Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The chemical behavior of the natural microporous manganese-oxide todorokite in actinides (Th, U, Pa) aqueous solutions

P. Misaelides[a]; T. Katranas[b]; A. Godelitsas[c]; H. Klewe-Nebenius; I. Anousis[d]
[a] Department of Chemistry, Aristotle University, Thessaloniki, Greece [b] Department of Chemistry, University of Ioannina, Ioannina, Greece [c] Univ. Münster, Münster, Germany [d] NRCPS "Demokritos", Aghia Paraskevi-Attiki, Greece

To cite this Article Misaelides, P. , Katranas, T. , Godelitsas, A. , Klewe-Nebenius, H. and Anousis, I.(2002) 'The chemical behavior of the natural microporous manganese-oxide todorokite in actinides (Th, U, Pa) aqueous solutions', Separation Science and Technology, 37: 5, 1109 — 1121

To link to this Article: DOI: 10.1081/SS-120002244

URL: http://dx.doi.org/10.1081/SS-120002244

SEPARATION SCIENCE AND TECHNOLOGY, 37(5), 1109–1121 (2002)

THE CHEMICAL BEHAVIOR OF THE NATURAL MICROPOROUS MANGANESE-OXIDE TODOROKITE IN ACTINIDES (Th, U, Pa) AQUEOUS SOLUTIONS

P. Misaelides,[1,*] **T. Katranas,**[1,†] **A. Godelitsas,**[1,#]
H. Klewe-Nebenius,[2] **and I. Anousis**[3]

[1]Department of Chemistry, Aristotle University,
GR-54006 Thessaloniki, Greece
[2]Forschungszentrum Karlsruhe, P.O. Box 3640,
D-76021 Karlsruhe, Germany
[3]NRCPS "Demokritos", GR-15310 Aghia Paraskevi-
Attiki, Greece

ABSTRACT

The chemical behavior of natural todorokite in Th and U aqueous solutions with initial concentrations between 10 and 1000 mg L^{-1} and pH higher than the point of zero charge (pH_{PZC}) of the mineral was investigated by instrumental neutron activation analysis and x-ray photoelectron spectroscopy. The experimental results indicated that considerable amounts of Th and U could be bound by todorokite through different sorption mechanisms

---

*Corresponding author. Fax: (3031) 0997753; E-mail: misailid@chem.auth.gr

†Current address: Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece.

#Current address: Inst. für Mineralogy, Univ. Münster, Correnstrasse 24, D-48140 Münster, Germany.

(especially surface precipitation) depending on the pH. The maximum sorption ratios (R_d) reached 697 and 94 mL g^{-1}, respectively. Exploratory experiments using ^{233}Pa in 1–0.001 *M* HCl solutions also indicated the ability of the material to interact with protactinium species even below its pH$_{PZC}$, exhibiting high R_d values ($2.4–63.5 \times 10^4$ mL g^{-1}). The precipitation of insoluble actinide hydrolysis products on the surface of the mineral can be attributed to the increase in pH due to simultaneous interaction with the H$^+$ cations.

Key Words: Todorokite; Manganese oxides; Actinides; Thorium; Uranium; Protactinium

INTRODUCTION

Natural Mn oxides/hydroxides/oxy-hydroxides are very common minerals in nature playing a very important role in the migration of heavy metals and radionuclides in the geosphere. Todorokite ($[Mn^{2+}, Ca, Mg]Mn_3^{4+}O_7 \cdot H_2O$) is a natural hydrated manganese oxide with a rather complicated chemical composition (1), occurring in large quantities along with other relative minerals (e.g., pyrolusite) in many areas of the world (2–6). Todorokite has also been identified as a major component of the so-called Mn nodules existing in huge quantities at the bottom of the oceans, consequently exhibiting a crucial economic importance (7–9). In addition, todorokite occurs with other Mn minerals in tuffaceous geological formations planned to be used for storage of high-level nuclear wastes (HLW) such as the Yucca Mountain, USA (10,11).

