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## The Solubility of Hydrrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model

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*Ion interaction / Thorium oxide / Solubility / Aqueous thermodynamics / Th<sup>4+</sup>(aq)*

### Abstract

The solubility of hydrrous Th(IV) oxide was measured in NaCl solutions ranging in concentration from 0.6 to 3.0 M and in KCl at 0.6 M, over a wide range of hydrogen ion concentration ( $p_{\text{CH}^+}$  3 to 11), and over equilibration times extending to more than one year. Our results show solubilities higher (by three to four orders of magnitude) than have been reported by other investigators in NaClO<sub>4</sub> media. Our thermodynamic modeling calculations indicate that these differences in solubility are a result of differences in the ionic media and the ionic strength of the solutions.

We have used the thermodynamic model of Pitzer and coworkers, which is valid to high ionic strengths, to analyze our data for solubility in both chloride and perchlorate media. The analysis required the use of specific ion-interaction parameters only for the bare Th<sup>4+</sup> ion with the bulk anion Cl<sup>-</sup>. The final thermodynamic model gives a good representation of all of our solubility data in NaCl and KCl solutions below  $p_{\text{CH}^+}$  of  $\sim 7$  as well as the solubility data in NaClO<sub>4</sub> media and the osmotic data for ThCl<sub>4</sub> solutions.

### Introduction

At low pH (<3), hydrrous Th(IV) oxides are highly soluble and the aqueous thermodynamics of Th(IV) can be studied by classical electromotive force (EMF) techniques. Not surprisingly, a large amount of precise EMF data is available on Th(IV) hydrolysis in a variety of electrolyte solutions [1–6]. The studies have been conducted almost exclusively at high total Th concentrations or with high concentrations of background electrolyte. The high Th concentrations cause the formation of polynuclear species, and the high concentrations of background electrolyte make extrapolation of these results to dilute solution difficult. The identity of the Th(IV) hydrolysis species in these studies has generally been inferred from least-squares statistical analysis of the experimental data. Past analyses have proposed numerous mononuclear and polynuclear hydrolysis species, including ThOH<sup>3+</sup>, Th(OH)<sub>2</sub><sup>2+</sup>, Th<sub>2</sub>(OH)<sub>2</sub><sup>6+</sup>, Th<sub>4</sub>(OH)<sub>8</sub><sup>8+</sup>, Th<sub>4</sub>(OH)<sub>12</sub><sup>4+</sup>, and Th<sub>6</sub>(OH)<sub>15</sub><sup>9+</sup>.

Most of these species are important only at high total dissolved Th(IV) concentrations and/or in acidic solutions (pH <3), and the mononuclear species in particular are usually relatively minor species in these

solutions. At higher pH values, the hydrrous oxides precipitate [7, 8] and dissolved Th concentrations decrease rapidly. In this higher-pH region, the dissolved Th concentrations are very low, and only the unhydrolyzed Th<sup>4+</sup> ion and/or mononuclear hydrolysis species (e.g., ThOH<sup>3+</sup>, Th(OH)<sub>2</sub><sup>2+</sup>) are expected to be important. Unfortunately, the low concentrations of dissolved Th(IV) and the possible presence of precipitated material make it difficult or even impossible to study these higher-pH solutions experimentally with classical EMF techniques. This is a particular problem because this pH region (pH >3) includes almost the entire range of possible solution pH values and almost the entire pH range of natural waters. Because of the difficulty of identifying the important hydrolysis species by EMF techniques, especially at low total Th concentrations and higher pH values, investigators have attempted to identify the mononuclear hydrolysis species more precisely by studying the solubility of Th(IV) oxides [7, 8]. Because Th(IV) oxides and hydrrous oxides are highly insoluble, solubility studies offer considerable promise for experimentally unraveling the aqueous chemistry of Th(IV) at higher pH values. Ideally, these studies would be conducted with well-characterized crystalline materials. Unfortunately, at low temperature, the well-characterized crystalline ThO<sub>2</sub>(c) equilibrates with the aqueous phase only very slowly, and it is difficult to establish that equilibrium has been achieved in such studies. Because of such difficulties, investigators have attempted to identify the mononuclear hydrolysis species more precisely by studying the solubility of hydrrous Th(IV) oxide, which can equilibrate with the aqueous phase rapidly, even though precipitates of Th(IV) oxide may be difficult to characterize exactly. Unfortunately, past investigators have disagreed sharply. Baes and Mesmer [9], in interpreting the solubility data of Nabivanets and Kudritskaya [8], concluded that Th(OH)<sub>2</sub><sup>2+</sup> and Th(OH)<sub>4</sub>(aq) were the dominant hydrolysis species. However, Ryan and Rai [7] recently found solubilities much lower than those of Nabivanets and Kudritskaya [8] and no convincing evidence for the formation of such mononuclear hydrolysis species.

In this paper, we report our findings on the solubility of hydrrous Th(IV) oxide in chloride solutions over wide ranges of  $p_{\text{CH}^+}$  and bulk electrolyte composition and over equilibration times extending to more

than a year. Our results are interpreted using a thermodynamic model that is valid to high ionic strength [10, 11].

### Experimental procedure

All experiments were conducted in a glovebox under an atmosphere of ultrapure argon. Precipitates were prepared according to the procedure used by Ryan and Rai [7]. A 100-g/l Th stock solution was prepared by dissolving reagent-grade  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  in 0.1 M  $\text{HNO}_3$ . A 0.625-ml (62.5 mg Th) aliquot of the stock solution was added to approximately 10 ml of boiled deionized water in each 50-ml polypropylene centrifuge tube, and the Th(IV) precipitates were formed by the addition of excess base,  $\sim 0.08$  ml of 10 M  $\text{CO}_2$ -free NaOH. The suspensions were centrifuged at about  $2000 \times g$  for 7 to 10 min and then washed twice with boiled deionized water. Thirty milliliters of NaCl or KCl was then added to each centrifuge tube containing precipitate, and the pH was adjusted to a range of values between 3 and 11 using either  $\text{CO}_2$ -free NaOH or HCl. The KCl was used primarily as a check on the NaCl results. All suspensions were placed on an orbital shaker inside the glovebox and shaken. Six sets of suspensions were prepared (three sets in 3 M NaCl, one set each in 0.6 and 1.2 M NaCl, and one set in 0.6 M KCl). The chloride solutions were prepared from reagent-grade chemicals and then acidified to pH  $\sim 4$  before use to remove any excess carbonate that may have been present in the reagent-grade chemicals. Each set was allowed to equilibrate for a different length of time before sampling. The sets in 3 M NaCl and 0.6 M KCl were sampled only once; the sets in 0.6 and 1.2 M NaCl were sampled twice.

