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THE CHEMISTRY OF URANIUM AND RELATED RADIONUCLIDES IN LAKE ONTARIO WATERS

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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, uranium probably exists as a strong uranyl carbonate complex.

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 environment³⁻⁸. A series of papers treats

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the solubilization of plutonium 9 and other high atomic number radioisotopes in the alkaline Mono Lake^{10,11}. A recent preprint¹² 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 1, and the transuranium radionuclides produced by nuclear reactors or weapons are given in Table 2. 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 concentration given in



Fig. 1. The decay schemes for the uranium /²³⁸U/, actinium /²³⁵U/ and thorium /²³²Th/ 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.

Tables 1 and 2 are our preliminary values which will be reported 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 Kuntz¹⁴ and Dobson¹⁵.

RESULTS AND DISCUSSION

2

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

S	eries	Half life	mBq l ⁻¹	Lake water log molarity	Likely form
238 _U 235 ₁₁	U	$4.5 \times 10^9 \text{ y}$	6	-8.7	$uo_2/co_3/_3^{4-}$
234 _U	AC U	$2.4 \times 10^5 \text{ y}$	0.5	(-11)	
231 _{Pa}	Ac	$3.2 \times 10^4 \text{ y}$		/-15/	Pa02
232 _{Th}	Th	1.4 x 10 ¹⁰ y		-8	ThO ₂
227 _{Ac}	AC	22 y		/-19/	
228 _{Ra}	Th	6.7 y			Ra ²⁺
²²⁶ Ra	U	1600 y	2	/-15.6/	
222 _{Rn}	U	3.8 d		/-17/	dissolved gas
210 _{PO}	U	138 d		-20	H ₂ PoO ₃
210 _{Bi}	U	5.0 đ		- 6	$Bi/OH/\frac{1}{2}$
210 _{Pb}	U	22 <u>y</u>	0,2	-8.3	Pb ²⁺

TABLE	1
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Predominant daughter products of uranium and thorium decay

336

TABLE	2
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Reactio	n [°] So	ource	mBq 2 ^{-]}	Lake water log molarity	Likely form
237 _{Np} /n,Y	/ + ß	235 _U			Np0 ⁺ 2
²³⁸ _{Pu} /π,γ ²³⁹ _{Pu} /π,γ ²⁴⁰ _{Pu} /π,γ ²⁴¹ _{Pu} /π,γ	/ + β / + β /	237 _{Np} 238 _U 239 _{Pu} 240 _{Pu}	10 ⁻³	~ 18	Pu02
²⁴¹ Am β ²⁴² Cm /n,γ	/ 1 β	241 _{Pu} 241 _{Am}	0.3	-17	Am ³⁺ proBably Cm ³⁺

Transuranics in lake water

given by, for example, Pourbaix¹⁶. 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 reaction¹⁸

$$H_{2}O_{2} + 2H^{+} + 2e^{-} + 2H_{2}O$$

with an H_2O_2 concentration of about 10^{-11} M. The pH is consistent with the carbonate system at equilibrium, $HCO_3^- = 10^{-3}$ M and $CO_3 = 10^{-5 \cdot 1}$ M.

The stability constants used to calculate concentrations were taken from the compilation of Sillen¹⁹. Where

2*

activity corrections were necessary, the following approximations were assumed for the activity coefficients¹: 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 1 and 2.

The lead concentration in the Great Lakes is about 1 ppb, or $10^{-8.3}$ M so that the solubility product for lead carbonate, $10^{-13.2}$ /Sillen¹⁸/, is nearly reached, unless the lead is solubilized by formation of the carbonate complex.

The solubility-product for bismuth hydroxide is 10^{-30} and limits the soluble Bi³⁺ to a concentration of 10^{-12} M, although two references 16,19 suggest a stable hydroxy complex, probably BiOH²⁺; 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 PO_3^{2-} 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 standpoint¹⁶. Both bismuth and polonium, if derived solely from ²¹⁰Pb would occur in very low concentrations - less than 10⁻¹⁹M.