The todorokite crystals possess a specific oxide-type structure with a framework consisting of triple chains of edge-sharing MnO_6 octahedra that corner-share to form tunnels with three octahedra on a side (12,13). The presence of tunnels (micropores), with dimensions 6.9×6.9 Å^2, allows the lattice to accommodate water molecules as well as possibly exchangeable cations (e.g., Na^+,Ca^{2+}) like zeolites. Consequently, natural todorokite is being explored as a potential sorbent for the separation of hazardous ions from contaminated aqueous media. Furthermore, the chemical behavior of the mineral towards dissolved actinide species is of additional importance, as mentioned above, due to its presence in potential HLW host rocks.

The published data concerning the interaction of actinides with todorokite, and generally with natural Mn oxides, are exceptionally limited compared to those for other geological materials such as clays and zeolites. Triay et al. (14) presented the interaction of Am with the Mn oxide romanechite, whereas recent experiments using synchrotron radiation techniques (15) indicated the strong affinity of Pu with mineral phases containing Mn oxides and provided spatially resolved information about its oxidation states and coordination environment. Even in the above works, associated with the Yucca Mountain Site Characterization Project (YMP), there are no references towards the chemical behavior of todorokite with respect to actinides including Th and U.

The present work also includes an exploratory investigation on the interaction of todorokite with protactinium obtained using trace amounts of ^{233}Pa in aqueous solutions of different HCl concentrations. Despite Th and U, Pa is one of the rather rare elements on earth. Its long-lived isotope, ^{231}Pa ($T_{1/2}$: 3.276×10^4 yr) is a member of the actinium natural radioactive series and can be found in small quantities in uranium minerals in equilibrium with ^{235}U (ca. 340 mg ton^{-1} of natural uranium). ^{231}Pa has also received attention recently because of its production during the operation of thorium-fuelled reactors (^{232}Th(n,2n)^{231}Th $\rightarrow$ ^{231}Pa nuclear reaction). The significance of ^{233}Pa ($T_{1/2}$: 27 days), that is produced additionally by means of the ^{232}Th(n,γ)^{233}Th $\rightarrow$ ^{233}Pa nuclear reaction, is limited due to its short half-life. Small amounts of ^{233}Pa are also produced in nuclear waste through the α-decay of ^{237}Np ($T_{1/2}$: 2.144×10^6 yr). Finally, it should be noted that inasmuch as there are no publications about the interaction of natural Mn oxides (including todorokite) with protactinium, the known facts regarding sorption of the element by any kind of geological material are also very limited (16,17), obviously due to its complicated aqueous chemistry.

EXPERIMENTAL

The representative natural todorokite sample used in the experimental work (kindly supplied by the Museum of Natural History, London, UK) was from the Montenegro mine, Cuba. The characterization of the above natural microporous Mn oxide, described in a previous contribution (18), was performed using a variety of analytical, thermal, and spectroscopic techniques. The cation exchange capacity (CEC) of the material was investigated using the $K^+ \leftrightarrow Cs^+$ method applied for other natural microporous minerals such as zeolites (19), while its point of zero charge (pH_{PZC}) and the specific surface area (SSA) were also determined by standard procedures. The main sorption characteristics of the particular todorokite sample, quite relevant for the understanding of its behavior either in aqueous or gaseous media, are summarized in Table 1.

The thorium and uranium solutions used for the experimental work were prepared by dissolution of appropriate amounts of $Th(NO_3)_4{\cdot}4H_2O$ and $UO_2(NO_3)_2{\cdot}6H_2O$ (Merck, KGaA, Darmstadt, Germany, pro analysi) in double distilled water. Six solutions with metal concentrations between 1000 and 10 mg L^{-1} were prepared by dilution of an initial standardized solution of 1000 mg L^{-1}. The concentrations in all the solutions were checked

Table 1. Sorption Characteristics of the Investigated Todorokite (18)

