Division Control No. ECD-74

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THE CHEMISTRY OF URANIUM AND RELATED RADIONUCLIDES IN LAKE ONTARIO WATERS

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NWRI Contribution No. 86-33

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EXECUTIVE SUMMARY

This paper decribes the predominant chemical forms of uranium, protactinium, thorium, actinium, radium, radon, polonium, bimuth, lead, neptunium, plotonium, americium, and curium in Lake Ontario.

LA CHIMIE DE L'URANIUM ET DES RADIONUCLÉIDES APPARENTÉS DANS LE LAC ONTARIO

R.F. Platford et S.R. Joshi

RÉSUMÉ À L'INTENTION DE LA DIRECTION

Cet article décrit les principales espèces chimiques de l'uranium, du protactinium, du thorium, de l'actinium, du radium, du radon, du polonium, du bismuth, du plomb, du neptunium, du plutonium, de l'américium et du curium dans le lac Ontario.

ABSTRACT

The chemistry of uranium and its eight associated daughters has been considered in Lake Ontario water along with that of selected transuranic elements. These transuranics arise mainly from fallout, and to a lesser extent from nuclear fuel reprocessing. Most exist as free ions or oxides of various kinds, although uranium probably exists as a strong uranyl carbonate complex.

RÉSUMÉ

On a étudié la chimie de l'uranium, de ses huit produits de filiation et de certains éléments transuraniens dans le lac Ontario. Les éléments transuraniens proviennent principalement des retombées et, dans une moindre mesure, du retraitement du combustible nucléaire. La plupart existe sous forme de divers types d'ions ou d'oxydes, mais l'uranium existe probablement sous forme d'un complexe stable de carbonate d'uranyle.

INTRODUCTION

The few studies of the uranium and thorium series radionuclides in aquatic ecosystems deal with physical rather than chemical behaviour, in spite of the fact that chemistry governs their lacustrine behaviour[1-2]. Of the transuranium elements, the chemical behaviour of plutonium has been considered most extensively in the aquatic environment[3-8]. A series of papers treats the solubilization of plutonium[9] and other high atomic number radioisotopes in the alkaline Mono Lake[10,11]. A recent preprint[12] deals with plutonium in the presence of humic acid. Information on the aqueous chemistry of all these radionuclides is useful in assessing both their removal by sorption on sedimenting particulates and availability for uptake by biota in a given aquatic ecosystem. These two factors, among other things, can significantly affect the routes by which humans receive radiation doses. The importance of such studies in Great Lakes waters arises from the presence of over 35 facilities incorporating various stages of the nuclear fuel cycle in the lakes basin and over 30 million inhabitants. The present article thus describes the elemental aqueous chemistry of members of the uranium series and selected transuranics in Lake Ontario waters.

MATERIALS AND METHODS

Figure 1 shows the relations among the various nuclides considered here. The parents ^{232}Th, ^{235}U and ^{238}U and their daughter products are given in Table I, and the transuranium radionuclides produced by nuclear reactors or weapons are given in Table II. The most abundant radioisotope for each element is given, excluding ^{207}Tl which is estimated to have a concentration of only about 10^{-25} M, if in equilibrium with ^{235}U.

The concentrations of ^{238}U, ^{226}Ra, ^{210}Pb and ^{241}Am were computed from the gamma-ray spectra of samples collected in 1985 and filtered through 0.45 μ Millipore filters. The spectra were accumulated using the system described elsewhere[13]. The concentrations given in Tables I and II are our preliminary values which will be reported on in detail at a later date. In the absence of measurements, we have assumed some of the radionuclides in the natural decay chains to be in equilibrium with their parents. The data on non-radioactive species in Lake Ontario were taken from KUNTZ[14] and DOBSON[15].

RESULTS AND DISCUSSION

The predominant chemical species for any element in aqueous solution can be derived from the redox potential and pH by reference to stability diagrams of the type given by, for example, POURBAIX[16].

