Pergamon

Geochimica et Cosmochimica Acta, Vol. 58, No. 2, pp. 613-623, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in the USA. All rights reserved
0016-7037/94 $6.00 + .00

On the influence of carbonate on mineral dissolution: III. The solubility of microcrystalline ThO_2 in CO_2–H_2O media

ERIK ÖSTHOLS,[1] JORDI BRUNO,[2] and INGMAR GRENTHE[1]
[1]Department of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden
[2]MBT Tecnologia Ambiental, CENT, E-08290 Cerdanyola, Spain

(*Received March* 12, 1993; *accepted in revised form August* 24, 1993)

Abstract—The solubility of microcrystalline ThO_2 as a function of pH has been studied under different partial pressures of CO_2 in aqueous media, in order to obtain qualitative and quantitative information on the complexation of Th^{4+} with carbonate. Based on the results of the study, the existence of a mixed thorium-hydroxo-carbonate complex, $Th(OH)_3CO_3^-$, as well as a thorium carbonate complex $Th(CO_3)_5^{6-}$ is proposed, and their stability constants and the solubility product of microcrystalline thorium dioxide ($ThO_2(act)$) are determined. The following equilibrium constants were determined in 0.5 M $NaClO_4$ at 25°C 1 atm.:

$$ThO_2(act) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O \quad \log K_S = 9.37 \pm 0.13$$

$$ThO_2(act) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^- \quad \log \beta_{1,3,1} = 6.11 \pm 0.19$$

$$ThO_2(act) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} \quad \log \beta_{1,0,5} = 42.12 \pm 0.32.$$

The errors are given as three standard deviations in the fitted constants. By extrapolation, the following constants are obtained for the infinite dilution standard state:

$$ThO_2(act) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O \quad \log K_s = 7.31 \pm 0.3$$

$$ThO_2(act) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^- \quad \log \beta_{1,3,1} = 6.78 \pm 0.3$$

$$ThO_2(act) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} \quad \log \beta_{1,0,5} = 39.64 \pm 0.4.$$

INTRODUCTION

THORIUM HAS LONG BEEN recognized as an important tracer element in natural waters because of its accurately known source terms, long half-life and single redox state (see e.g., SANTSCHI and HONEYMAN, 1989). Thorium is, therefore, a suitable analogue for other tetravalent actinides. Also, data on Th content exist for oceans and lakes in many cases where data for other actinides are not available.

In order to correlate the behaviour of Th to that of other actinides in natural aquatic environments, it is important that the speciation, adsorption behaviour and scavenging processes of Th be well known. Many workers have been investigating scavenging processes of Th in natural waters (HUNTER et al., 1988; LAFLAMME and MURRAY, 1987; MORAN and BUESSELER, 1992; MENAGER et al., 1988; BASKARAN et al., 1992), and insights have been gained into different sorption and colloid related processes of importance for the migration of Th in natural environments. In order to make quantitative models for these processes, however, it is necessary to possess good knowledge of the basic equilibrium processes affecting Th.

Studies (LAFLAMME and MURRAY, 1987) of the thorium content in alkaline waters from Soap Lake in Eastern Washington, USA, and Mono Lake in California, USA (ANDERSON et al., 1982; SIMPSON et al., 1982) have yielded thorium concentrations that exceed those expected from the solubility of crystalline $ThO_2(c)$ by several orders of magnitude. LAFLAMME and MURRAY (1987) found that the rise in solubility can be qualitatively explained partly by decreased thorium surface adsorption through competition for surface sites by HCO_3^- and CO_3^{2-}, and partly by the influence on the solubility of $ThO_2(c)$ of dissolved Th carbonate complexes. Further modelling, however, was prevented by lack of reliable data on the Th(IV) − H_2O − $CO_2(g)$ system and specifically the dissolution behaviour of $ThO_2(c)$ in the presence of carbonates.

Quantitative data on Th complexation with carbonates are scarce. Some studies have been made that indicate the formation of thorium carbonate species in solution (FAUCHERRE and DERVIN, 1962; GRENTHE and LAGERMAN, 1991; RYACHIKOV et al., 1963). The only reliable quantitative study found by the authors is by JOÃO et al. (1987), who studied the thorium carbonate complexation at high pH and carbonate concentrations using liquid-liquid extraction methods.

Crystal structure determinations (VOLIOTIS and RIMSKY, 1975) show the structure of a mononuclear pentacarbonate complex in some solid phases. The lack of quantitative thermodynamic information and reliable studies of speciation of thorium carbonate complexes, in connection with the apparent dominance of $Th(OH)_4^0$ at pH values above 6 has led LANGMUIR and HERMAN (1980) to conclude that thorium carbonate complexes are unlikely to be of any significance. However, it has long been known (CLEVE, 1874) that the presence of carbonates increases the solubility of ThO_2. The homogeneous ternary system Th(IV) − H_2O − $CO_2(g)$ has been studied earlier (GRENTHE and LAGERMAN, 1991). The data have not been fully interpreted, but clearly indicate the formation of carbonate complexes. The existence of U(IV) carbonate species (GRENTHE et al., 1992, and references therein) also clearly indicates the possibility of Th carbonate complex formation.

Based on the investigations of CHAFEE et al. (1973), a general scheme for the stepwise formation of carbonate complexes from metal hydroxide complexes has been proposed (BRUNO, 1986). This scheme suggests that one should expect increasing numbers of CO_3^{2-} ligands with rising carbonate concentration, with the carbonate ligands eventually totally replacing the hydroxo ligands. Thus, one would expect formation of mixed complexes at low and medium carbonate concentrations, and formation of pure carbonate complexes at higher carbonate concentrations.

The purpose of this study is to obtain quantitative information on the thorium speciation in aqueous solution in the presence of carbonates.

EXPERIMENTAL

Reagents

P.a. grade $Th(NO_3)_4 \cdot 5H_2O$ from E. Merck was used for preparing the solid phase. Puriss. NaOH from EKA Chemicals was used for the precipitation. The ionic medium used was prepared from Merck p.a. grade $HClO_4$ and Merck p.a. grade Na_2CO_3, or Merck p.a. grade solid $NaClO_4$. The ionic medium was prepared by neutralizing the $NaClO_4$ dissolved, or the salt resulting from mixing the sodium carbonate with the perchloric acid, adding ashless tablets for complexing dissolved ions, and letting the resulting mixture settle for a minimum of three days. The mixture was then filtered on a G4 glass filter funnel and analyzed. P.a. grade water free $Na_2CO_3(s)$ and $NaHCO_3(s)$ was used in the batch experiments. For the Th analysis, Merck p.a. grade HCl, Merck p.a. grade Na_2CO_3, and Arsenazo III metal indicator, also from Merck, were used. The CO_2 and nitrogen gases were delivered by AGA Sweden. The water used was purified using a Milli-Q water purifier supplied by Millipore Inc.

Preparation of Solid Phases

Well crystallized thorium oxide is very insoluble in aqueous media (BAES and MESMER, 1976), and the kinetics of dissolution is slow in the absence of very strong acids (TAKEUCHI et al., 1971). Hence, it is not possible to study the solubility of a well crystallized thorium oxide under conditions relevant in natural waters. A procedure for producing a thorium oxide/hydroxide of low crystallinity was adopted in this study. $Th(NO_3)_4 \cdot 5H_2O$ was dissolved in water and a concentrated solution of NaOH was quickly added under vigorous stirring until a pH of approximately 9–10 was reached. The precipitate was then filtered on a G4 glass filter funnel and washed with water until the filtrate was neutral. The solid was dried at room temperature for one week in a vacuum desiccator. The solid was taken out and gently ground to a powder in a mortar before use.

General Procedure

Two different experimental procedures were used, one in which continuous titrations of aqueous solution (0.5 M $NaClO_4$) in contact with the solid were performed under constant partial pressure of CO_2 and varying pH, and one in which sealed tubes containing ionic medium and buffer solutions of carbonate/bicarbonate of different pH's at constant total carbonate concentration, in contact with the solid, were agitated to attain equilibrium.