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 $^{218}\text{At}_2$ 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 monovalent ion.

Our measurements of radium in Lake Ontario give typical concentrations of 2 mBq ℓ^{-1} /10⁻¹⁶M/²²⁶Ra, about one third the activity of its parent ²³⁸U just as is the case in Mono Lake¹⁰. The element is stable only as a 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 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. 230 Th arising from the decay of 238 U is insignificant in comparison with 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 ThO₂; its can, however, exist as soluble ThCO₃/OH/₂ in alkaline carbonates such as Mono Lake¹¹.

Protactinium, like its daughter actinium, occurs mainly as a decay product of 235 U. it should exist as the pentavalent Pa0⁺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



pН



the predominant state is the uranyl ion. There is enough carbonate in lake water and the very strong $UO_2/CO_3/\frac{4}{3}$ complex forms, more than 99% of the uranyl ion is in this form¹⁹.

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 covered⁶⁻¹¹. 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 the 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 ²²⁶Ra activity recommended under Canadian National Health and Welfare guidelines is 100 mBg l^{-1} ; it would appear that ⁹⁰Sr, which occurs at a level of 24-45 mBg l^{-1} in Lake Ontario, contributes a greater dose to drinking water than do any of the uranium and transuranium series of elements²⁰.

341

REFERENCES

- R.M. Garrels, C.L. Christ, Mineral Equilibria, Harper, New York, 1965.
- 2. D.R. Champ, J.L. Young, D.E. Robertson, K.H. Abel, Water Poll. Res. J. Canada, 19 /1984/ 35.
- J.B. Andelman, T.C. Rozzell, Adv. in Chem. Series, 93, ACS, Washington, 1970.
- W.R. Schell, R.L. Watters, <u>Health Physics</u>, 29 /1975/ 589.
- J.J. Alberts, M.A. Wahlgren, D.M. Nelson, P.J. Jehn, Envir. Sci. Technol., 11 /1977/ 673.
- D. Rai, R.J. Serne, J.L. Swanson, <u>J. Environmental</u> Quality, 9 /1980/ 417.
- 7. S.R. Aston, Marine Chem., 8 /1980/ 319.
- D.M. Nelson, W.R. Penrose, J.O. Karttunen, P. Mehlhaff, Env. Sci. Technol., 19 /1985/ 127.
- 9. H.J. Simpson, R.M. Trier, J.R. Toggweiler, G. Mathieu, B.L. Deck, C.R. Olsen, D.E. Hammond, C. Fuller, T.L. Ku, Science, 216 /1982/ 516.
- 10. R.F. Anderson, M.P. Bacon, P.G. Brewer, <u>Science</u>, 216 /1982/ 516.
- 11. J.M. Cleveland, T.F. Rees, K.L. Nash, <u>Science</u>, 222 /1983/ 1323.
- 12. R.A. Roberts, G.R. Choppin, A.C.S. Sept. 1985, Chicago.
- 13. S.R. Joshi, Anal. Chem., 57 /1985/ 1023.
- 14. K.W. Kuntz, Inland Waters Directorate Report, Dec. 1984, Burlington, Ontario.
- 15. H.F.H. Dobson, Lake Ontario Nater Chemistry Atlas, Scientific Series No. 139, 1984, Burlington, Ontario.
- M. Pourbaix, Atlas of Electrochemical Equilibria, 1966, Pergamon, Oxford.

- 17. R.L. Thomas, A.L.W. Kemp, C.F.M. Lewis, J. Sed. Petrol., 42 /1972/66.
- 18. W.G. Breck, J. Marine Res., 30 /1972/ 121.
- 19. L.G. Sillen, Stability Constants of Metal Ion Complexes, Chemical Society, London, 1964.
- 20. R.N. McNeeley, Water Quality Sourcebook, Inland Waters Directorate, Ottawa, Ontario, 1979.

AR-066