Cation exchange capacity (CEC)	15 meq 100 g^{-1}
Specific surface area (SSA)	25 $m^2 g^{-1}$ (150°C), 39 $m^2 g^{-1}$ (250°C), 59 $m^2 g^{-1}$ (350°C), 37 $m^2 g^{-1}$ (450°C)
Point of zero charge (pH_{PZC})	2.4
Potential exchangeable cations (w/w)	Na (1.75%), Ba (1.06%), Ca (1.04%), Sr (0.65%), K (0.4%)

spectrophotometrically using the Arsenazo(III) method (20). The above-mentioned concentration range was selected mostly in order to simulate real actinide-contaminated nuclear wastes, such as those of BNFL at Springfields, UK, containing 180–750 mg L^{-1} thorium. For the individual sorption experiments, 50 mg of powdered todorokite was shaken for 24 hr with 10 mL of the individual solutions in polystyrene centrifuge tubes at room temperature (batch-type procedure). Preliminary tests indicated that the duration of the treatment was sufficient for the establishment of the final equilibrium. After the treatment the solid phases were separated using Nuclepore membrane filters, washed several times with double distilled water, and air-dried. The pH of the solutions was measured before and at the end of the treatment. The Th and U content of the separated solid phases was determined by means of instrumental neutron activation analysis (INAA) combined with high resolution γ-ray spectrometry using a high purity germanium detector (CANBERRA Industries, Meriden, CT, REGe-detector, efficiency 20%, resolution 2.1 keV for the 1.332 MeV ^{60}Co line) connected to a standard computer-based γ-ray spectroscopy set-up. The quantitative determination of Th and U was performed by means of the γ-radiation ^{233}Pa and ^{239}Np using IAEA Soil-7 as reference material. The irradiations were performed at 5 MW research reactor of the NRCPS "Demokritos", Athens, Greece (flux: 5×10^{13} cm^{-2} sec^{-1}).

The investigation of the interaction of todorokite with protactinium was performed using ^{233}Pa ($T_{1/2}$: 27.4 days), which was prepared by irradiation of a small amount of $Th(NO_3)_4 \cdot 4H_2O$ by thermal neutrons in the above-mentioned research reactor. The ^{233}Pa is a decay product of ^{233}Th ($T_{1/2}$: 23.3 min) and can be separated from the irradiated thorium nitrate by means of ion exchange using procedures described in the literature (21). The method used is based on the fact that protactinium forms in concentrated HCl solutions (8 *M*) negatively charged chloride complexes (22,23) reacting with an anion anionic exchanger (in this work Dowex 1 × 2 resin), while thorium remains as cation in the solution. The elution of the retained protactinium takes place by passing solutions of lower HCl concentration

(4 *M* and lower) through the ion-exchanger column. Protactinium-233 solutions in 1–0.25 *M* HCl were prepared for the sorption experiments. In a further experiment, ^{233}Pa was separated from the irradiated thorium nitrate dissolved in 3 *M* HCl by extraction using methyl-isobutyl-ketone (MIBK, Merck, KGaA, Darmstadt, Germany,) and re-extraction by 0.1 *M* HCl. Pa solutions in 0.01 and 0.001 *M* HCl were prepared by dilution of the solution in 0.1 *M* HCl. The ^{233}Pa concentration of the individual solutions was determined by γ-ray spectrometry. The contact time of todorokite with the protactinium solutions was 8 hr.

The x-ray photoelectron spectroscopy (XPS) spectra were obtained at the Institute of Instrumental Analysis (IFIA) at the Research Centre Karlsruhe, Germany, using a VG ESCALAB-5 instrument (Thermo VG Scientific, Imberhorn Grinstead, UK) equipped with a Mg K_α x-ray source. The correction for the charging of the nonconducting sample was made taking into account the C1s photopeak at 285 eV assigned to surface contamination by the atmosphere.