Sampling consisted of measuring either the pH or the hydrogen ion concentration, as we will describe, and centrifuging and filtering the supernatants. Filtration was through Amicon type F-25 Centriflo membrane cones with effective 2500-molecular-weight cut-offs and approximately 0.0018- $\mu\text{m}$  pore sizes. Rai and others [7, 12, 13] have shown that these membranes are effective in separating solids from solutions. The membranes were pretreated in the following manner: First, all membranes were soaked in  $\sim 0.01$  M HCl overnight. Next, the membranes were washed with deionized water and then in turn with small aliquots of deionized water, pH-adjusted deionized water (at the approximate pH of the sample), and finally an aliquot of the sample. Such pretreatment should both saturate any adsorption sites on the filters and prevent dissolution of the precipitate upon contact with the filters.

Filtrates were analyzed for Th by inductively coupled plasma mass spectrometry (ICP-MS). The high NaCl or KCl concentration interfered with the ICP-MS analysis. As a result, the Th had to be extracted from the chloride matrix before analysis. Extraction of the Th from the chloride filtrates was accomplished

Table 1. Parameters for correcting pH(obs) to  $p_{\text{cH}^+}$ <sup>a</sup>

Aqueous solution	<i>A</i>
3.0 M NaCl	0.46
1.2 M NaCl	0.16
0.6 M NaCl	0.04
0.6 M KCl	-0.08

$$^a p_{\text{cH}^+} = \text{pH}(\text{obs}) + A.$$

by the use of thenoyltrifluoroacetone (TTA) in acetate buffer solution, as described by Bertrand and Choppin [14] and Schramke *et al.* [15]. This procedure was tested and yielded quantitative extractions over the ranges of NaCl and total Th concentrations encountered in this study. With the exception of analyses near the analytical detection limit ( $\sim 0.5$   $\mu\text{g/l}$  Th), ICP-MS analyses were highly precise with errors usually  $< 10\%$ .

The concentration of hydrogen ions in NaCl and KCl solutions was calculated from the observed pH meter reading, according to a modified Gran titration procedure [16–19]. In this method, the observed pH [pH(obs)] is related to the concentration of hydrogen ions by the equation

$$\text{pH}(\text{obs}) = p_{\text{cH}^+} - A \quad (1)$$

where  $\text{cH}^+$  is the hydrogen ion concentration in molarity units. The constant *A* is defined by

$$A = \log \gamma_{\text{H}^+} + \frac{F}{2.303RT} \Delta E_j \quad (2)$$

where  $\gamma$  is the convention-dependent molarity-scale activity coefficient of  $\text{H}^+$ , *F* is Faraday's constant, *R* is the ideal gas constant, and  $\Delta E_j$  is the difference in liquid junction potential between standards and solutions. Although neither term on the right side of Eq. 2 can be measured experimentally, the combination of them, *A*, in Eq. 2 can be measured.

Rewriting Eq. 1 in terms of logarithms and then taking the antilog of both sides yields

$$\text{H}^+(\text{obs}) = 10^A \text{c}_{\text{H}^+}. \quad (3)$$

The constant *A* is then obtained by a modified Gran titration, in which the number of moles of acid added per liter is plotted against  $\text{H}^+(\text{obs})$ , which is the negative of the antilog of the pH meter reading. The logarithm of the slope of this curve is the correction factor *A* needed to convert the observed pH to  $p_{\text{cH}^+}$ .

The calculated values for the constant *A* to be used in Eq. 1 are listed in Table 1. The  $p_{\text{cH}^+}$  determinations were in general highly precise, with errors generally  $\leq 0.05 p_{\text{cH}^+}$  units.

### Results and discussion

The solubilities of the Th(IV) precipitates in 0.6 to 3.0 M NaCl, over a broad range of hydrogen ion concentrations ( $p_{\text{cH}^+}$  3 to 11), and over equilibration times

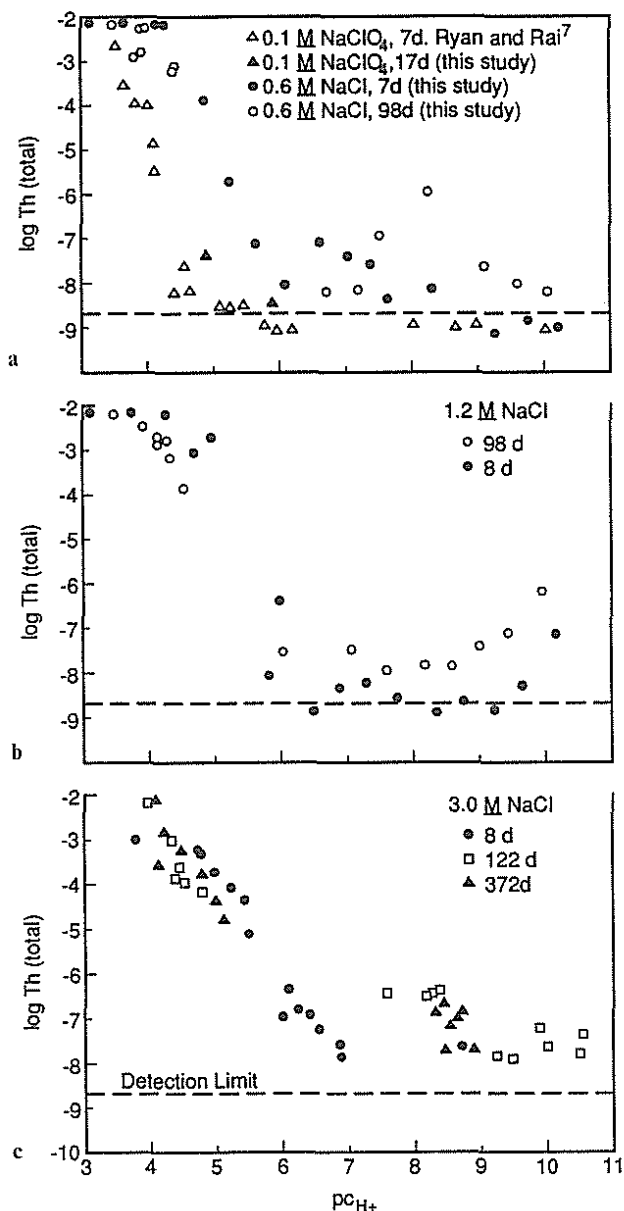


Fig. 1. Hydrated Th(IV) oxide solubilities in (a) 0.1 M NaClO<sub>4</sub> and 0.6 M NaCl solutions; (b) in 1.2 M NaCl; and (c) in 3 M NaCl.

