In *Comprehensive Inorganic Chemistry, Vol. 5, Actinides, Master Index*, pp. 465–635. Pergamon Press.

ALLEN K. A. and MCDOWELL W. J. (1963) The thorium sulfate complexes from di-*n*-decylamine sulfate extraction equilibria. *J. Phys. Chem.* **65**, 1138–1140.

AMES L. L. and RAI D. (1978) Processes influencing radionuclide mobility and retention, element chemistry and geochemistry, conclusions and evaluation. In *Radionuclide Interactions with Soil and Rock Media*. Vol. 1, Sect. 3, pp. 211–220. Final Report for Contract 68-03-2514. EPA 520/6-78-007, U.S. Environmental Protection Agency.

ANON. (1976) *Environmental Analysis of the Uranium Fuel Cycle: Part IV—Supplemental Analysis, 1976*, 130 pp. U.S. Environmental Protection Agency, Office of Radiation Programs.

AYRES J. A. (edl) (1970) *Decontamination of Nuclear Reactors and Equipment*. Ronald Press.

BAES C. F. JR and MESMER R. E. (1976) *The Hydrolysis of Cations*, 489 pp. Wiley-Interscience.

BAUMAN E. W. (1970) Thermodynamic parameters of thorium–fluoride complexes from measurements with the fluoride-selective electrode at 5, 25 and 45°C. *J. Inorg. Nucl. Chem.* **32**, 3823–3830.

BONDIETTI E. A. (1974) Adsorption of U(+4) and Th(+4) by soil colloids. *Agron. Abstr.*

BUSEY R. H. and MESMER R. E. (1977) Ionization equilibria of silicic acid and polysilicate formation in aqueous sodium chloride to 300°C. *Inorg. Chem.* **16**, 2444–2450.

BUTLER J. N. (1964) *Ionic Equilibrium: A Mathematical Approach*. Addison–Wesley.

CERRE P. and MESTRE E. (1970) Treatment and disposal of decontamination wastes. In *Decontamination Of Nuclear Reactors And Equipment*. (ed. J. A. Ayres), pp. 280–329. Ronald Press.

CODATA Task Group on Key Values for Thermodynamics (1976) Recommended Key Values for Thermodynamics, 1975. *J. Chem. Thermodyn.* **8**, 603–605.

CODATA Task Group on Key Values for Thermodynamics (1977) Recommended Key Values for Thermodynamics, 1976. *J. Chem. Thermodyn.* **9**, 705–706.

DAHLMAN R. C., BONDIETTI E. A. and EYMAN L. D. (1976) Biological pathways and chemical behavior of plutonium and other actinides in the environment. In *Actinides in the Environment*. (ed. A. M. Friedman), Chap. 4, pp. 47–80. ACS Symp. Ser. 35, Am. Chem. Soc.

DAVIS J. A. and LECKIE J. O. (1979) Speciation of adsorbed ions at the oxide/water interface. In *Chemical Modelling in Aqueous Systems* (ed. Everett A. Jenne), Chap. 15, pp. 299–317. ACS Symp. Ser. No. 93.

DEMENTYEV V. S. and SYROMYATNIKOV N. G. (1965) Mode of occurrence of thorium isotopes in ground waters. *Geokhimiya* **2**, 211–218.

DROZDOVSKAYA A. A. and MEL'NIK Y. P. (1968) New experimental and calculated data on the migration of thorium under supergene conditions. *Geokhimiya* **4**, 151–167.

FOURNIER R. O. (1976) The solubility of amorphous silica at high temperatures and high pressures. *Conf. Scale Management Geothermal Energy Development*, San Diego, August 2–4, 1976, pp. 19–23.

FUGER J. and OETTING F. L. (1976) The chemical thermodynamics of actinide elements and compounds. Part 2, *The Actinide Aqueous Ions*, part 2, pp. 16–60. Int. At. Energy Agency.

GRAUSTEIN W. C., CROMACK K. JR and SOLLINS P. (1977) Calcium Oxalate: Occurrence in Soils and Effect on Nutrient and Geochemical Cycles. *Science* **198**, 1252–1254.