RESULTS AND DISCUSSION

The results of the thorium and uranium uptake by the investigated todorokite sample are given in Figs. 1 and 2. The absolute thorium uptake was found to be in the range 1.1–42.8 mg g^{-1}, whereas the corresponding values for uranium were 0.64–25.8 mg g^{-1}. The analysis of the initial material by INAA also indicated the presence of 7 μg g^{-1} of uranium (18). No thorium was detected during the analysis of the initial todorokite sample. The uranium uptake values (Γ) were found to obey a Freundlich-type relation $\Gamma = 0.12[C_{eq}]^{0.8123}$, $[C_{eq}]$ denoting the equilibrium uranium concentration in the solution. The thorium uptake by the investigated material does not seem to obey a similar relation. The sorption ratio values (R_d) for the case of thorium calculated from the

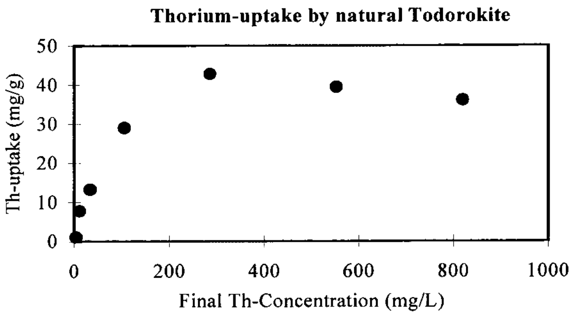

Figure 1. Thorium uptake (mg g^{-1}) by todorokite.

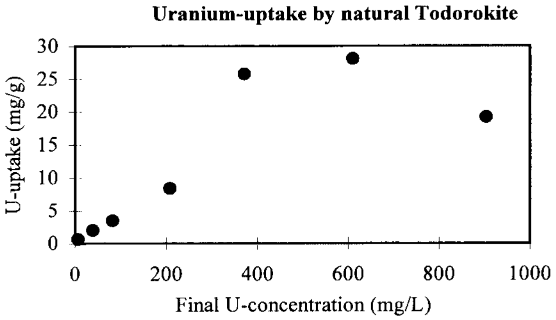

Figure 2. Uranium uptake ($mg\,g^{-1}$) by todorokite.

concentration of the element in the solid and liquid phase ranged between $44\,mL\,g^{-1}$ (for the $1000\,mg\,L^{-1}$ solution) and $697\,mL\,g^{-1}$ (for the $50\,mg\,L^{-1}$ solution). The R_d values for uranium were found to be lower varying in the region between 21 and $94\,mL\,g^{-1}$ (for the 1000 and $10\,mg\,L^{-1}$ solutions, respectively).

The thorium uptake by todorokite cannot be justified by the rather low CEC ($15\,meq\,100\,g^{-1}$) of this natural microporous mineral, and most probably is due to other processes rather than ion exchange. The initial pH of the thorium solutions ($1000-10\,mg\,L^{-1}$) varied between 2.9 and 4.0 whereas the final pH varied between 2.7 and 7.9 (Fig. 3) evidently due to the simultaneous sorption of H^+ cations causing an unfavorable intense hydrolysis of the initial Th^{4+} ions. Therefore, surface precipitation of thorium solid hydrolysis products and adsorption of species such as $[Th(OH)]^{3+}$ could be the sorption mechanisms

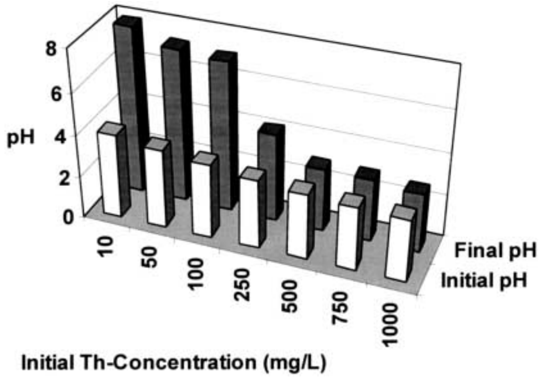

Figure 3. Variation of the pH of the thorium aqueous solutions during their interaction with todorokite.

responsible for the considerable amount of thorium bound by the material. Thorium solid hydrolysis products, including $Th(OH)_4$, generally are indistinct amorphous compounds and their precise identification on surfaces even spectroscopically is rather difficult. The surface precipitation of Th compounds has also been demonstrated on the basis of relevant experiments including other microporous minerals such as natural zeolites (24,25).