ranging from 8 d to more than a year are shown in Fig. 1. The data show that the precipitates are highly soluble below  $p_{CH^+} \sim 4$ . The solubility decreases rapidly over the  $p_{CH^+}$  range from 4 to 7, and appears to become independent of hydrogen ion concentration when  $p_{CH^+}$  is greater than  $\sim 7$ .

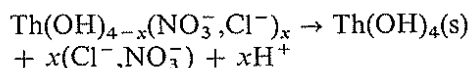
The data in Fig. 1 show another interesting feature: the solubilities obtained are at least three to four orders of magnitude higher than the solubilities in 0.1 M NaClO<sub>4</sub> media observed by Ryan and Rai [7] (see Fig. 1a). These large differences in solubility must be a result of differences either in the nature of the solid precipitates or in the aqueous ion interactions or ion-complexation reactions that occur in the aqueous solutions.

The precipitates in this study were prepared in the same way as those of Ryan and Rai [7] and therefore

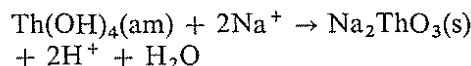
Table 2. Changes in  $p_{CH^+}$  that occurred in 0.6 M NaCl solutions upon aging

Sample	$p_{CH^+}$		Change in $p_{CH^+}$
	7 d	98 d	
J227	3.10	2.83	-0.17
J228	3.74	3.46	-0.28
J229	4.26	3.92	-0.34
J230	4.68	4.33	-0.35
J231	4.95	4.53	-0.42
J232	5.84	4.24	-1.60
J233	5.99	4.15	-1.84
J234	6.54	4.13	-2.41
J235	6.92	6.07	-0.85
J236	7.32	7.08	-0.24
J237	7.79	7.63	-0.16
J238	8.37	8.21	-0.16
J239	8.80	8.60	-0.20
J240	9.25	9.04	-0.21
J241	9.68	9.46	-0.22
J242	10.19	9.96	-0.23

should, at least initially, have been similar in chemical composition. It is possible that the chemical composition of the precipitates could have been altered after the NaCl was added to the samples, and in particular Na<sup>+</sup> or Cl<sup>-</sup> ions could have been incorporated into the precipitates. Several efforts were made to determine the precise chemical composition of the precipitates, including acid digestion and X-ray fluorescence (XRF) analysis. However, the high concentrations of Na<sup>+</sup> and Cl<sup>-</sup> in the solutions required that the precipitates be washed before analysis; even then, small amounts of adsorbed or occluded solution could have markedly affected the analysis. Nevertheless, these results show that only small amounts of Na or Cl at most could have been included in the precipitates. For example, after only two days of aging, selected precipitates in 0.6 M NaCl contained only about 6% Cl; after times longer than 3 months, all samples analyzed showed Cl at less than 1% and Na less than 0.1% (these samples included 6 from 3 M NaCl solutions). However, the presence of small amounts of foreign ions, either Na<sup>+</sup> or Cl<sup>-</sup>, or even some NO<sub>3</sub><sup>-</sup> from the original stock solution, is evidenced by changes in  $p_{CH^+}$  that occurred in certain samples after extended periods of aging. An example of these changes in 0.6 M NaCl solutions is shown in Table 2. These changes in hydrogen ion concentration could be caused by either the loss of some acidic occluded solutions, the loss of small amounts of NO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup> from the precipitates by means of such a reaction as



or the incorporation of minor amounts of Na<sup>+</sup> by means of such a reaction as



**Table 3.** Most complete XRD pattern<sup>a</sup> for a precipitate from a 3 M NaCl solution after 1 yr of aging (all peaks were broad)

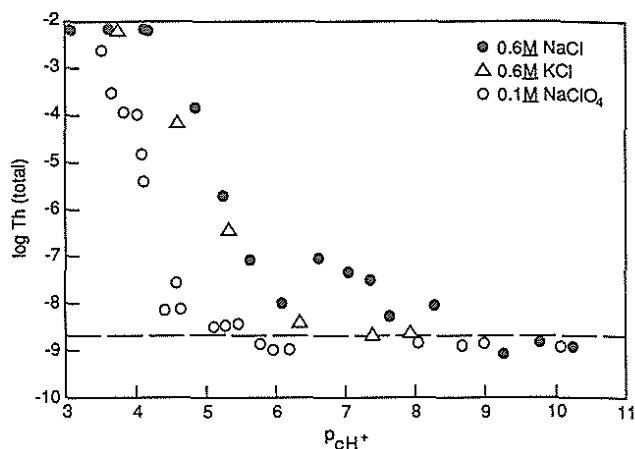
ThO <sub>2</sub> precipitate <i>d</i> Spacing Å	<i>I</i> / <i>I</i> <sup>0</sup>	ThO <sub>2</sub> (c) <sup>b</sup> <i>d</i> Spacing Å	<i>I</i> / <i>I</i> <sup>0</sup>
4.54 <sup>c</sup>	80		
3.25	90	3.23	100
		2.80	35
2.53	40		
1.99	40	1.98	58
1.82	40		
1.69	40	1.69	64
		1.62	11
1.41	30	1.40	8
1.28	30	1.28	26
		1.25	17
		1.14	20
		1.08	19

<sup>a</sup> Most complete patterns from eight samples taken after 1 yr of aging. Most samples were amorphous or showed one or two broad lines.

<sup>b</sup> Standard pattern from Joint Committee on Powder Diffraction Standards (JCPDS).