The experimental setup for the continuous titration consisted of a PTFE or glass vessel with a combined glass electrode or a separate glass electrode and an Ag/AgCl reference electrode for pH measurements. A platinum net and a mercury counter electrode connected to a constant current source were used for coulometric variation of the total acidity of the test solution. The pH measurements and the coulometric acid/base additions were both controlled by a computer. The batch experiments were carried out in polypropylene tubes sealed with screwcaps.

The 100% $CO_2(g)$ titration was carried out in a thermostated room, at a temperature of 23.78°C ± 0.24. The following experiments were made in a thermostated box, at a temperature of 25.04°C ± 0.06, and at atmospheric pressure. The batch solubility experiments were made in a thermostated room at 25°C ± 0.5.

The temperature variation will give rise to variations in solubility and errors in the potential readings. These variations, however, can safely be neglected when compared to errors in the electrode calibrations and Th concentration measurements.

The coulometric setup was used for calibrating the glass electrode system and for increasing the total alkalinity in the solubility experiments up to pH values of around 6.5, as well as for acidifying the solubility experiment at low pH. To increase the alkalinity above pH 6.5, Na_2CO_3 solutions adjusted to 0.5 M ionic strength with $NaClO_4$ stock were used.

The electrode calibrations were made coulometrically in 0.5 M $NaClO_4$ using the Gran II method (GRAN, 1952). During the electrode calibrations, N_2 gas was bubbled through the solutions. The N_2 gas was washed in 10% sulphuric acid and then bubbled through 0.5 M $NaClO_4$ in order to saturate the gas with water vapour.

Two different types of glass pH electrodes were tried in the experiments, one with a built in reference electrode and one which requires a separate reference electrode. The separate reference electrode features a double junction connection between reference solution and test solution. The inner compartment of the reference (as well as the only compartment of the combined electrode) was filled with a 0.01 M $AgClO_4$, 0.5 M $NaClO_4$ solution, and the outer compartment with 0.5 M $NaClO_4$ solution. This type of cell has been studied before (BIEDERMANN and DOUHÉRET, 1980), and the diffusion potential for 0.5 M $NaClO_4$ was found to be $-133 \cdot [H^+]$ mV at 25 deg. C. The order of magnitude of this value was confirmed in the present work by electrode calibrations at low pH. This translates to less than 0.003 pH units in the experiments, and hence the diffusion potential can be neglected.

Since the continuous titration experiments sometimes took several months to complete, the stability of the pH electrode systems over time was checked. The separate reference electrode cells appear to be more stable with time than combined glass electrodes, and were consequently used in all continuous titration experiments except the very first one. The uncertainty for the combined electrode over 2–3 months, defined as three standard deviations, was typically 9 mV (approx. 0.1 pH units), and for the separate electrode system typically 2.5 mV (approx. 0.04 pH units). If there are any trends in the variation of the electrode calibration results over long times, they are smaller than the errors quoted above. The electrodes were calibrated before and after each experiment to check for changes in the reference potentials. For the batch experiments, where long term stability of the electrode potentials is of little importance, combined glass electrodes calibrated using the procedure outlined above were used.

After calibrating the electrode, a few grams of solid phase were introduced in the Teflon/glass vessel containing around 150 ml 0.5 M $NaClO_4$, and CO_2 bubbling was started. The CO_2 gas was washed in the same way as the N_2 gas. 100% CO_2, 10% CO_2 90% N_2, and 100% N_2 gas mixtures were used, giving (after correction for water vapour pressure) 0.97, 0.1 and 0 atm. CO_2 pressure, respectively.

For the batch experiments, around 0.5 g solid was weighed into each test tube together with sodium carbonate, sodium bicarbonate, and sodium perchlorate stock solution in calculated amounts to give a total carbonate concentration of 0.1 M and a total ionic strength of 0.5 M, and the tubes were filled with water to a total volume of 44 mL. Care was taken to leave as little air as possible in the tubes.

In the first 0.97 atm CO_2 continuous titration experiment, the pH range from 2 to 6.5 was investigated. This investigation suggested a minimum solubility at a pH of approximately 4.5, and in the subsequent studies, the experiments were started at this pH. This procedure was used to prevent precipitation, which might introduce new solid phase in the reaction vessel. In the first experiment, some precipitation did occur, since the pH of minimum solubility was not known at this time, and had to be determined from the experiment. Since the conditions for precipitation in the vessel resemble those used in the preparation of the solid, there is no reason to believe that the solid formed during the experiment should differ significantly from the original one.

Sampling

Continuous titrations

The pH of the solution was continuously monitored (every 10 or 30 minutes), and when no tendency to pH drift in a particular direction could be detected, the system was assumed to be in equilibrium. For the 0.97 atm. CO_2 experiments, this was usually the case after some 48 hours, and for the 0 and 0.1 atm. CO_2 experiments, after approximately one week. In the pH range below 4, the equilibration time was a minimum of one week. The very first sample in each experiment was taken, at the earliest, 10 days after the solid phase was added to the reaction vessel, since it is reasonable to assume that the first equilibration takes longer than the subsequent ones.

The samples were taken using a 10 mL polypropylene syringe connected to a Teflon capillary submerged into the solution, in order to avoid opening the vessel for sampling. The samples were then filtered through a Millex GV 0.22 μm filter unit from Millipore S.A. and weighed into polypropylene test tubes, to which 0.2 g of concentrated $HClO_4$ was added. The test tubes were then sealed until the time of analysis. The filter was attached directly to the syringe after sampling, and the sample pressed through the filter directly into the test tube, to avoid exposure to air. The vessel was refilled with ionic medium to replace the volumes removed when sampling at intermediate pH values. At high pH (above 6.5) the sample volume was replaced with the carbonate solution mentioned above. The volumes of the samples were calculated using the known weights of the samples and a density of 1.037 kg/L for 0.5 M $NaClO_4$ at 25°C. Immediately before sampling, the pH, air pressure, and temperature of the test solution were registered.

Batch experiments

In the batch experiments, the sample tubes were shaken for minimum of one month to attain equilibrium. Then the tubes were opened, and the pH was measured immediately. 10 mL fractions of the tube contents were taken out and filtered with 0.22 μ Millipore G.V. filters into test tubes and acidified with $HClO_4$. The tubes containing the conserved and filtered samples were then sealed until the time of analysis.

Filtering

To check the possible influence of the filtering procedure on the sample concentrations, some tests were made using different pore sizes and filtering samples twice to check for possible Th adsorption in the filters. The changes in the measured Th concentration with changing filter sizes down to 0.01 μm was within the experimental error. No change in concentration was found when filtering twice. This indicates that the measurements are not affected by colloids or adsorption in the filters.

Sample Analysis

The analysis of the total concentration of thorium was made using a modified version of the spectrophotometric method with the Arsenazo III reagent described by SAVVIN (1961). A stock solution of $Th(NO_3)_4$ was prepared by dissolving $Th(NO_3)_4 \cdot 5H_2O$ in water. The exact concentration was determined gravimetrically by heating crucibles with weighed amounts of stock to 950°C, producing $ThO_2(c)$. This stock solution was then used to prepare a second, more dilute stock from which standards were prepared by diluting weighed amounts of stock solution with 0.5 M $NaClO_4$ and some 2 g concentrated $HClO_4$ per 100 mL final standard solution. The standards were in the range 10^{-4} to $10^{-7.5}$ M of total Th concentration. Arsenazo III reagent was prepared by dissolving 0.5 g of Arsenazo III in 500 mL of water that had been alkalified by the addition of Na_2CO_3 (to increase the solubility of the Arsenazo III). 40 mL of the Arsenazo III solution was mixed with conc. HCl and water to 2 L to obtain a 6 M HCl reagent mixture. This concentration was used to obtain high sensitivity of the spectrophotometric method (SAVVIN, 1961). Approx. 10 mL of each standard was then weighed into 100 mL volumetric flasks and diluted to the mark with the reagent mixture. The absorbance was measured against a reagent blank at 661.4 nm in a Varian Cary 219 spectrophotometer, using 10 cm quartz glass cuvettes. Polypropylene volumetric flasks from Nalgene were used for all standards and samples. The absorbance was plotted against the total number of moles of Th in the flasks, and a standard curve was obtained. The standard curve was linear in the range $10^{-4.5}$ M–10^{-7} M total Th. The samples were analyzed in a similar manner immediately after the calibration. The extinction coefficient found in our experiments (typically 125000 $M^{-1} \cdot cm^{-1}$) is in fair agreement with the one given by SAVVIN (1961), 130000, which is obtained in 9 M acid, where the extinction coefficient is slightly higher than in the 6 M acid solution used in this work.