The uranium sorption by todorokite depends strongly on its aqueous chemistry also related to the pH of the used solutions ($1000-10\,\mathrm{mg\,L^{-1}}$). The hydrolysis of the uranyl ions begins practically at $pH > 3$ and mononuclear (e.g., $[UO_2(OH)^+]$) as well as polynuclear (e.g., $[(UO_2)_2(OH)_2]^{2+}$, $[(UO_2)_3(OH)_5]^+$) hydrolysis products of the general type $[(UO_2)_x(OH)_y]^{(2x-y)+}$ are formed. The occurrence of species $U_2O_5^{2+}$, $U_3O_8^{2+}$ and polymeric species of the type $UO_2(UO_3)_n^{2+}$ has also been proposed (26,27). At $pH < 4$, the most dominant species is the hydrated uranyl cation (28,29), which can be sorbed through ion exchange by natural microporous materials (30). The initial pH of the U solutions used during this work was between 3.5 and 5.4, whereas the final pH was between 3.9 and 8.0 (Fig. 4) attributed to the sorption of H^+ cations by the material. Therefore, one could expect a contribution of ion exchange of uranyl cations only in the case of the sorption from the most concentrated solutions. The removal of uranium by todorokite from solutions of lower concentration most probably is due to other sorption mechanisms such as surface precipitation of neutral solid hydrolysis products (in fact distinct U phases) or even adsorption of positively-charged species of the type $[(UO_2)(OH)]^+$. Similar phenomena, concerning an evident surface precipitation of particular U phases, have been observed in the case of other minerals, such as zeolites, galena, and pyrite (31,32).

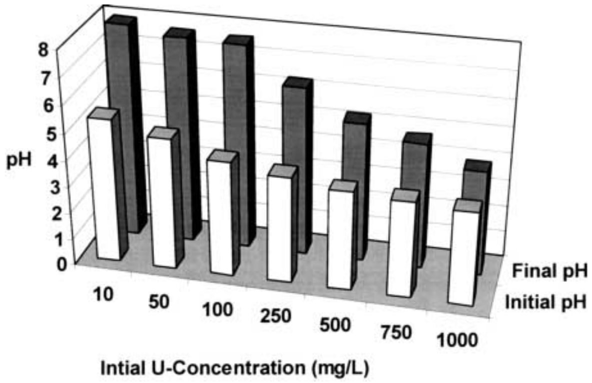

Figure 4. Variation of the pH of the uranium aqueous solutions during their interaction with todorokite.

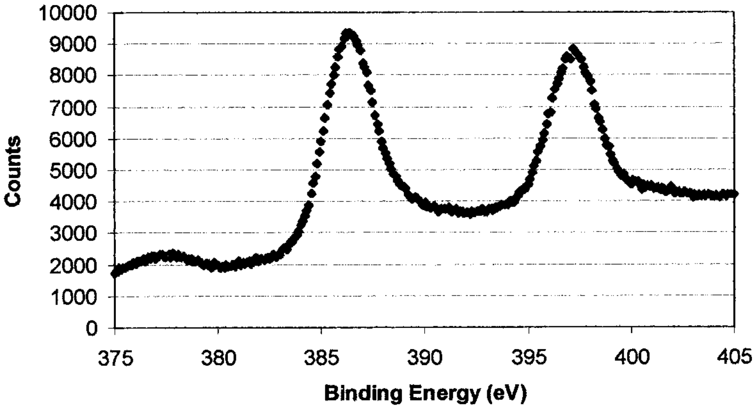

Figure 5. Raw XPS data concerning U-phases bound on the surface of the interacted todorokite crystals. Two main peaks assigned to U-4$f_{7/2}$ (381.7 eV) and U-4$f_{5/2}$ (392.6 eV) binding energies can be recorded after the appropriate correction (−4.6 eV), due to the charging of the nonconducting samples, taking into account the standard C1s photopeak at 285 eV.