The portion of the diagrams pertaining to natural waters is shown in Fig. 1 for six of the more important elements in the uranium decay series, and for three transuranium elements. We have assumed averaged values of 0.5 ± 0.1 volt for the E_h and 8 ± 0.5 for the pH. These values are representative of many natural surface waters[1,17,18]. The E_h value is consistent with a slow reaction[18].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

with an H_2O_2 concentration of about 10^{-11} M. The pH is consistent with the carbonate system at equilibrium and HCO_3^- = 10^{-3} M and $CO_3^=$ = $10^{-5.1}$ M.

The stability constants used to calculate concentrations were taken from the compilation of SILLEN[19]. Where activity corrections were necessary, the following approximations were assumed for the activity coefficients[1]: uncharged species, $\gamma = 1$; monovalent ion, $\gamma = 0.93$; divalent ion, $\gamma = 0.75$; trivalent ion $\gamma = 0.50$.

The form in which each element is likely to occur in lake water is given in Tables I and II.

The lead concentration in the Great Lakes is about 1 ppb, or $10^{-8.3}$ M so that the solubility product for lead carbonate, $10^{-13.2}$ (SILLEN[18]), is nearly reached, unless the lead is solublized by formation of the carbonate complex.

The solubility product for bismuth hydroxide is 10^{-30} and limits the soluble Bi^{+3} to a concentration of 10^{-12}M, although two references[16,19] suggest a stable hydroxy complex, probably $BiOH^{++}$; the bismuth arising from ^{210}Pb decay would in any event be at a low enough concentration to be soluble.

The chemistry of polonium resembles that of tellurium, in that the most stable form in aqueous solution is the +4 oxidation state; elemental polonium can be coprecipitated with tellurium from solution by reduction of the normally occurring $PoO_3^{=}$ ion. The high specific activity of polonium can convert oxygen to ozone and lead to self oxidation to a higher oxidation state than would be expected from a purely chemical standpoint[16]. Both bismuth and polonium, if derived solely from ^{210}Pb would occur in very low concentrations - less than 10^{-19} M.

Astatine is a minor branch member of the uranium decay chain; its concentration will be less than 10^{-20} of the uranium concentration if in secular equilibrium. Astatine should exist as $^{218}At_2$ in solution except that its concentration corresponds to only one atom per hundred tonnes of lake water, rendering dimerization statistically improbable.

Radon is very soluble in water (10^{-2} M) and will exist in the gaseous state.

Francium occurs in nature only as a minor branch in the decay chain of ^{235}U, to the extent of 10^{-26} M ^{223}Fr, all of which is soluble as the monovalent ion.

Our measurements of radium in Lake Ontario give typical concentrations of 2 mBq L^{-1} (10^{-16} M) ^{226}Ra, about one third the activity of its parent ^{238}U just as is the case in Mono Lake[10]. The element is stable only as the divalent ion.

The longest lived actinium isotope, ^{227}Ac with a half life of 22 y, is a daughter product of ^{235}U. Actinium behaves like lanthanum and will precipitate as the trivalent hydroxide at concentrations above about 10^{-11} M. If in secular equilibrium with uranium, however, its concentration in lake water should be only about 10^{-18} M and it should exist as the trivalent ion.

There are two sources of thorium. The ^{230}Th arising from decay of ^{238}U is insignificant in comparison with the ^{232}Th which is the parent of the series, and which occurs in a concentration of about 10^{-8} M. Because the solubility of the oxide is so low, virtually all of the thorium will exist as ThO_2; it can, however, exists as soluble $ThCO_3(OH)_2$ in alkaline carbonates such as Mono Lake[11].

Protactinium, like its daughter actinium, occurs mainly as a decay product of ^{235}U. It should exist as the pentavalent PaO_2^+. Its stability diagram has not been accurately defined and was assumed to resemble that of niobium.

The chemistry of uranium, though complicated, is well known. It can be seen from its stability diagram that the predominant state is the uranyl ion. There is enough carbonate in lake water to form the very strong $UO_2(CO_3)_3^{-4}$ complex; more than 99% of the uranyl ion is in this form[19].