HANSEN R. O. (1970) Radioactivity of a California terrace soil. *Soil Sci.* **110**, 31–38.

KAMATH P. R., KHAN A. A., RAO S. R., PILLAI T. N. V., BARKAR M. L. and GANAPATHY S. (1964) Environmental natural radioactivity measurements at Trombay Establishment. In *The Natural Radiation Environment* (eds

J. A. S. Adams and W. M. Lowder), pp. 957–978. Univ. Chicago Press.

KATZ J. J. and SEABORG G. T. (1957) *The Chemistry of the Actinide Elements*, 508 pp. Wiley.

KAUFMAN R. F., EADIE G. G. and RUSSELL C. R. (1976) Effects of uranium mining and milling on ground water in the Grants Mineral Belt, New Mexico. *Ground Water* **14**, 296–308.

KILDAY M. V. and PROSEN E. J. (1973) The enthalpy of solution of low quartz (α-quartz) in aqueous hydrofluoric acid. *J. Res. Natl. Bur. Stand.* **77A**, 205–215.

LAKIN H. W. (1979) Sharpen your tools. In *Geochemical Exploration 1978* (eds J. R. Watterson and P. I. Theobald), pp. 1–7. *Proc. 7th Int. Geochem. Explor. Symp.*, Assoc. Explor. Geochem.

LANGMUIR D. and OZSVATH D. (1980) The n-power exchange function. A general model for metal adsorption onto geological materials. *Abstr. Am. Chem. Soc. Nat Meet.*, Houston, March, 1980. COL 013.

LEAVENS P. (1968) New data on whewellite. *Am. Mineral.* **53**, 455.

LIND C. and HERR J. (1975) Effects of Organic Solutes on Chemical Reactions of Aluminum. *U.S. Geol. Survey Water Supply Pap.* 1827-G.

MALCOLM R. L. (1980) Personal Communication. U.S. Geol. Surv.

MARTELL A. E. and SMITH R. M. (1977) *Critical Stability Constants, Other Organic Ligands*, Vol. 3. Plenum.

MCKEAGUE J. A., ROSS G. J., and GAMBLE D. S. (1976) Properties, criteria of classification, and concepts of genesis of podzolic soils in Canada. *Proc. Quarternary Soils Symp.*, York Univ., May 21–23, 1976.

MEANS J. L., CRERAR D. A. and DUGUID J. O. (1978) Migration of radioactive wastes: Radionuclide mobilization by complexing agents. *Science* **200**, 1477–1481.

MIYAKE Y., SUGIMURA and TSUBOTA H. (1964) Content of uranium, radium, and thorium in river waters in Japan. In *The Natural Radiation Environment* (eds J. A. S. Adams and W. M. Lowder), pp. 219–225. Univ. Chicago Press.

MOFFETT D. and TELLIER M. (1978) Radiological investigations of an abandoned uranium tailings area. *J. Environ. Qual.* **7**, 310–314.

MOORE W. S. and SACKETT W. M. (1964) Uranium and thorium inequilibrium in sea water. *J. Geophys. Res.* **69**, 5401–5405.

MOORE W. S. and SWAMI S. K. (1973) Thorium, element and geochemistry. In *The Encyclopedia of Geochemistry and Environmental Sciences* (ed. Rhodes W. Fairbridge), Vol. IV A, pp. 1183–1188. Van Nostrand.

MOREY G. W., FOURNIER R. O. and ROWE J. J. (1962) The solubility of quartz in water in the temperature interval from 25° to 300°C. *Geochim. Cosmochim. Acta* **26**, 1029–1043.

MOSKVIN A. I., ESSEN L. N. and BUKHTIYAROVA T. N. (1967) The formation of thorium (IV) and uranium (IV) complexes in phosphate solutions. *Russ. J. Inorg. Chem.* **12**, 1794–1795.

NAUMOV G. B., RYZHENKO B. N. and KHODAKOVSKY I. L. (1974) *Handbook of Thermodynamic Data*, 328 pp. Nat. Technical Info. Service, U.S. Dept. of Commerce.