Additional information about the chemical behavior of todorokite in the U aqueous solutions, resulting in the metal uptake by the mineral predominantly through surface precipitation, can be obtained by the XPS measurements performed on the interacted solid. Figure 5 shows a plot of the raw XPS data obtained during these measurements. The two peaks of this graph belong to U-4$f_{7/2}$ and U-4$f_{5/2}$ binding energies appearing, after charging correction, at 381.7 and 392.6 eV. The correction for the charging of the nonconducting samples made taking into account the C1s photopeak at 285 eV amounts to −4.6 eV. The U-4$f_{7/2}$ binding energy of 381.7 eV corresponds to the presence of a U-phase of the type UO_3 (33) bound to the surface of the todorokite particles. The same crystalline U oxide was observed in the case of interaction of natural zeolite crystals with uranyl nitrate solutions (34). Relevant results involving surface precipitation were presented for the case of the uranium sorption on colloidal hematite, where extended x-ray absorption fine structure (EXAFS) measurements gave spectra very similar to the phase $UO_2(OH)_2{\cdot}H_2O$, which is known as schoepite (35). The XPS measurements also indicated that the oxidation state of the framework manganese ions (Mn^{4+}) on the surface of todorokite crystals remained unchanged after the interaction with the U-containing aqueous solution (binding energy of Mn-2$p_{3/2}$: 642.3 eV).

The recent information on the protactinium aqueous chemistry is rather restricted compared to other lower actinides. Most of the studies in the literature were performed using ^{233}Pa, because of the limited availability of ^{231}Pa and its long half-life. On the other hand, the ^{233}Pa studies in solutions have been conducted at very low concentrations mainly because of its high radioactivity and polymerization tendency. The most stable oxidation state in solutions is the Pa(V), which tends to hydrolyze, forming oxy-hydroxide species (36) and finally precipitates as a hydrated oxide ($Pa_2O_5 \cdot x H_2O$) unless strong complex compound forming agents are present. The hydrolysis of pentavalent protactinium, increasing with the pH of the solution, is extremely complicated and not yet understood completely. The presence of actinyl(V) ions (PaO_2^+) could be possible in solutions of very high acidity eventually and even be formulated as $PaO(OH)_2^+$ (23). Complexing agents in very strong solutions replace the oxygen atoms of protactinyl ion forming anionic halide species such as PaX_6^- and PaX_7^{2-} (where X: F, Cl...). Extraction studies (22,37) have indicated that, at HCl concentrations higher than $6\,M$, the formation of $PaCl_6^-$ and $PaCl_7^{2-}$ is possible (also leading to the Pa separation using anionic ion exchangers). At lower acid concentrations (below $6\,M$) negatively (e.g., $Pa(OH)Cl_5^-$, $Pa(OH)_2Cl_4^-$) and positively (e.g., $Pa(OH)Cl_3^+$) charged hydroxy-chloride species are formed. The formation of neutral species (e.g., $Pa(OH)_2Cl_3$) is also possible.

The R_d values for the uptake of protactinium from 1, 0.5, 0.25, 0.01, and $0.001\,M$ HCl solutions, calculated from the concentration of ^{233}Pa in the solid and liquid phase, are given in Table 2. The initial pH of the investigated solutions was lower than the pH_{PZC} (2.4) of the mineral (18). At pH values lower than 2.4, the studied todorokite is positively charged, and is able to sorb anionic species, whereas at pH values higher than 2.4 the mineral is negatively charged and can act as a cationic sorbent. However, the use of the todorokite sample as anionic sorbent (in low pH solutions) is limited by the dissolution phenomena apparently leading to a prompt release of Mn from its crystal structure (18). The obtained R_d values could

Table 2. Sorption Ratio (R_d) Values Calculated for the Removal of Protactinium from Aqueous Solutions of Different Concentrations by the Todorokite Sample Under Investigation

HCl Concentration (M)	Initial Pa Concentration ($ng\,L^{-1}$)	R_d-Value ($\times 10^4\,mL\,g^{-1}$)
1	0.64	2.4
0.5	0.18	1.6
0.25	0.15	1.1
0.01	0.05	0.2
0.001	0.004	63.5

reflect the diminishing amount of anionic Pa species macroscopically in 1, 0.5, 0.25, and 0.01 *M* HCl solutions. Although the values of Table 2 have a rather qualitative character, they indicate the high sorption ability of the material against low concentrations of Pa anionic species. Pa sorption experiments performed using 0.001 *M* HCl solutions lead to almost total removal of the element assigned to the surface precipitation of the insoluble protactinium hydrolysis products (38). In the last case, the pH of the solution was increased drastically by todorokite (pH ~ 6) fundamentally due to the simultaneous uptake of H^+ cations, as also took place in the case of the Th and U solutions.