The Transuranic Elements

Neptunium is produced in reactors by successive neutron capture by ^{235}U, followed by beta decay. The most stable form in lake water is likely to be the pentavalent NpO_2^+ ion which will form a weak uncharged bicarbonate complex.

The four plutonium isotopes with mass numbers from 238 to 241 inclusive are all significant sources of radioactivity. The chemistry of plutonium in the aquatic environment has been extensively covered[6-11]. The predominant solution species is probably PuO_2^+, although uncertainty in the diagram precludes ruling out the hexavalent form. If the solubility is exceeded, plutonium usually exists as the tetravalent dioxide, associated with suspended solids.

Our measurements indicate that ^{241}Am, the most important isotope of that element, occurs to the extent of about 10^{-17} M in Lake Ontario. The stable form is trivalent, with no strong complexes expected.

We have not enough information on curium in the Great Lakes to state its concentration or its form; it is usually trivalent in aqueous solution.

Of the radionuclides considered here, radium is the most likely to be a health hazard in our drinking water. Even so, the maximum ^{226}Ra activity recommended under Canadian National Health and Welfare guidelines is 100 mBq L^{-1}; it would appear that ^{90}Sr, which occurs at a level of 25-45 mBq L^{-1} in Lake Ontario, contributes a

greater dose to drinking water than do any of the uranium and transuranium series of elements[20].

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Table I. Predominant daughter products of uranium and thorium decay

	Series	Half Life	mBq L^{-1}	Lake Water Log Molarity	Likely Form
^{238}U	U	$4.5 \times 10^{9}y$	6	-8.7	$UO_2(CO_3)_3^{-4}$
^{235}U	Ac	$7.0 \times 10^{8}y$	0.3	(-11)	
^{234}U	U	$2.4 \times 10^{5}y$			
^{231}Pa	Ac	$3.2 \times 10^{4}y$		(-15)	PaO_2^{+}
^{232}Th	Th	$1.4 \times 10^{10}y$		-8	ThO_2
^{227}Ac	Ac	22y		(-19)	
^{228}Ra	Th	6.7 y			Ra^{++}
^{226}Ra	U	1600 y	2	(-15.6)	
^{222}Rn	U	3.8 d		(-17)	dissolved gas
^{210}Po	U	138 d		-20	H_2PoO_3
^{210}Bi	U	5.0 d		-6	$Bi\ OH_2^{++}$
^{210}Pb	U	22 y	0.2	-8.3	Pb^{++}

Values in parenthesis are estimates based on sea water concentrations, or by assuming secular equilibrium with a mother source.