<sup>c</sup> Peak could be characteristic of trace amount of Na<sub>2</sub>ThO<sub>3</sub> (see JCPDS). Precipitates contain <0.1% Na.

which could have changed the  $p_{\text{CH}^+}$  of these poorly buffered solutions. Similar changes in  $p_{\text{CH}^+}$  were also observed by Ryan and Rai (unpublished data) in 0.1 M NaClO<sub>4</sub> solutions after 45 days of aging. Of special interest is the fact that the observed solubilities at given  $p_{\text{CH}^+}$  levels are similar after extended periods of aging (Fig. 1), despite the changes in  $p_{\text{CH}^+}$  that may have occurred in certain samples, indicating that the same solid phase material controls the solubility even after extended periods of aging in NaCl. Since the same solid phase appears to control the solubility both before and after the possible incorporation or loss of minor amounts of foreign ions from the precipitates, these foreign ions do not appear to be participating in the equilibrium reactions involving Th(IV). Of the possible substituting foreign ions (i.e., Na<sup>+</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>), incorporation of Na<sup>+</sup> would appear to be the most likely possibility, because Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> would tend to form only very soluble materials and because XRD analysis showed the possible formation of minor quantities of Na<sub>2</sub>ThO<sub>3</sub>(c) in certain 3 M NaCl solutions (see Table 3). Therefore, as a final test, we measured the solubility of precipitates prepared in the same manner in 0.6 M KCl solutions, where Na<sup>+</sup> substitution reactions cannot occur. These results (Fig. 2) show that the solubilities in 0.6 M KCl are very similar to the results in 0.6 M NaCl and indicate that the same solid phase or a solid phase of similar solubility does in fact control solubility in KCl media where Na<sup>+</sup> substitution reactions cannot occur. Taken all together, these results indicate that the large differences in solubility between chloride and perchlorate media (Fig. 1) are best explained by aqueous phase ion interactions or ion complexation reactions. How-

**Fig. 2.** Hydrous Th(IV) oxide solubilities in 0.6 M NaCl, 0.6 M KCl, and 0.1 M NaClO<sub>4</sub>.

ever, it is possible that the precipitates crystallized more rapidly in NaClO<sub>4</sub> than in NaCl or KCl and that differences in crystallinity could have caused the large differences in solubility. Crystalline ThO<sub>2</sub>(c) is extremely stable and insoluble ( $\log K_{\text{sp}} = -54.2$ ) [20]. To evaluate whether differences in the crystallinity of precipitates equilibrated in NaClO<sub>4</sub> and NaCl solutions could account for the differences in solubility, we set up two samples of our precipitates in the 0.1 M NaClO<sub>4</sub>, as used by Ryan and Rai [7], and measured the solubility after 17 d of equilibration. The results were in excellent agreement with those of Ryan and Rai [7] (Fig. 1a), and both precipitates were amorphous to X-rays. X-ray diffraction (XRD) analysis of selected precipitates in 0.6 M NaCl after 4 months and precipitates in 3.0 M NaCl after 3 months in this study also showed the precipitates to be amorphous.<sup>1</sup> Only the samples in 3 M NaCl that had been aged for more than one year showed any crystalline pattern. Although most of these samples had only one or two broad lines and were probably largely amorphous, some samples showed the presence of at least some ThO<sub>2</sub>(c) and possibly trace amounts of Na<sub>2</sub>ThO<sub>3</sub> (Table 3). However, these samples (Fig. 1c) do not show significantly decreased solubilities, indicating that an amorphous precipitate still controls the solubility, despite crystallization of some of the material. Thus differences in crystallinity cannot account for the large differences in observed solubility between chloride and perchlorate media.

Given these results, we conclude that differences in aqueous phase ion interactions or ion-complexation reactions and in ionic strength must explain the large differences in solubility between chloride and perchlorate solutions. This conclusion is also supported by the adsorption data of Hunter *et al.* [21], who studied the adsorption of Th onto iron oxide in 0.42 M NaCl. Hunter *et al.* [21] found no evidence of precipi-

<sup>1</sup> XRD analysis required washing the precipitates in deionized water to prevent halite formation, which occurred during XRD analysis of unwashed precipitates.

tation in their experiments below pH 5; such precipitation should have occurred if the hydrous oxide is as insoluble as the NaClO<sub>4</sub> data indicate.

Although some of the precipitates may have contained small amounts of foreign ions, we believe that the observed differences in solubilities can be adequately modeled by assuming that hydrous Th(IV) oxide is in equilibrium with the aqueous solutions. This conclusion is supported by the following facts: (1) solubilities in NaCl solution, at the same hydrogen ion concentration, were similar before and after changes in solution pH that could have been caused by loss or incorporation of foreign ions; (2) the solubility data of Ryan and Rai [7] can be adequately represented by the simple reaction  $\text{ThO}_2 \cdot x\text{H}_2\text{O} + 4\text{H}^+ \rightleftharpoons \text{Th}^{4+} + (2+x)\text{H}_2\text{O}$ ; (3) solubilities were similar in NaCl and KCl media; and (4) our aqueous phase thermodynamic model, which uses ThO<sub>2</sub>(am) as the equilibrating phase, explains well the solubility both in perchlorate [7] and in chloride media (this study).

### Thermodynamic analysis

Our principal objective in this section is to develop the simplest thermodynamic model of the aqueous phase that will satisfactorily account for all of the experimental solubility data on hydrous Th oxide in dilute solution, NaClO<sub>4</sub> solution, and NaCl solutions (which are similar to KCl), as well as the existing osmotic coefficient data for ThCl<sub>4</sub> solutions [22].

As mentioned in the introduction, the hydrous Th oxide solubility data [7] in 0.1 M NaClO<sub>4</sub> and in dilute solution ( $I \sim 0.05$ ) support the hypothesis that only the unhydrolyzed Th<sup>4+</sup> ion is dominant in their solutions, at least at low total Th concentrations. Such a highly charged species would be likely to interact strongly with the bulk anions, in this case Cl<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>. Such interactions can significantly influence the solubility of the Th(IV) precipitates, and it is possible that such interactions can explain the large differences in solubility between different ionic media.

We will confine our thermodynamic analysis to the region where  $p_{\text{cH}^+} < 7$ , principally because this is the  $p_{\text{cH}^+}$  region where the changes in solubility are most pronounced and because the measured Th concentrations are well above the detection limits. At higher  $p_{\text{cH}^+}$  values, most of the solubilities are at the analytical detection limit or too close to it for definitive calculations to be made.