Solid Phase Analysis

To monitor possible changes in the solids during the experiments, such as aging and incorporation of carbonate, the solid phases used in the experiments were analyzed before and after experiments, after washing with water, filtering, and drying. The solid phases were investigated using X-ray powder diffraction (XPD), scanning electron microscope (SEM) in combination with X-ray fluorescence, and BET isotherms for determination of specific surface area as well as porosity. We also tried to estimate the water content of the solid gravimetrically.

Gravimetric analysis

A weighed amount of a solid phase prepared at 25°C was heated to 800°C overnight, allowed to cool in a desiccator, and weighed. If the weight loss is taken to be due to evaporation of H_2O only, this would correspond to the composition $ThO_2 \cdot 2.4H_2O$, which is in good agreement with the observations by DZIMITROWICZ et al. (1984), who found values around $n = 2.5$ for $ThO_2 \cdot nH_2O$ prepared by rapid precipitation of ThO_2 from thorium nitrate solution by addition of KOH.

XPD measurements

The XPD measurements show that the solid phases prepared at room temperature were microcrystalline with a very low degree of crystallinity. DZIMITROWICZ et al. (1984) found a similar microcrystalline solid in their study. The solid prepared at room temperature showed no sign of becoming significantly more crystalline after being used in an experiment for 2 months.

BET measurements

Several amorphous solid batches were prepared as described above. The essentially amorphous solid samples had BET surface area values between 16–76 m^2/g. Different fractions of the same solid sometimes had BET areas differing by as much as 40 m^2/g, but normally the variation was around 10–20 m^2/g. These variations are probably due to inhomogeneities in the samples, which were only lightly ground in order not to produce fine powders that might show anomalous solubility behaviour. The BET surface area of a solid phase used in the second 0.1 atm CO_2 experiment was measured to 16 m^2/g after the experiment. A fraction of the unused solid had a value of 32 m^2/g. This difference is within the range of uncertainty for the measurements due to minor inhomogeneities as mentioned above, showing that the solid does not age significantly during the experiments. The values for 25°C are also in fair agreement with the analyses of DZIMITROWICZ et al. (1984), who found a BET surface area of 22 m^2/g for microcrystalline ThO_2 prepared as described above.

As can be seen from the BET results in Table 1, aging of the solid and heating gives an initial increase in surface area accompanied by an increase in porosity, when crystallization of the amorphous solid sets in, followed by a decrease in surface area with further crystallization.

Porosity measurements

In conjunction with the BET surface area measurements, the total pore area per unit weight of solid was measured for some solids using

Table 1

Results of BET $ThO_2(s)$ analyses			
Temp. of prepn. (°C)	Aging (months)	BET surf. area (m^2/g)	Max. pore area (m^2/g)
100	0	222	22.0
25	0	32	5.0
25	2	16	2.1
25	6	216	-
900	0	0.3	-

adsorption isotherms of $N_2(g)$. The results are summarized in Table 1. One can see that the increase in surface area is accompanied by an increase in pore area.

X-ray fluorescence measurements

Samples of solid used in experiments for 2–3 months were analyzed using energy dispersive X-ray fluorescence equipment in an SEM together with unused solid samples. The acceleration voltage used gives a penetration depth of approx. 1–2 μm. The results in Fig. 5 do not indicate any increase in carbon content as a result of exposure to carbonate containing solution in this layer. The place where the carbon peak would have appeared is marked in the graph. The method is not sensitive enough to detect carbon contents of less than 1–2%. A separate scan of a wider energy range (not shown) revealed no peaks beside those for thorium and oxygen, indicating that no major impurities resulting from the method of preparation were present.

MODELLING OF DATA

Continuous Titrations

The measured total concentration of Th is plotted against $-\log[H^+]$ for different partial pressures of CO_2 in Fig. 1. The solubility measurements were influenced by kinetic factors, as well as aging and washing of solids before use. One series of data at 10% CO_2 was judged unreliable and has not been used in the modelling, as indicated in Fig. 1, since we suspect that the solid contained residues of the thorium nitrate mother liquor due to incomplete washing of the solid. Furthermore, some experiments at 0.01 atm. CO_2 partial pressure have been excluded, since the dissolution kinetics was too slow to obtain stable solubilities within reasonable time. In the pH range below 4, it was very difficult to get stable and reproducible solubility values. This may be due to slow precipitation kinetics in cases where acid additions to change pH give rise to minor oversaturations. One measurement series in this pH range is shown in Fig. 1, together with the theoretical solubility curve in the same range. These data have not been used for modelling. Finally, only freshly precipitated solids have been used, in order to avoid solids that have aged and reached higher degrees of crystallinity.

The increase in solubility with increased pH in carbonate solutions observed in the continuous titration experiments could not be reproduced in the absence of carbonates. In the carbonate free experiments, the solubility was too low to be measured accurately at pH's above 4 and up to 10, probably due to slow dissolution kinetics. This carbonate effect on solubility clearly indicates the formation of one or more thorium carbonate complexes. A preliminary graphical analysis of the data indicated the formation of a complex with charge −1 at pH > 5. The dependence of solubility on p_{CO_2} indicates that one CO_2 ligand is incorporated in the complex as a carbonate. Since the concentrations of Th^{4+} and carbonate cannot be varied independently in this experiment, it is not possible to establish the nuclearity of thorium carbonate complexes from this study alone. However, at the low Th concentrations in the study, we find it reasonable to assume the formation of a mononuclear mixed complex $Th(OH)_3CO_3^-$. The stability constant of this mixed complex and the solubility product of microcrystalline thorium dioxide

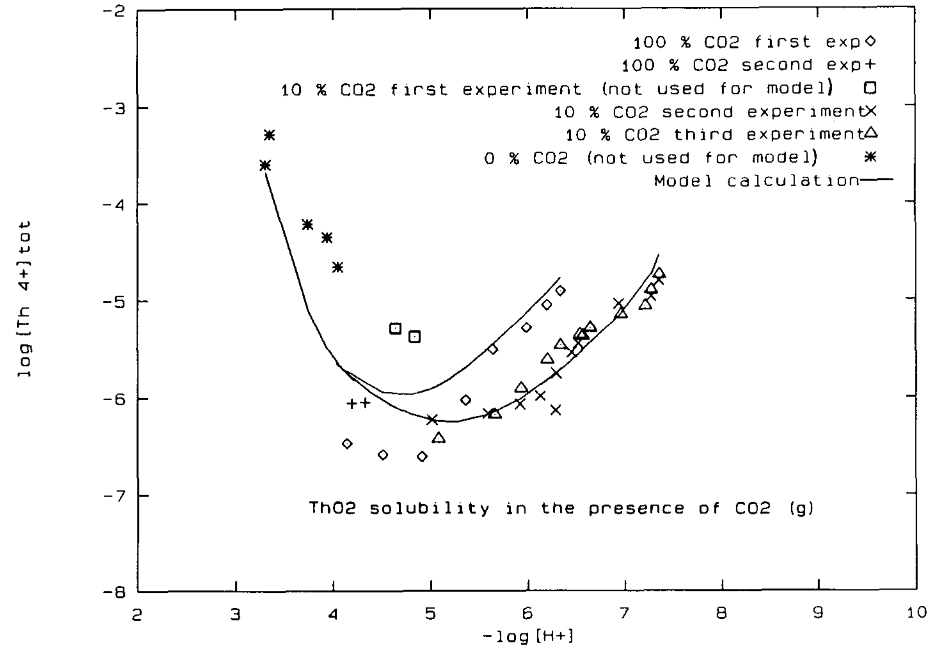

FIG. 1. Measured and calculated solubilities of microcyrstalline ThO_2 at different partial pressures of CO_2. The lines represent the calculated solubilities using the stability constants determined in this work.