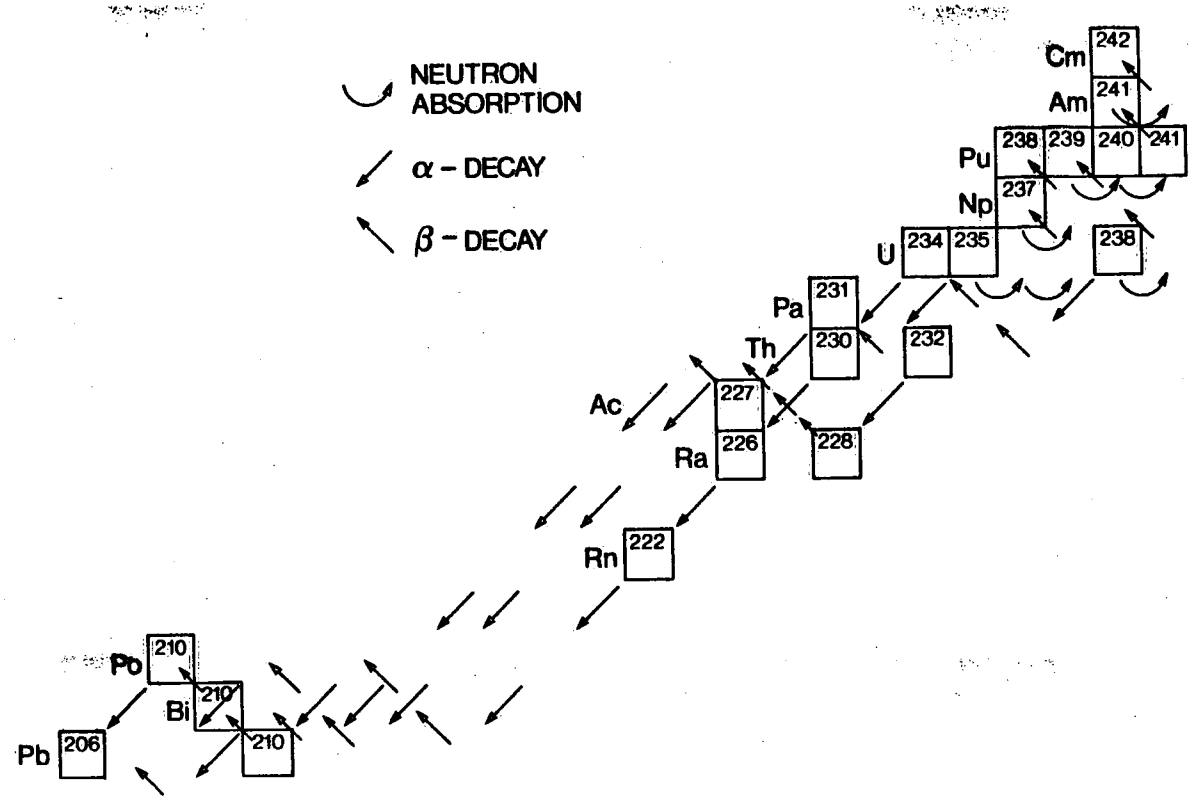
Table II. Transuranics in lake water

	Reaction	Source	mBq L^{-1}	Lake Water Log Molarity	Likely Form
^{237}Np	$(n,\gamma) + \beta$	^{235}U			NpO_2^+
^{238}Pu	$(n,\gamma) + \beta$	^{237}Np			PuO_2^+
^{239}Pu	$(n,\gamma) + \beta$	^{238}U			
^{240}Pu	(n,γ)	^{239}Pu	10^{-3}	-18	
^{241}Pu	(n,γ)	^{240}Pu			
^{241}Am	β	^{241}Pu	0.3	-17	Am^{+3}
^{242}Cm	$(n,\gamma) + \beta$	^{241}Am			probably Cm^{+3}

FIGURES

Fig. 1 The decay schemes for the uranium (^{238}U), actinium (^{235}U) and thorium (^{232}Th) series; only those nuclides which occur in significant concentrations are shown in blocks. Also shown are the transuranic nuclides arising from neutron irradiation of uranium fuel (from T.H. PIGFORD and K.P. ANG, Health Phys. 29 (1975) 451).

Fig. 2 Stability diagrams for nine of the elements considered in this paper. The E_h is given in volts relative to the normal hydrogen electrode at 25°C. The effect of temperature in natural solutions is generally smaller than the uncertainty in the diagram fields.