Our solubility data for hydrous Th(IV) oxide extend to high ionic strengths (3 M). Therefore, to conduct an accurate thermodynamic analysis of this system, the thermodynamic model must also be valid to high ionic strengths. Pitzer's [10, 11] ion-interaction model for the excess solution free energy has been shown to accurately calculate solubilities of the solid phases of actinides and other elements in multicomponent electrolyte solutions ranging from zero to high concentrations [16, 23–27]. Pitzer's model emphasizes a detailed description of the specific

Table 4. Pitzer ion-interaction parameters used in this study

	Binary parameters				Reference
	$\beta^0$	$\beta^1$	$\beta^2$	$C^\phi$	
Na <sup>+</sup> , Cl <sup>-</sup>	0.0765	0.2644	0.0	0.00127	26
Na <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup>	0.0554	0.2755	0.0	-0.00118	28
Na <sup>+</sup> , OH <sup>-</sup>	0.0864	0.253	0.0	0.0044	26
H <sup>+</sup> , Cl <sup>-</sup>	0.1775	0.2945	0.0	0.0008	26
H <sup>+</sup> , ClO <sub>4</sub> <sup>-</sup>	0.1747	0.2931	0.0	0.00819	28
Th <sup>4+</sup> , Cl <sup>-</sup>	1.014	13.3	-200	-0.103	This study
Common-ion ternary parameters					Reference
$\Theta_{\text{Na}^+, \text{H}^+} = 0.036$					26
$\Theta_{\text{Cl}^-, \text{OH}^-} = -0.050$					26
$\Psi_{\text{Na}^+, \text{H}^+, \text{Cl}^-} = -0.004$					26
$\Psi_{\text{Na}^+, \text{Cl}^-, \text{OH}^-} = -0.006$					26

ion interactions in the solution. The effects of the specific ion interactions on the excess solution free energy are represented within the activity coefficient expressions. The activity coefficients are expressed in a virial-type expansion as

$$\ln \gamma_i = \ln \gamma_i^{\text{DH}} + \sum_j \beta_{ij}(I)m_j + \sum_{j,k} C_{ijk}m_jm_k + \dots \quad (4)$$

where  $m$  is molality and  $\gamma_i^{\text{DH}}$  is a modified Debye-Hückel activity coefficient that is a universal function of ionic strength.  $\beta_{ij}(I)$  and  $C_{ijk}$  are specific for each ion interaction. Pitzer [10] has given explicit phenomenological expressions for  $\beta$ ; the form of  $\beta$  is different for like, unlike, and neutral ion interactions. The third virial coefficient,  $C$ , is taken to be independent of ionic strength. A detailed description of the form of Eq. 4 has been given elsewhere [16, 25, 26]. The complete set of parameters defining the non-ideal behavior of electrolytes is given by  $\beta^0$ ,  $\beta^1$ ,  $\beta^2$ , and  $C^\phi$  for each cation-anion pair,  $\Theta_{ij}$  for each cation-cation or anion-anion pair,  $\Psi_{ijk}$  for each cation-cation-anion and anion-anion-cation triplet, and  $\lambda_{in}$  and  $\delta_{ijn}$  for each ion-neutral and ion-ion-neutral interaction. The ion-interaction parameters used in this study are summarized in Table 4.

In our experimental solutions, strong specific ion interactions are likely to occur between the tetrapositive Th<sup>4+</sup> ion and the bulk anions Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup>. Pitzer and Mayorga [28] have obtained the necessary Th<sup>4+</sup>-Cl<sup>-</sup> ion-interaction parameters (i.e.,  $\beta^0$ ,  $\beta^1$ , and  $C^\phi$ ) from an analysis of osmotic coefficient data for ThCl<sub>4</sub> solutions. The standard chemical potential of Th<sup>4+</sup> was calculated from the free energy of formation given by Fuger and Oetting [29] (i.e.,  $\mu^0/RT = -284.227$ ).

Using this relatively simple model, we calculated the solubility product of hydrous Th(IV) oxide from the data of Ryan and Rai [7] for a low-total-Th-concentration ( $\sim 1 \times 10^{-5}$  M) dilute solution ( $I \sim 0.005$ ). In this calculation, the low total Th concentration means that polynuclear species should not be important, and we have at least temporarily neglected

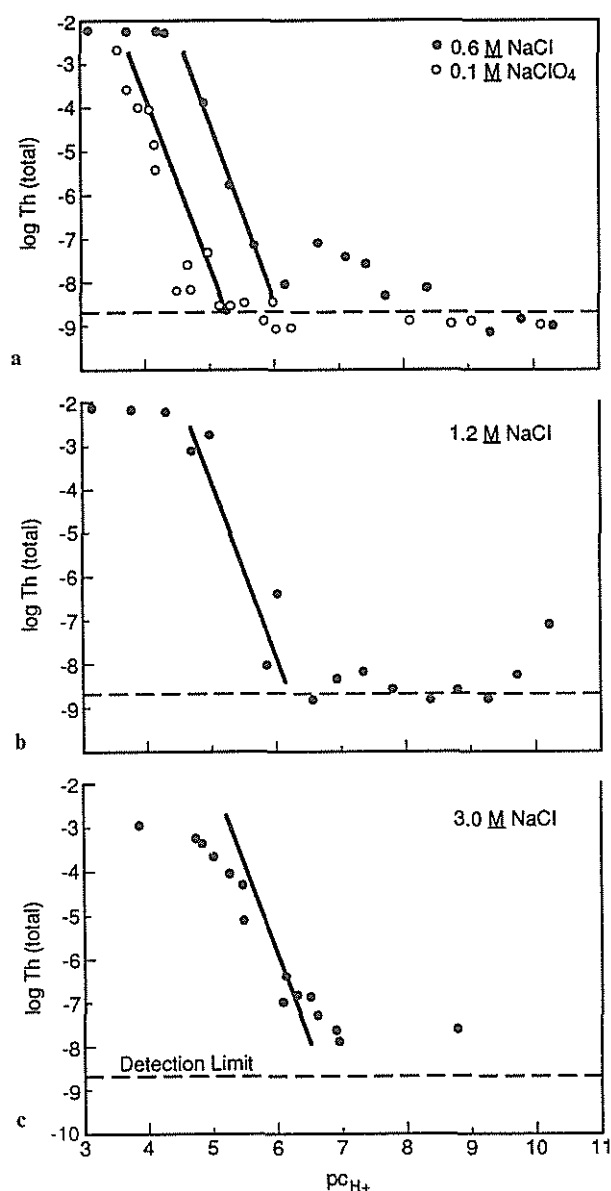
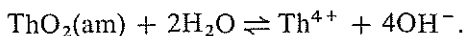