were fitted to the data with the newly written C-Letagrop program system (ÖSTHOLS, 1991) which can estimate stability constants, solubility products, and surface complex stability constants from experimental data. The Th hydrolysis constants used were recently determined in 3 M $NaClO_4$ (GRENTHE and LAGERMAN, 1991) and corrected to 0.5 M $NaClO_4$ using the specific ion interaction theory (GRENTHE et al., 1992). The acidity constants for the carbonate used in this work were interpolated to 0.5 M $NaClO_4$ from data published earlier (FRYDMAN et al., 1958, SPAHIU, 1983, BRUNO et al., 1992b) using the specific ion interaction theory. Unknown interaction coefficients were estimated from analogies with U(IV) species. The ionic product of water in 0.5 M $NaClO_4$ was taken from SILLÉN and MARTELL (1964). The stability constants used in the fitting procedure are shown in Table 4. The residual of the logarithm of the measured total concentration of thorium in solution was used for the nonlinear least squares fitting. Two other mixed complexes were also tried, $Th(OH)_2CO_3(aq)$ and $Th(OH)_4CO_3^{2-}$, but inclusion of these species does not improve the fit to the experimental data.

One solubility product fits all the data quite well, indicating that the solids prepared on different occasions are nearly identical. This is also confirmed by the batch experiments discussed below. The fitted concentrations are shown together with the measured values in Fig. 1.

Standard deviations in the fitted parameters were obtained using Monte Carlo analysis (PRESS et al., 1988) with the errors in pH chosen as explained above. The standard deviations in the measured pressures were estimated to $3 \cdot 10^{-3}$ atm., and the errors in the fitted Th concentrations assigned using the formula

$$\sigma^2 = \sum_{i=1}^{N} (\log[Th]_{tot,i}(obs) - \log[Th]_{tot,i}(calc))^2/(N - M), \quad (1)$$

where σ is the average standard deviation for a set of N data points with M fitting parameters, $\log\,[Th]_{tot,i}(obs)$ is the measured solubility of thorium for data point i, and $\log\,[Th]_{tot,i}(calc)$ is the fitted solubility of thorium for data point i. The Monte Carlo analysis is integrated in the C-Letagrop program.

The distribution diagram for thorium obtained with our model for the pH range 3–8. CO_2 pressure is shown in Fig. 2.

Batch Experiments

The log of the obtained total concentration of Th in solution corrected for the formation of $Th(OH)_4^0$ and $Th(OH)_3CO_3^-$ is plotted against $\log\,[CO_3^{2-}]$ in Fig. 3. The results from two different experiments are shown, using solid phases prepared at two different occasions. As can be seen, the results are fairly similar, supporting the conclusion that the solid phase preparation method gives reproducible results. Attempts to make batch experiments at 0.01 M total CO_3^{2-} concentration failed to yield reproducible solubilities, probably owing to slow dissolution kinetics.

All the complexes and constants used in the continuous titrations were included in the modelling of the batch experiments. In addition, an attempt to include the complexes $Th(CO_3)_5^{6-}$, $Th(CO_3)_4^{4-}$, $Th(OH)_2CO_3(aq)$, and $Th(OH)_4CO_3^{2-}$ in the model was made. The best fit was obtained by adding only the pentacarbonate complex to the existing model from the continuous titrations. The fitted concentrations are shown in Fig. 3 together with the measured solubilities. The concentrations used in the fitting procedure, as in the modelling of the continuous titrations, are the logarithms of the total thorium concentrations in solution. The total carbonate concentrations used in the modelling were calculated from the weighed amounts of solid carbonate and bicarbonate added, and are thus not exactly the same for all data points.

In the Monte Carlo simulation giving the estimated error in the fitted stability constant, the pH errors were assigned as discussed above, the assigned standard deviations in the total carbonate concentrations were $3 \cdot 10^{-3}$ M, and the uncertainties in the fitted concentrations were estimated using Eqn. 1.

The distribution of thorium obtained with our model at $[CO_3^{2-}]_{tot} = 0.1$ M in the pH range investigated in the batch experiments is shown in Fig. 4.

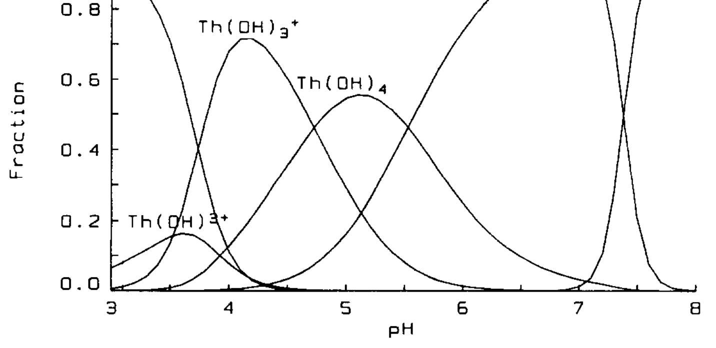

FIG. 2. Distribution diagram for thorium at $p_{CO_2} = 0.10$ atm. in the pH range covered by the continuous titration experiments.

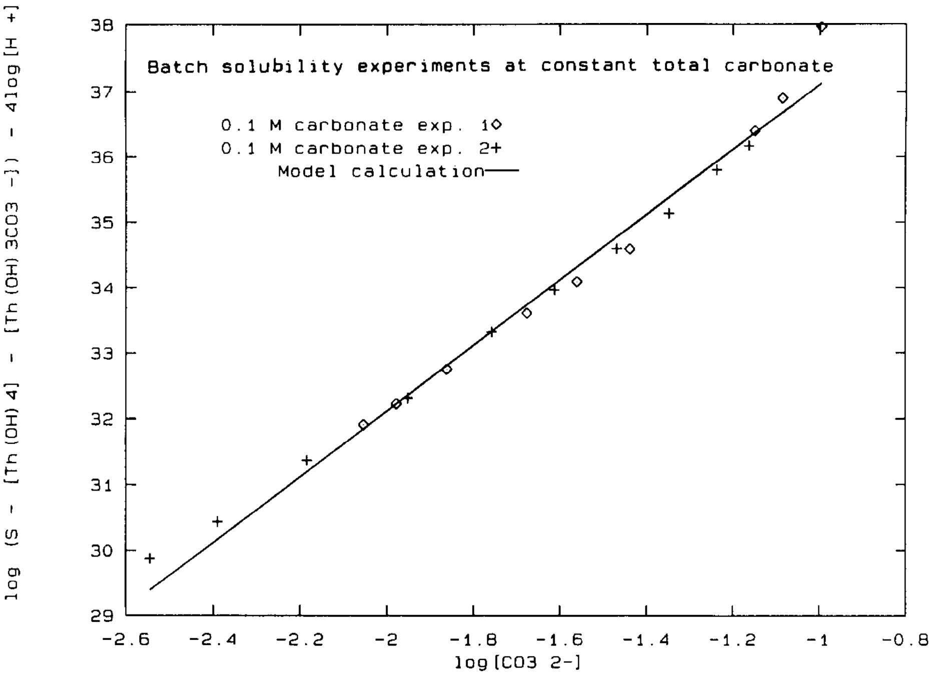

FIG. 3. Measured and calculated solubilities of microcrystalline ThO_2 in batch experiments for constant total carbonate concentrations. The line represents the calculated solubility using the stability constants determined in this work.