OSMOND J. K. (1964) The distribution of the heavy radioelements in the rocks and waters of Florida. In *The Natural Radiation Environment* (eds J. A. S. Adams and W. M. Lowder), pp. 153–159. Univ. Chicago Press.

PARKER V. B., WAGMAN D. D. and GARVIN D. (1976) Selected thermochemical data compatible with the CODATA recommendations. NBSIR 75-968, Interim Report, Office of Standard. Ref. Data, Nat. Bur. Standards, 31 pp.

RAI D. and SERNE R. J. (1978) *Solid Phases and Solution Species of Different Elements in Geologic environments.* Battelle, PNL-2651/UC-70.

RAND M. H. (1975) Thorium: Physico-chemical properties of its compounds and alloys, Part I. *Thermochemical Properties*, Special Issue No. 5, pp. 7–85. Int. At. Energy Agency.

RANCON D. (1973) The behavior in underground environments of uranium and thorium discharged by the nuclear industry. In *Environmental Behavior of Radionuclides released in the Nuclear Industry*, pp. 333–346. IAEA-SM-172/55 (in French).

RANKAMA K. and SAHAMA T. H. (1950) *Geochemistry.* Univ. of Chicago Press.

REUTER J. H. and PERDUE E. M. (1977) Importance of heavy metal–organic solute interactions in natural waters. *Geochim. Cosmochim. Acta* **41**, 325–334.

ROBINS R. G. (1967) Hydrothermal precipitation in solutions of thorium nitrate, ferric nitrate and alluminum nitrate. *J. Inorg. Nucl. Chem.* **29**, 431–435.

ROGERS J. J. W. and ADAMS J. A. S. (1969) *Handbook of Geochemistry* (ed. K. H. Wedepohl), II/4, 90-D-3. Springer-Verlag.

ROSLER H. J. and LANGE H. (1972) *Geochemical Tables*, 468 pp. Elsevier.

SHCHERBINA V. V. and ABAKIROV S. A. (1967) On the mode of transport of thorium in the hydrothermal solutions. *Geokhimiya* **2**, 161–166.

SCHNITZER M. and KHAN S. U. (1978) Soil Organic Matter. *Developments in Soil Science*, Vol. 8, 319 pp. Elsevier.

SILLEN L. G. and MARTELL A. E. (1971) *Stability Constants of Metal-Ion Complexes*, Suppl. No. 1. Spec. Publ. No. 25, The Chem. Soc.

SOMAYAJULU B. L. K. and GOLDBERG E. D. (1966) Thorium and uranium isotopes in sea water and sediments. *Earth Planet. Sci. Lett.* **1**, 102–106.

THURBER D. (1965) The concentrations of some natural radioelements in the waters of the Great Basin. *Bull. Volcanol.* **28**, 195–201.

VYDRA F. and GALBA J. (1967) Sorption von Metall-Komplexen an Silicagel III. Sorption von Hydrolsenprodukten des Th^{4+}, Fe^{3+}, Al^{3+} und Cr^{3+}: Collection Czechoslov. *Chem. Commun.* **32**, 3530–3536.

WAGMAN D. D., EVANS W. H., PARKER V. B., HALOW I., BAILEY S. M. and SCHUMM R. H. (1968) Selected values of chemical thermodynamic properties. Nat. Bur. Standards Technical Note 270-3, 264 pp.

WAGMAN D. D., EVANS W. H., PARKER V. B., HALOW I., BAILEY S. M. and SCHUMM R. H. (1969) Selected values of chemical thermodynamic properties. Nat. Bur. Standards Technical Note 270-4, 141 pp.

WAGMAN D. D., SCHUMM R. H. and PARKER V. B. (1977) A computer-assisted evaluation of the thermochemical data of compounds of thorium. NBSIR 77-1300, 93 pp. Nat. Bur. Standards, Dept. Commerce.

WAGMAN D. D., EVANS, W. H., PARKER V. B., HALOW I., BAILEY S. M. and CHURNEY K. L. (1971) Selected values of chemical thermodynamic properties. Nat. Bur. Standards Technical Note 270-5, 49 pp.

WEBER J. H. (1980) Personal Communication. Univ. of New Hampshire.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720