Fig. 3. Calculated and experimental hydrous Th oxide solubilities in (a) 0.6 M NaCl (7 d) and 0.1 M NaClO<sub>4</sub> (17 d); (b) 1.2 M NaCl (8 d); and (c) 3.0 M NaCl (8 d).

mononuclear hydrolysis species. The calculation yields  $\log K = -45.5$  for the reaction



This value for  $\log K$  is in excellent agreement with that of Ryan and Rai [7], if their correction for hydrolysis species is neglected. Using this solubility product and the ion-interaction parameters for  $\text{Th}^{4+}\text{-Cl}^-$  as analogs for  $\text{Th}^{4+}\text{-ClO}_4^-$ , which is not an unreasonable assumption given that the numerical values for  $\beta^0$  and  $\beta^1$  for 3:1  $\text{ClO}_4^-$  electrolytes differ from the  $\text{Cl}^-$  values by only 20% [34], the calculated solubilities are in very good agreement with the 0.1 M NaClO<sub>4</sub> data obtained by Ryan and Rai [7] and the few data points obtained in this study (Fig. 3a). In addition, preliminary calculations without these interaction parameters showed poor agreement with the 0.1 M NaClO<sub>4</sub> data. These

calculations indicate that the  $\text{Th}^{4+}\text{-Cl}^-$  values are reasonable analogs for the  $\text{Th}^{4+}\text{-ClO}_4^-$  values.

Using this very simple model, which assumes the presence of only  $\text{Th}^{4+}$  ions, an amorphous Th oxide, and specific ion-interaction parameters for  $\text{Th}^{4+}$  with  $\text{Cl}^-$ , we calculated the solubility of the hydrous oxide expected in our NaCl solutions. As expected, given the differences between NaClO<sub>4</sub> and NaCl solutions, at a given  $p_{\text{CH}^+}$  value, the calculated solubilities were approximately three orders of magnitude too low, even in our 0.6 M NaCl solutions. Important aqueous ion interactions are obviously being neglected. The most obvious neglected interaction to be added would involve mononuclear hydrolysis species, such as  $\text{ThOH}^{3+}$  and  $\text{Th}(\text{OH})_2^{2+}$ , or much stronger interaction between  $\text{Th}^{4+}$  and  $\text{Cl}^-$  than has previously been assumed. Combinations of these species and ion-interaction parameters for these species and  $\text{Cl}^-$  [e.g.,  $\text{ThOH}^{3+}\text{-Cl}^-$ ,  $\text{Th}(\text{OH})_2^{2+}\text{-Cl}^-$ ] were derived and tested. The combination that fit our solubility data for NaCl media was  $\text{Th}(\text{OH})_2^{2+}$  and ion-interaction parameters for  $\text{Th}(\text{OH})_2^{2+}\text{-Cl}^-$ . However, when this hydrolysis species was included, no combination of ion-interaction parameters for either  $\text{Th}^{4+}$  or  $\text{Th}(\text{OH})_2^{2+}$  and no solubility products for the hydrous oxide could be found that gave even qualitative agreement with either the dilute solution data or the 0.1 M NaClO<sub>4</sub> data of Ryan and Rai [7]. This result showed that, at least below  $p_{\text{CH}^+} \sim 6.5$ , inclusion of mononuclear hydrolysis species and ion-interaction parameters for  $\text{Cl}^-$  with such species cannot entirely explain the  $\text{ThO}_2(\text{am})$  solubility data in both NaCl and NaClO<sub>4</sub> media. In addition, although the data for solubility in NaCl can be fit using a ternary ion-interaction parameter such as  $\Theta_{\text{Na}^+, \text{Th}^{4+}}$ , the calculated values are both negative and extremely large ( $\Theta_{\text{Na}^+, \text{Th}^{4+}}, \sim -4.6$ ), and such ternary ion interactions still would not explain the large differences between NaCl and NaClO<sub>4</sub> media. Therefore, the large differences in solubility for the hydrous oxide observed in the different ionic media must be caused by stronger specific ion interaction between  $\text{Th}^{4+}$  and  $\text{Cl}^-$  than that indicated by just the  $\text{ThCl}_4$  osmotic data. This conclusion is supported by the inclusion of Th-Cl ion pairs in thermodynamic data reviews [20].

Strong specific ion interactions are usually accounted for in the Pitzer ion-interaction approach by evaluating the  $\beta^2$  ion-interaction parameter [11, 16, 26, 30]. The effect of including  $\beta^2$  is only important at low ionic strength because the contribution of  $\beta^2$  to the activity coefficient is determined by an expression that decreases rapidly as a function of ionic strength.

We have determined the value of  $\beta_{\text{Th}^{4+}\text{-Cl}^-}^2$  from our 0.6 M NaCl solubility data in the region where  $p_{\text{CH}^+} < 7$  and then used NONLIN<sup>2</sup> to refit the  $\text{ThCl}_4$

<sup>2</sup> NONLIN, developed by A. R. Felmy, uses the MINPACK nonlinear least-squares programs in combination with a chemical equilibrium program based on the Gibbs free-energy minimization procedure of Harvie *et al.* [31]. The mathematical development has been outlined by Harvie [32].



osmotic coefficient data with this value included. Our calculated values for  $\beta^0$ ,  $\beta^1$ , and  $C^\phi$  from the osmotic coefficient data in  $\text{ThCl}_4$  are very similar to those of Pitzer and Mayorga [28]. This similarity indicates that, as expected,  $\beta^2$  has little effect on the calculated higher-ionic-strength osmotic coefficients [30, 34]. Using this model, which includes only ion-interaction parameters for  $\text{Th}^{4+}\text{-Cl}^-$ , with a value of  $\beta^2 = -200$  gives good agreement with our solubility data for 0.6, 1.2 and even 3.0 M NaCl (Fig. 3), and this is the simplest model that satisfactorily explains all of these data.