ACKNOWLEDGMENTS

The authors would like to thank Drs. A. M. Clark and E. Valsami-Jones (British Museum of Natural History, UK) for providing the investigated todorokite sample as well as Dr. D. Bish (Los Alamos National Laboratory, USA) for the constructive discussions on the subject of the present work.

REFERENCES

1. Ostwald, J. Some Observations on the Chemical Composition of Todorokite. Mineral. Mag. **1986**, *50*, 336–340.
2. Frondel, C.; Marvin, U.B.; Ito, J. New Occurrences of Todorokite. Am. Mineral. **1960**, *45*, 1167–1173.
3. Straczec, J.A.; Horen, A.; Ross, M.; Warshaw, C.M. Studies of the Manganese Oxides. IV. Todorokite. Am. Mineral. **1960**, *45*, 1174–1184.
4. Larson, L.T. Zinc-Bearing Todorokite from Philipsburg, Montana. Am. Mineral. **1962**, *47*, 59–66.
5. Radtke, A.S.; Taylor, C.M.; Hewett, D.F. Aurorite, Argentian Todorokite and Hydrous Silver-Bearing Lead Manganese Oxide. Econ. Geol. **1967**, *62*, 186–206.
6. Finkelman, R.B.; Evans, H.T., Jr.; Matzko, J. Manganese Minerals in Geodes from Chihuahua, Mexico. Mineral. Mag. **1974**, *39*, 549–558.
7. Burns, V.M.; Burns, R.G. Post-depositional Metal Enrichment Processes Inside Manganese Nodules from the North Equatorial Pacific. Earth Planet. Sci. Lett. **1978**, *39*, 341–348.
8. Burns, R.G., (Ed.) Reviews in Mineralogy. In *Marine Minerals*; M.S.A.: Washington, 1979; Vol. 6.
9. Burns, R.G.; Burns, V.M.; Stockman, H.W. A Review of the Todorokite–Buserite Problem: Implications to the Mineralogy of Marine Manganese Nodules. Am. Mineral. **1983**, *68*, 972–980.