Final Model

In the final stage of the modelling, the two carbonate complex stability constants as well as the solubility constant for amorphous thorium oxide were simultaneously fitted to all data except those indicated above. The uncertainties in the fitted parameters were obtained using Monte Carlo simulations for all data points, again excluding the low pH data. The uncertainties quoted are the individual errors in the estimated parameters, obtained by fixing all other fitting parameters.

RESULTS

The least squares fitting of our solubility data yields the following results for 0.5 M $NaClO_4$ at 25°C 1 atm. pressure:

$$ThO_2(act) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O \log K_s = 9.37 \pm 0.13, \quad (2)$$

$$ThO_2(act) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^- \log \beta_{1,3,1} = 6.11 \pm 0.19, \quad (3)$$

$$ThO_2(act) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} \log \beta_{1,0,5} = 42.12 \pm 0.32. \quad (4)$$

The uncertainties quoted for the constants are equal to three standard deviations. By extrapolation using the specific ion interaction theory (GRENTHE et al., 1992), the following constants are obtained for the infinite dilution standard state:

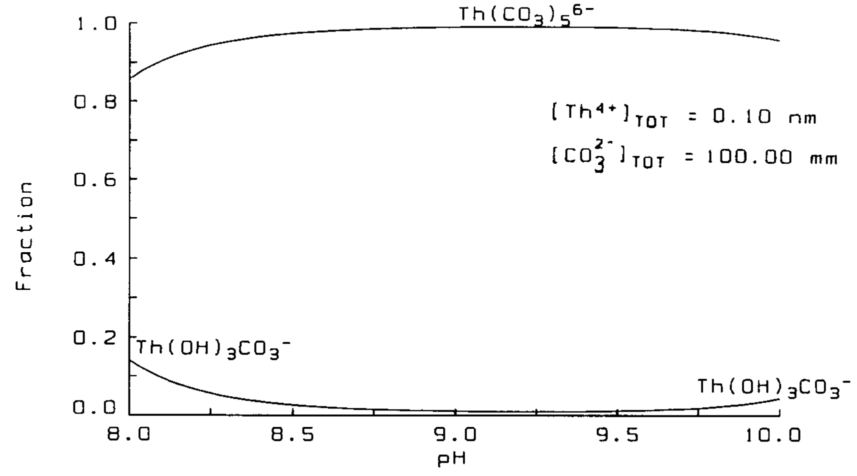

FIG. 4. Distribution diagram for thorium at $[CO_3^{2-}]_{tot} = 0.1$ M in the pH range covered by the batch experiments.

Table 2

Solubility data from continuous titrations

pCO_2	$\log[H^+]$	$\log[Th^{4+}]_{tot}$
0	-4.05	-4.660
0	-3.94	-4.351
0	-3.74	-4.218
0	-3.31	-3.599
0.1 atm CO_2, experiment 1		
0.1	-7.28	-4.899
0.1	-7.36	-4.742
0.1	-4.84	-5.38
0.1	-4.64	-5.28
0.1 atm CO_2, experiment 2		
0.1	-5.23	-5.936
0.1	-5.28	-5.876
0.1	-5.01	-6.229
0.1	-5.59	-6.163
0.1	-5.92	-6.066
0.1	-6.29	-6.132
0.1	-6.13	-5.986
0.1	-6.29	-5.749
0.1	-6.45	-5.536
0.1	-6.52	-5.445
0.1	-6.94	-5.035
0.1	-7.27	-4.966
0.1	-7.35	-4.801
0.1 atm CO_2, experiment 3		
0.1	-5.08	-6.426
0.1	-5.66	-6.175
0.1	-5.93	-5.900
0.1	-6.20	-5.611
0.1	-6.34	-5.466
0.1	-6.54	-5.352
0.1	-6.57	-5.368
pCO_2	$\log[H^+]$	$\log[Th^{4+}]_{tot}$
0.1	-6.65	-5.283
0.1	-6.65	-5.287
0.1	-6.65	-5.290
0.1	-6.97	-5.145
0.1	-7.22	-5.062
1 atm CO_2, experiment 1		
0.97	-4.14	-6.472
0.97	-4.51	-6.558
0.97	-4.91	-6.576
0.97	-5.36	-6.027
0.97	-5.64	-5.503
0.97	-5.99	-5.288
0.97	-6.20	-5.052
0.97	-6.34	-4.908
1 atm CO_2, experiment 2		
0.97	-4.19	-6.059
0.97	-4.33	-6.048

$$ThO_2(act) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O \quad \log K_s = 7.31 \pm 0.3,$$

$$ThO_2(act) + H^+ + H_2O + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^- \quad \log \beta_{1,3,1} = 6.78 \pm 0.3,$$

$$ThO_2(act) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} \quad \log \beta_{1,0,5} = 39.64 \pm 0.4.$$

The theoretical solubilities using these constants as well as the measured solubilities are depicted in Figs. 1 and 3. The measured solubilities are also tabulated in Tables 2 and 3.

DISCUSSION

Heterogeneous equilibria usually have slower kinetics than homogeneous equilibria, and the dissolution of ThO_2 is no exception. The equilibria are clearly getting slower as the $[CO_3^{2-}]$ decreases, as indicated by the fact that a few days was usually enough to reach equilibrium in the 0.97 atm. CO_2 experiment, whereas attempts to carry out experiments with 0.01 atm CO_2 were discontinued because equilibrium could not be reached within two weeks. A similar dependence of dissolution rate on carbonate concentration has been observed in a kinetic study of the dissolution of $Fe_2O_3(s)$ in bicarbonate solution (BRUNO et al., 1992a). This, together with the fact that solubility equilibria are slower at low solubilities, probably accounts for the less satisfactory fit at the lowest solubilities. However, the fitted stability constants for the carbonate complexes are well determined from the more accurate data at higher solubility. As indicated in Fig. 1, the data obtained at low pH, although of lower quality as discussed above, are not entirely incompatible with the theoretical solubility curve.

Mixed complexes of the type $Me_p^{n+}(OH)_q(CO_2)_r^{pn-q}$ have been found for several metal ions (BRUNO, 1990), and it is not unexpected to find one for Th considering the available data for U(IV) (GRENTHE et al., 1992). ALLARD (1982) suggested the possibility of formation of tetravalent actinide complexes of the type $An(OH)_3CO_3^-$ from Pu(IV) solubilities in carbonate solutions. He estimated the stability constant for the reaction

$$Th^{4+} + 3OH^- + CO_3^{2-} \rightleftharpoons Th(OH)_3CO_3^- \qquad (5)$$

to be 10^{42} at 0 ionic strength. In the present work we obtain $10^{41.5}$.