NEUTRON ABSORPTION
α - DECAY
β - DECAY
Cm
242
Am
241
Pu
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237
U
234
235
238
Pa
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Th
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Pb
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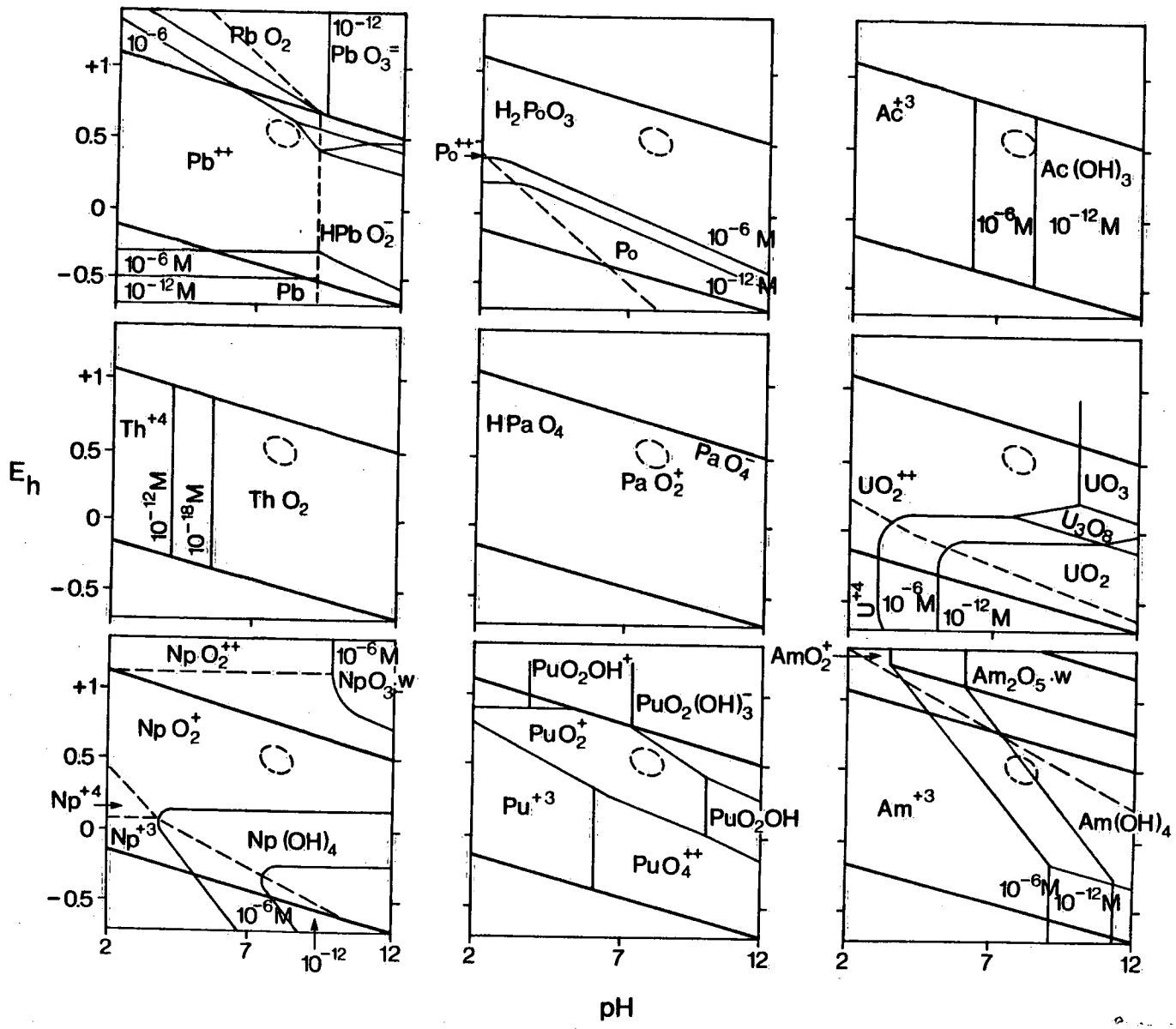
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10^-6
Pb++
HPb O2-
10^-6 M
10^-12 M
Pb
H2PoO3
Po++
Po
10^-6 M
10^-12 M
Ac+3
Ac (OH)3
10^-6 M
10^-12 M
Th+4
10^-12 M
10^-18 M
Th O2
HPa O4
Pa O2+
Pa O4-
UO2++
UO3
U3O8
UO2
U+4
10^-6 M
10^-12 M
Np O2++
10^-6 M
NpO3·w
Np O2+
Np+4
Np+3
Np (OH)4
10^-6 M
10^-12
PuO2OH+
PuO2(OH)3-
PuO2+
Pu+3
PuO2OH
PuO4++
AmO2+
Am2O5·w
Am+3
Am(OH)4
10^-6 M
10^-12 M
Eh
pH
+1
0.5
0
-0.5
2
7
12