In summary, the model we have developed is relatively simple, in that only ion-interaction parameters for  $\text{Th}^{4+}\text{-Cl}^-$  are required, and yet it gives satisfactory results for the solubility of hydrous Th oxide in NaCl solutions ranging in concentration from 0.6 to 3.0 M and over a range of  $p_{\text{CH}^+}$  values from 3 to almost 7. In addition, the model is consistent with the hydrous oxide solubility data for dilute solution, 0.1 M  $\text{NaClO}_4$ , and 0.6 M KCl, and accurately describes the osmotic coefficient data for  $\text{ThCl}_4$  solutions.

At higher  $p_{\text{CH}^+}$  values ( $> 7$ ), mononuclear hydrolysis species could well be important, and in fact our solubility data even in 3 M NaCl tend to show a slope of less than 4 on the  $\log \text{Th}$  versus  $p_{\text{CH}^+}$  curve, possibly indicating that in the  $> 6 p_{\text{CH}^+}$  region, mononuclear hydrolysis species of Th [i.e.,  $\text{ThOH}^{3+}$  or  $\text{Th}(\text{OH})_2^{2+}$ ] are becoming important. More studies at higher NaCl concentrations and perhaps in different ionic media would be required to firmly establish the importance of such species in predicting the solubility of the hydrous oxide. However, such hydrolysis species are not required to explain our NaCl data to 3.0 M, nor the 0.1 M  $\text{NaClO}_4$  data.

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### References

- Baes, C. F., Jr., Meyer, N. J., Roberts, C. E.: The Hydrolysis of Thorium(IV) at 0 and 95°C. *Inorg. Chem.* **4**, 518 (1965).
- Brown, P. L., Ellis, J., Sylva, R. N.: The Hydrolysis of Metal Ions. Part 5. Thorium(IV). *J. Chem. Soc. Dalton Trans.* **31** (1983).
- Milic, N. B.: Studies on the Hydrolysis of Metal Ions. 61. Hydrolysis of the Thorium(IV) Ion in Lithium, Potassium, and Magnesium Nitrate Media. *Acta Chem. Scand.* **25**, 2487 (1971).
- Hietanen, S., Sillen, L. G.: Studies on the Hydrolysis of Metal Ions. 22. Equilibrium Studies in Self-Medium; Application to the Hydrolysis of  $\text{Th}^{4+}$ . *Acta Chem. Scand.* **13**, 533 (1959).
- Hietanen, S., Sillen, L. G.: Studies on the Hydrolysis of Metal Ions. 60. Hydrolysis of the Thorium(IV) Ion in 3 M (Na)Cl Medium. *Acta Chem. Scand.* **22**, 265 (1968).
- Kraus, K. A., Holmberg, R. W.: Hydrolytic Behavior of Metal Ions. III. Hydrolysis of Thorium(IV). *J. Phys. Chem.* **58**, 325 (1954).
- Ryan, J. L., Rai, Dhanpat: Thorium(IV) Hydrous Oxide Solubility. *Inorg. Chem.* **26**, 4140 (1987).
- Nabivanets, B. I., Kudritskaya, L. N.: Hydroxy Complexes of Thorium(IV). *Ukr. Khim. Zh.* **30**, 891 (1964).
- Baes, C. F., Jr., Mesmer, R. E.: *The Hydrolysis of Cations*, Wiley, New York 1976.
- Pitzer, K. S.: Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **77**, 268 (1973).
- Pitzer, K. S.: *Activity Coefficients in Electrolyte Solutions*, Vol. 1, CRC Press, Boca Raton, Florida 1979.
- Rai, Dhanpat, Strickert, R. G., Moore, D. A., Ryan, J. L.: Am(III) Hydrolysis Constants and Solubility of Am(III) Hydroxide. *Radiochim. Acta* **33**, 201 (1983).
- Rai, Dhanpat: Solubility Product of Pu(IV) Hydrous Oxide and Equilibrium Constants of Pu(IV)/Pu(V), Pu(IV)/Pu(VI), and Pu(V)/Pu(VI) Couples. *Radiochim. Acta* **35**, 97 (1984).
- Bertrand, P. A., Choppin, G. R.: Separation of Actinides in Different Oxidation States by Solvent Extraction. *Radiochim. Acta* **31**, 135 (1982).
- Schramke, J. A., Rai, Dhanpat, Fulton, R. W., Choppin, G. R.: Determination of Aqueous Plutonium Oxidation States by Solvent Extraction. *J. Radioanal. Nucl. Chem. Articles* **130**, 333 (1989).
- Felmy, A. R., Rai, Dhanpat, Schramke, J. A., Ryan, J. L.: The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines. *Radiochim. Acta* **48**, 29 (1989).
- McBryde, W. A. E.: The pH Meter as a Hydrogen-Ion Concentration Probe. *Analyst* **94**, 337 (1969).
- McBryde, W. A. E.: The pH Meter as a Hydrogen-Ion Concentration Probe. *Analyst* **96**, 739 (1971).
- Dickson, A. F.: Ph. D. Dissertation, University of Liverpool, Liverpool, United Kingdom 1977.
- Wagman, D. D., Schumm, R. H., Parker, V. B.: *A Computer Assisted Evaluation of the Thermochemical Data of Thorium*, NBSIR77-1300, U.S. National Bureau of Standards, Washington, D.C., 1977.
- Hunter, K. A., Hawke, D. J., Choo, L. K.: Equilibrium Adsorption of Thorium by Metal Oxides in Marine Electrolytes. *Geochim. Cosmochim. Acta* **52**, 627 (1988).
- Robinson, R. A., Stokes, R. H.: *Electrolyte Solutions*, Butterworth Publishers, London 1965.
- Rai, Dhanpat, Felmy, A. R., Ryan, J. L.: Uranium(IV) Hydrolysis Constants and Solubility Product of  $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ . *Inorg. Chem.* **29**, 260 (1990).
- Felmy, A. R., Rai, Dhanpat, Amonette, J. E.: The Solubility of Barite and Celestite in Sodium Sulfate: Evaluation of Thermodynamic Data. *J. Soln. Chem.* **19**, 175 (1990).
- Felmy, A. R., Weare, J. H.: The Prediction of Borate Mineral Equilibria in Natural Waters: Application to Searles Lake, California. *Geochim. Cosmochim. Acta* **50**, 2771 (1986).
- Harvie, C. E., Moller, N., Weare, J. H.: The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O System to High Ionic Strengths at 25°C. *Geochim. Cosmochim. Acta* **48**, 723 (1984).
- Harvie, C. E., Weare, J. H.: The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O System from Zero to High Concentration at 25°C. *Geochim. Cosmochim. Acta* **44**, 981 (1980).
- Pitzer, K. S., Mayorga, G.: Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Elec-