The pentacarbonate complex structure is well established in solid phase investigations (VOLIOTIS and RIMSKY, 1975). This clearly shows that the thorium ion is capable of coordinating five carbonate ions. The value found for the stability

Table 3

Solubility data from batch experiments

$[CO_3^{2-}]_{tot}$	$\log[H^+]$	$\log[Th^{4+}]_{tot}$
0.0857	-8.77	-3.135
0.0898	-8.83	-3.078
0.0890	-8.97	-3.102
0.0957	-9.16	-3.028
0.0949	-9.32	-3.166
0.0999	-9.47	-3.264
0.1109	-9.94	-3.334
0.1101	-10.14	-3.639
0.1157	-10.45	-4.014
0.1041	-8.21	-2.945
0.1015	-8.36	-2.987
0.1012	-8.56	-2.873
0.1043	-8.80	-2.878
0.1011	-9.04	-2.817
0.1045	-9.20	-2.849
0.1028	-9.41	-3.030
0.1029	-9.59	-3.229
0.1035	-9.80	-3.377
0.1015	-10.00	-3.801

constant of the limiting pentacarbonate complex of Th at zero ionic strength can be recalculated to the reaction

$$Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}, \qquad (6)$$

giving a log stability constant of 32.3, which can be compared to the value found for the corresponding reaction for U(IV) (GRENTHE et al., 1992), 34.0 ± 0.9. (JOÃO et al., 1987) have determined a stability constant for the above reaction through liquid extraction methods. Their study confirms the stoichiometry of the pentacarbonate complex. They obtained a log stability constant of 26.2 in 1 M carbonate media, which is considerably lower than our value of 32.8 in 0.5 M $NaClO_4$. However, the former value is based on the assumption that the thorium-EDTA complex formed at high pH is ThY. This is not correct. The predominant complex is Th(OH)Y as shown by the equilibrium constant log $K = 7.04$ (SMITH and MARTELL, 1989) for the reaction

$$ThY + H_2O \rightleftharpoons Th(OH)Y + H^+. \qquad (7)$$

Using this to recalculate the result of JOÃO et al. (1987) gives log $\beta = 33.2$ for reaction 6, which is in good agreement with our value.

FAUCHERRE and DERVIN (1962) have estimated the log of the stability constant for the reaction 6 to be 1.36 from measurements of freezing point depressions. However, there is no independent assessment of the dominant reaction in solution which is postulated to be 6. Moreover, the treatment of data assumes the existence of free Th^{4+} in solution, and given the high alkalinity and high carbonate concentrations of the solutions used, this is not a valid assumption.

Several workers (GAYER and LEIDER, 1954; GREILING and LIESER, 1984; RYAN and RAI, 1987) have studied the solubility of $ThO_2(s)$ in aqueous media. These solubility measurements have produced results that seem to differ by as much as three orders of magnitude in the minimum solubility at higher pH, but they all indicate a sharp decrease of solubility with increasing pH, yielding what seems to be a constant solubility at neutral to alkaline pH. The observed differences in the total Th concentration data obtained in this region may partly be due to differing degrees of crystallinity of the solid phase (BAES and MESMER, 1976). It is obvious from earlier studies (BAES and MESMER, 1976, GREILING and LIESER, 1984, PRASAD et al., 1967, DZIMITROWICZ et al., 1984) that the solubility and properties of the solid phase change with the method of preparation in terms of temperature and degree of supersaturation, and that aging with time takes place in the cases where the initially formed solid is not perfectly crystalline. As one would expect, with increased temperature the solubility decreases due to formation of larger crystals with smaller specific surface area and less surface layer −OH groups. Therefore, the degree of crystallinity and surface area should be considered when judging solubility data (BRUNO, 1989). Different filtering methods can also influence the solubility values obtained, since thorium may form colloidal particles in aqueous media (DZIMITROWICZ et al., 1984).

Considering what is known about the dissolution kinetics of $UO_2(s)$ (BRUNO et al., 1991), one might expect increasing dissolution rates with increasing proton concentration for thorium dioxide. This might account for the difficulties in getting reliable data in the low pH range, where the solubility starts increasing, since the dissolution rate increases but not the reprecipitation rate. This makes it difficult to obtain equilibrium if for some reason the solution becomes oversaturated, which might happen if acid is added too quickly. In the absence of ligands other than hydroxide, one also expects slow dissolution kinetics above pH 4, where the solubility is very low.

The formation of large thorium carbonate clusters even at low pH in solutions with high total thorium concentration (GRENTHE and LAGERMAN, 1991) shows that probably the presence of carbonate increases the rate of precipitation, as well as the rate of dissolution as discussed above. One would, therefore, expect it to be considerably easier to attain solubility equilibrium in the presence of carbonates.

The log of the solubility product found for amorphous thorium oxide at infinite dilution in this study, 7.42, is several logarithmic units lower than the value proposed by BAES and MESMER (1976), 9.4. However, the latter value is strongly dependent on the hydrolysis model used, which is different from the one used in this study. The minimum solubility above pH 4.5 used in BAES and MESMER (1976), taken from a work using hydrous thorium oxide at 17 deg. C and 0.1 M $NaClO_4$ (NABIVANETS and KUDRITSKAYA, 1964) is $10^{-6.32}$ M in the absence of carbonate. This correlates well with our estimate in 0.1 M $NaClO_4$ and 25°C which is $10^{-6.56}$ M. We note that the hydrous thorium dioxide used by NABIVANETS and KUDRITSKAYA (1964) has been produced in much the same way as in our study. Also, the limiting solubility at high pH found by GAYER and LEIDER (1954), again using a procedure similar to ours for producing the solid phase, is approximately 10^{-6} M at 25°C in 0.3–0.8 M NaOH solutions. However, RYAN and RAI (1987) found minimum solubilities at high pH in 0.1 M $NaClO_4$ at 25 deg. C of approximately 10^{-9} M for hydrous thorium dioxide. In our work we also found the solubility at high pH in the absence of carbonate to be below our detection limits. Possible causes for the differences have been discussed above, but it is not clear what the exact reason for this discrepancy is. In this study, the lower limit of the value obtained for the solubility product K_s, is dependent on our measurements in the pH range below 6 at relatively low carbonate concentrations and low thorium solubilities. Still, because of the good agreement of our model at high pH with several previous studies (GAYER and LEIDER,

Table 4

Hydrolysis constants used for fitting corrected to 0.5 M $NaClO_4$. All equilibria written as:

$$pTh^{4+} + qH_2O + rCO_2(g) \rightleftharpoons Th_p(OH)_q(CO_2)_r^{4p-q} + qH^+$$

p,q,r	log $\beta_{p,q,r}$
0,1,0	-13.75
0,1,1	-7.57
0,1,1	-17.23(a)
1,1,0	-4.16
1,3,0	-11.22
1,4,0	-15.95
2,2,0	-6.71
2,3,0	-8.22

(a) Second acidity constant for H_2CO_3

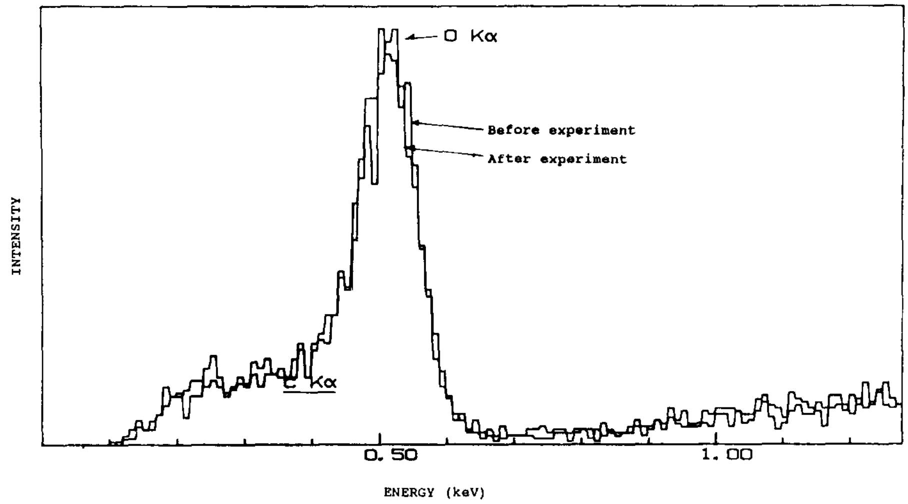

FIG. 5. Energy dispersive X-ray fluorescence spectrum of solid phase before and after solubility experiment. Intensity plotted vs. fluorescence wavelength.

1954; NABIVANETS and KUDRITSKAYA, 1964), we select our fitted solubility product as the best to use in our model.

In the absence of complexing ligands other than OH^-, the solubility of thorium oxide at pH above 4–5 is governed by the reaction

$$ThO_2(act) + 2H_2O \rightleftharpoons Th(OH)_4(aq). \quad (8)$$

The determination of the solubility product K_s as written in Eqn. 2, from solubility measurements of this type, requires an independent determination of the stability constant for the formation of the complex $Th(OH)_4(aq)$. Few such determinations are available, and as mentioned above we have chosen the one by GRENTHE and LAGERMAN (1991). The stability constants for the thorium carbonate complexes proposed in this study are in any case not very sensitive to the hydrolysis constants chosen.

The X-ray Powder Diffraction data in our study show no detectable increase in crystallinity for the solid phase over the time of the experiments, and this together with the BET analyses supports the conclusion that the aging of the solid during the experiments is negligible.

There are several reports of solid phases of thorium containing carbonates (CLEVE, 1874; CHERNYAEV et al., 1958; VOLIOTIS and RIMSKY, 1975). These solids contain some additional ion, such as sodium or potassium, and are usually produced by evaporation of solutions of high carbonate concentrations. Their thermodynamic stability vs. thorium dioxide is uncertain (AHRLAND et al., 1973). Our X-ray fluorescence data indicate that no bulk changes in thorium dioxide take place even if the solid is in contact with carbonate media for several months, indicating a higher thermodynamic stability of the oxide than of the solids containing carbonate.

IMPLICATIONS FOR THE BEHAVIOUR OF THORIUM IN NATURAL WATERS

In Fig. 6, we compare the measured concentrations of ^{232}Th in some alkaline lakes in the U.S. where elevated Th concentrations have been found (LAFLAMME and MURRAY, 1987; SANCHEZ et al., 1986; SIMPSON et al., 1984), with predictions using the stability constants for the carbonate complexes determined in this work, and the hydrolysis data in Table 4. The lakes are, in order of increasing carbonate concentration, Lake Abert and Mono Lake in Eastern Washington, and Soap Lake in California, USA. The pH range for these lakes is rather narrow, 9.6–10.0, and the total carbonate

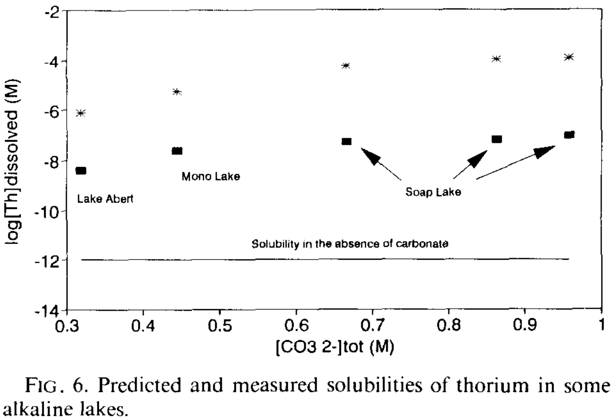

FIG. 6. Predicted and measured solubilities of thorium in some alkaline lakes.

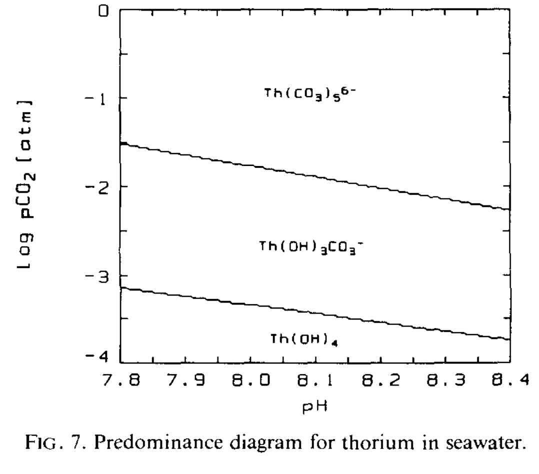

FIG. 7. Predominance diagram for thorium in seawater.

concentrations vary from 0.3 to 0.96 M. In an effort to estimate the solubility product for crystalline $ThO_2(s)$, we have used free energy of formation data (CODATA, 1976; CODATA, 1977). This gives $\log K = 1.8$ for reaction 2, which is close to the value suggested by ALLARD (1982) for An(IV) oxide solubility products, 2. The choice of solubility product is somewhat arbitrary, since crystallinity and coprecipitation will probably influence the value. We have chosen the value 2, and corrected it to 0.5 M ionic strength to be consistent with the other constants used. This corrected value was used to produce Fig. 5. We contend that our model can predict the trend in the data rather well. The dominating complex in all of the cases shown in Fig. 6 is the pentacarbonate complex. We have not attempted any corrections for varying ionic strengths in the lakes, since the salinity is quite high in all the lakes, and the influence of salinity on the total solubility of Th in carbonate solutions is rather small. The thermodynamic data underlying the diagram do not include any other ligands for Th than OH^- and CO_3^{2-}. The systematic difference between the predicted solubility and the reported can be corrected by a lowering of the solubility product. Such a lowering is expected for trace elements like thorium which may form coprecipitates with solid phases of major geochemical elements.

The importance of carbonate complexes for Th speciation in seawater has been discussed by BRUNO (1990). We have recalculated the predominance diagram for thorium in seawater using the constants obtained in this work, again without corrections for ionic strengths. The result is shown in Fig. 7. It is clear from the diagrams that contrary to the conclusions of LANGMUIR and HERMAN (1980), thorium carbonate complexes cannot be neglected when modelling the distribution of thorium in natural waters. It is very likely that other tetravalent actinides will show a similar behavior.

Acknowledgments—The authors wish to thank Dr. Kastriot Spahiu for valuable suggestions and calculations regarding the carbonate chemistry of tetravalent actinides. The SEM photographs were taken at the Department of Material Sciences, RIT, with the kind help of Dr. Nils Lange. The X-ray fluorescence measurements were made at the Institute of Concrete and Building Materials Research in Stockholm with the assistance of Dr. Manfred Meier, and the BET and porosity measurements were made by Dr. Sven-Ingvar Andersson and coworkers at the Dept. of Technical Chemistry, Chalmers Institute of Technology in Gothenburg. The work was financed by the SKB (Swedish Nuclear Fuel and Waste Management Co.).

Editorial handling: R. H. Byrne

REFERENCES

AHRLAND et al. (1973) *The Chemistry of the Actinides.* Pergamon Press.

ALLARD B. (1982) Solubilities of Actinides in Neutral or Basic Solutions. In *Actinides in Perspective* (ed. N. M. EDELSTEIN), pp. 553–580. Pergamon Press.

ANDERSON R. F., BACON M. P., and BREWER P. G. (1982) Elevated concentrations of Actinides in Mono Lake. *Science* **216**, 514–516.

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

BASKARAN M., SANTSCHI P. H., BENOIT G., and HONEYMAN B. D. (1992) Scavenging of thorium isotopes by colloids in seawater of the Gulf of Mexico. *Geochim. Cosmochim. Acta* **56**, 3375–3388.

BIEDERMANN G. and DOUHÉRET, G. (1980) Studies of Cells with Transference. *Chem. Scripta* **16**, 144–153.

BRUNO J. (1986) Stoichiometric and Structural Studies on the $Be^{2+} - H_2O - CO_2(g)$ System. Ph.D. dissertation, Royal Inst. of Techn.

BRUNO J. (1989) A Reinterpretation of the Solubility Product of Solid Uranium(IV) Dioxide. *Acta Chem. Scand.* **43**, 99–100.

BRUNO J. (1990) The Influence of Dissolved Carbon Dioxide on Trace Metal Speciation in Seawater. *Marine Chem.* **30**, 231–240.

BRUNO J., GRENTHE I., and ROBOUCH P. (1989) Studies of Metal Carbonate Equilibria. 20. Formation of Tetra(carbonato)-uranium(IV) Ion, $U(CO_3)_4^{4-}$, in Hydrogen Carbonate Solutions. *Inorg. Chim. Acta* **158**, 221–226.