- trolytes with One or Both Ions Univalent. *J. Phys. Chem.* **77**, 2300 (1973).
29. Fuger, J., Oetting, F. L.: *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 2. The Actinide Aqueous Ions*, International Atomic Energy Agency, Vienna, Austria 1976.
  30. Pitzer, K. S., Silvester, L. F.: Thermodynamics of Electrolytes. 11. Properties of 3:2, 4:2, and Other High-Valence Types. *J. Phys. Chem.* **82**, 1239 (1978).
  31. Harvie, C. E., Greenberg, J. P., Weare, J. H.: A Chemical Equilibrium Algorithm for Highly Non-Ideal Multiphase Systems: Free Energy Minimization. *Geochim. Cosmochim. Acta* **51**, 1045 (1987).
  32. Harvie, C. E.: Ph. D. Dissertation, University of California, San Diego, La Jolla, California 1981.
  33. Reardon, E. J.: Ion Interaction Parameters for  $\text{AlSO}_4$  and Application to Prediction of Metal Sulfate Solubility in Binary Salt Systems. *J. Phys. Chem.* **92**, 6426 (1988).
  34. Pitzer, K. S., Peterson, J. R., Silvester, L. F.: Thermodynamics of Electrolytes. IV. Rare Earth Chlorides, Nitrates, and Perchlorates. *J. Soln. Chem.* **7**, 45 (1978).

## APPENDIX

## Complete data listing

0.6 M NaCl						0.6 M KCl		
7 days			98 days			7 days		
pH(obs)	$p_{\text{CH}^+}$	logTh(T)	pH(obs)	$p_{\text{CH}^+}$	logTh(T)	pH(obs)	$p_{\text{CH}^+}$	logTh(T)
3.02	3.06	-2.15	2.87	2.91	-2.17	3.83	3.75	-2.19
3.59	3.63	-2.16	3.42	3.46	-2.18	4.68	4.60	-4.17
4.09	4.13	-2.17	3.86	3.90	-2.29	5.42	5.34	-6.43
4.14	4.18	-2.19	3.91	3.95	-2.28	6.05	5.97	-9.00
4.81	4.85	-3.87	4.38	4.42	-3.14	6.44	6.36	-8.41
5.21	5.25	-5.73	3.86	3.90	-2.77	7.48	7.40	-8.68
5.59	5.63	-8.53	3.77	3.81	-2.86	8.03	7.95	-8.67
6.06	6.10	-7.97	4.35	4.39	-3.21	-2.86		
6.58	6.62	-7.08	6.69	6.73	-8.15			
7.01	7.05	-7.36	7.18	7.22	-8.12			
7.34	7.38	-8.38	7.5	7.54	-6.92			
7.61	7.65	-8.30	8.21	8.25	-5.92			
8.26	8.30	-8.07	9.08	9.12	-7.60			
9.23	9.27	-9.09	9.58	9.62	-7.97			
9.74	9.78	-8.82	10.04	10.08	-8.16			
10.20	10.24	-8.95						

1.2 M NaCl					
7 days			98 days		
pH(obs)	$p_{\text{CH}^+}$	logTh(T)	pH(obs)	$p_{\text{CH}^+}$	logTh(T)
2.94	3.10	-2.16	2.67	2.83	-2.20
3.58	3.74	-2.16	3.30	3.46	-2.19
4.10	4.26	-2.20	3.76	3.92	-2.48
4.52	4.68	-3.09	4.17	4.33	-3.16
4.79	4.95	-2.73	4.37	4.53	-3.90
5.68	5.84	-7.69	4.08	4.24	-2.83
5.83	5.99	-6.39	3.99	4.15	-2.75
6.38	6.54	-8.90	3.97	3.97	-4.13
6.76	6.92	-8.30	5.91	6.07	-7.51
7.16	7.32	-8.20	6.92	7.08	-7.46
7.63	7.79	-8.57	7.47	7.63	-7.90
8.21	8.37	-8.83	8.05	8.21	-7.80
8.64	8.80	-8.62	8.44	8.60	-7.82
9.09	9.25	-8.80	8.88	9.04	-7.38
9.52	9.68	-8.25	9.30	9.46	-7.08
10.03	10.19	-7.10	9.80	9.96	-6.14

## 3.0 M NaCl

8 days			122 days			372 days		
pH(obs)	$p_{\text{H}^+}$	logTh(T)	pH(obs)	$p_{\text{H}^+}$	logTh(T)	pH(obs)	$p_{\text{H}^+}$	logTh(T)
3.36	3.82	-2.95	3.56	4.02	-2.17	3.61	4.07	-2.09
4.27	4.73	-3.30	3.87	4.33	-3.03	3.69	4.15	-3.56
4.32	4.78	-3.33	3.98	4.44	-3.61	3.81	4.27	-2.87
4.52	4.98	-3.71	3.95	4.41	-3.90	4.05	4.51	-3.28
4.76	5.22	-4.09	4.02	4.48	-3.94	4.36	4.82	-3.77
4.96	5.42	-4.32	4.32	4.78	-4.10	4.56	5.02	-4.40
5.0	5.46	-5.13	7.12	7.58	-6.47	4.65	5.11	-4.79
5.58	6.04	-6.98	7.77	8.23	-6.44	7.89	8.35	-6.85
5.61	6.01	-6.39	7.82	8.28	-6.43	7.98	8.44	-6.66
5.81	6.27	-6.84	7.93	8.39	-6.37	8.20	8.66	-6.96
5.99	6.45	-6.94	8.82	9.28	-7.84	8.11	8.57	-7.09
6.12	6.58	-7.28	9.00	9.46	-7.92	8.04	8.50	-7.73
6.41	6.87	-7.61	9.47	9.93	-7.20	8.05	8.51	-7.73
6.42	6.88	-7.62	9.58	10.04	-7.66	8.24	8.70	-6.83
6.44	6.90	-7.89	10.06	10.52	-7.83	8.48	8.94	-7.68
8.27	8.73	-7.64	10.10	10.56	-7.45			