BRUNO J., CASAS I., and PUIGDOMÈNECH I. (1991) The kinetics of dissolution of UO_2 under reducing conditions and the influence of an oxidized surface layer (UO_{2+x}): Application of a continuous flow-through reactor. *Geochim. Cosmochim. Acta* **55**, 647–658.

BRUNO J., STUMM W., WERSIN P., and BRANDBERG F. (1992a) On the influence of carbonate in mineral dissolution: I. The thermodynamics and kinetics of hematite dissolution in bicarbonate solutions at T = 25°C. *Geochim. Cosmochim. Acta* **56**, 1139.

BRUNO J., WERSIN P., and STUMM W. (1992b) On the influence of carbonate in mineral dissolution: II. The solubility of $FeCO_3(s)$ at 25°C and 1 atm. total pressure. *Geochim. Cosmochim. Acta* **56**, 1149–1155.

CHAFEE E., DASGUPTA T. P., and HARRIS G. M. (1973) Kinetics and mechanism of aquation and formation reactions of carbonato complexes V. Carbon dioxide uptake by hydroxopentaamminecobalt(III) ion. *J. Chem. Soc.* **95**, 4169.

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.

CHERNYAEV I. I., GOLOVNYA V. A., and MOLODKIN A. K. (1958) On hydrated forms of sodium penta-carbothoriate. *Zhur. Neorg. Khim.* **3**, 2671.

CLEVE P.-T. (1874) Sur les combinaisons du thorium. *Bull. Soc. Chim.* **21**, 115.

DANESI P. R., MAGINI M., MAGHERITA S., and D'ALLESANDRO G. (1968) Hydrolytic behaviour of concentrated thorium nitrate and perchlorate solutions. *Energ. Nucl.* **15**, 335.

DZIMITROWICZ D. J., WISEMAN P. J., and CHERNS D. (1984) An electron Microscope Study of Hydrous Thorium Dioxide $ThO_2 \cdot nH_2O$. *J. Coll. Interf. Sci.* **103**, 170–177.

FAUCHERRE J. and DERVIN J. (1962) Sur la constitution en solution des thoricarbonates complexes. *Compt. Rend. Acad. Sci.* **255**, 2264–2266.

FRYDMAN M., NILSSON G., RENGEMO T., and SILLÉN L. G. (1958) Some solution equilibria involving calcium sulfite and carbonate III. The acidity constants of H_2CO_3 and H_2SO_3 and $CaCO_3 + CaSO_3$ equilibria in $NaClO_4$ medium at 25 deg. C. *Acta Chem. Scand.* **12**, 878–884.

GAYER K. H. and LEIDER H. (1954) The Solubility of Thorium Hydroxide in Solutions of Sodium Hydroxide and Perchloric Acid at 25°C. *J. Amer. Chem. Soc.* **76**, 5938.

GRAN G. (1952) Determination of the equivalence point in potentiometric titrations. *Analyst* **77**, 661.

GREILING H.-D. and LIESER K. H. (1984) Properties of ThO_2, UO_2 and PuO_2 as Function of Pretreatment and their Dissolution in HNO_3. *Radiochim. Acta* **35**, 79–89.

GRENTHE I. and LAGERMAN B. (1991) Studies on Metal Carbonate Equilibria. 23. Complex Formation in the $Th(IV) - H_2O - CO_2(g)$ System. *Acta. Chem. Scand.* **45**, 231–238.

GRENTHE I. et al. (1992) *Chemical Thermodynamics of Uranium (NEA-OECD).* North-Holland Elsevier Sci. Publ.

HUNTER K. A., HAWKE D. J., and CHOO, L. K. (1988) Equilibrium adsorption of thorium by metal oxides in marine electrolytes. *Geochim. Cosmochim. Acta* **52**, 627–636.

JOÃO A., BIGOT S., and FROMAGE F. (1987) Etude des carbonates complexes des éléments IVB I-Détermination de la constante de stabilité du pentacarbonatothorate(IV). *Bull. Soc. Chim. Fr.* **1**, 42–44.

LAFLAMME B. D. and MURRAY J. W. (1987) Solid/solution interaction: The effect of carbonate alkalinity on adsorbed thorium. *Geochim. Cosmochim. Acta* **51**, 243–250.

LANGMUIR D. and HERMAN J. S. (1980) The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta* **44,** 1753–1766.

MENAGER M.-T., PARNEIX J.-C., PETIT J.-C., and DRAN J.-C. (1988) Migration of U, Th and REE in an Intragranitic Hydrothermal System: Implications for the Mobility of Actinides Around a Radwaste Repository. *Radiochim. Acta* **44/45,** 291–297.

MORAN S. B. and BUESSELER, K. O. (1992) Short residence time of colloids in the upper ocean estimated from U-Th disequilibria. *Nature* **359,** 221–223.

NABIVANETS B. I. and KUDRITSKAYA L. N. (1964) Hydrocomplexes of Th(IV). *Ukr. Khim. Zh.* **30,** 891–895.

ÖSTHOLS E. (1991) *The C-Letagrop program system TRITA-OOK-2051.* Roy. Inst. Technol.

PRASAD R., BEASLEY M. L., and MILLIGAN W. O. (1967) Aging of Hydrous Thoria Gels. *J. Electron Micr.* **16,** 101–119.

PRESS W. H., FLANNERY B. P., TEUKOLSKY, S. A., and VETTERLING W. T. (1988) *Numerical Recipes in C.* Cambridge Univ. Press.

RYACHIKOV D. I., VOLYNETS M. P., ZARINSKIJ V. A., and IVANOV V. I. (1963) *Zhur. Analit. Khim.* **18,** 348.

RYAN J. L. and RAI D. (1987) Thorium(IV) Hydrous Oxide Solubility. *Inorg. Chem.* **26,** 4140–4142.

SANCHEZ A. L., MURRAY J. W., SCHELL W. R., and MILLER L. G. (1986) Fallout plutonium in two oxic-anoxic environments. *Limnol. Oceanogr.* **31(5),** 1110–1121.

SANTSCHI P. H. and HONEYMAN B. D. (1989) Radionuclides in Aquatic Environments. *Radiat. Phys. Chem.* **34(2),** 213–240.

SAVVIN S. B. (1961) Analytical Use of Arsenazo III. *Talanta* **8,** 673–685.

SILLÉN L. G. and MARTELL A. E. (1964) *Stability Constants of Metal-Ion Complexes Sect. I; The Chemical Society, Spec. Publ. No. 17,* London.

SIMPSON H. J., OLSEN C. R., HAMMOND D. E., FULLER C., KU T. L., TRIER R. M., TOGGWEILER J. R., MATHIEU G., and DECK B. L. (1982) Radionuclides in Mono Lake, California. *Science* **216,** 512–514.

SIMPSON H. J., TRIER R. M., LI Y-H., ANDERSON R. F., and HERCZEG A. L. (1984) *Field experiment determinations of distribution coefficients of actinide elements in alkaline lake environments.* NUREG/CR-3940 Report U.S. Nuclear Reg. Commission.

SMITH R. M. and MARTELL A. E. (1989) *Critical Stability Constants,* Vol. 6. Plenum Press.

SPAHIU K. (1983) Carbonate Complex Formation in Lanthanoid and Actinoid Systems. Ph.D. Dissertation Royal Inst. Technol.

TAKEUCHI T., HANSON K., and WADSWORTH M. E. (1971) Dissolution of Thorium Oxide in Hydrofluoric acid and Nitric Acid Mixtures. *J. Inorg. Nucl. Chem.* **33,** 1089–1098.

VOLIOTIS S. and RIMSKY A. (1975) Etude Structurale des Carbonates Complexes de Cérium et de Thorium III. *Acta Crystallogr., Sect. B* **31,** 2615.