10. Carlos, B.A.; Chipera, S.J.; Bish, D.L.; Craven, S.J. Fracture-Lining Manganese Oxide Minerals in Silicic Tuff, Yucca Mountain, Nevada, U.S.A. Chem. Geol. **1993**, *107*, 47–69.
11. Triay, I. R.; Cotter, C. R.; Kraus, S. M.; Huddleston, M. H.; Chipera, S. J.; Bish, D. L. *Radionuclide Sorption in Yucca Mountain Tuffs with J-13 Well Water: Neptunium, Uranium and Plutonium, Yucca Mountain Site Characterization Program Milestone 3383*; Los Alamos National Laboratory, Report LA-12956-MS, 1996.
12. Post, J.E.; Bish, D.L. Rietveld Refinement of the Todorokite Structure. Am. Mineral. **1988**, *73*, 861–869.
13. Lindsley, D.H. (Ed.) Reviews in Mineralogy. In *Oxide Minerals: Petrologic and Magnetic Significance*; M.S.A.: Washington, 1991; Vol. 25.
14. Triay, I.R.; Meijer, A.; Cisneros, M.R.; Miller, G.C.; Mitchell, A.J.; Ott, M.A.; Hobart, D.E.; Palmer, P.D.; Perrin, R.E.; Aguilar, R.D. Sorption of Americium in Tuff and Pure Minerals Using Synthetic and Natural Groundwaters. Radiochim. Acta **1991**, *52/53*, 141–145.
15. Bertsch, P. M.; Hunter, D. B.; Duff, M. Micro/Spatially Resolved XRF and XAFS by the In-Situ Interrogation of Radionuclide Distribution and Speciation in Environmental Samples. In *Proceedings of the Euroconference and NEA Workshop on the Speciation, Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources*; Paris: NEA-OECD, 1999; 81–82.
16. Kulmala, S.; Hakanen, M.; Lindberg, A. Sorption of Protactinium on Finnish Bedrock. Radiochemistry **1998**, *40*, 501–503.
17. Baston, G.M.N.; Berry, J.A.; Brownsword, M.; Heath, T.G.; Ilett, D.J.; McCrohon, R.; Tweed, C.J.; Yui, M. The Sorption of Polonium, Actinium and Protactinium onto Geological Materials. *Proceedings Volume 556*; Materials Research Society: Pittsburgh, 1999; 1107–1114.
18. Godelitsas, A.; Misaelides, P.; Katranas, T.; Triantafyllidis, C.; Klewe-Nebenius, H.; Pavlidou, E. Characterization of Natural Manganese Oxides: the Case of Todorokite. In *Natural Microporous Materials in the Environmental Technology*; Misaelides, P., Macasek, F., Pinnavaia, T.J., Colella, C., Eds.; Kluwer: Dordrecht, 1999; 445–461.
19. Ming, D.W.; Allen, E.R.; Galindo, C., Jr.; Henninger, D.L. Methods for Determining Cation Exchange Capacities and Compositions of Native Exchangeable Cations for Clinoptilolite. In *Zeolites '91, Part 2*; Fuentes, G.R., Gonzalez, J.A., Eds.; Havana: International Conference Center, 1991; 31–37.
20. Savvin, S.B. Analytical Applications of Arsenazo-III–II. Determination of Thorium, Uranium, Protactinium, Neptunium, Hafnium and Scandium. Talanta **1964**, *11*, 1–6.

21. Nesmeyanov, A.N. *A Guide to Practical Radiochemistry*; Mir Publishers: Moscow, 1984; Vol. 2, 171–173.
22. Casey, A.T.; Maddock, A.G. The Chemistry of Protactinium V: A Comparison of the Extraction of Protactinium, Niobium and Tantalum. J. Inorg. Nucl. Chem. **1959**, *10*, 289–305.
23. Ahrland, S.; Liljenzin, J.O.; Rydberg, J. Solution Chemistry. In *Comprehensive Inorganic Chemistry*; Bailar, J.C., Jr., Emeleus, H.J., Nyholm, Sir R., Trotman-Dickenson, A.F., Eds.; Pergamon: Oxford, 1973; Vol. 5 (Actinides).
24. Dyer, A.; Jozefowicz, L.C. The Removal of Thorium from Aqueous Solutions Using Zeolites. J. Radioanal. Nucl. Chem. **1992**, *159*, 47–62.
25. Godelitsas, A.; Misaelides, P.; Charistos, D.; Filippidis, A.; Anousis, I. Interaction of HEU-Type Zeolite Crystals with Thorium Aqueous Solutions. Chem. Erde **1996**, *56*, 143–156.
26. Sutton, J. Hydrolysis of Uranyl Ion, Part I. J. Chem. Soc. **1949**, 275–286.
27. Grindler, J. A. The Radiochemistry of Uranium, NAS-NS 3050, 1962
28. Madic, C.; Den Auwer, C.; Guillaumond, R. Application of X-Ray Absorption Spectroscopy (XAS) to Actinide Solution Chemistry. In *Proceedings of the Euroconference and NEA Workshop on the Speciation, Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources*; Paris: NEA-OECD, 1999; 69–79.
29. Baes, C.F.; Mesmer, R.E. *The Hydrolysis of Cations*; Krieger: Malabar, 1986; 490.
30. Misaelides, P.; Godelitsas, A. Interaction of Actinides with Natural Microporous Materials. In *Natural Microporous Materials in the Environmental Technology*; Misaelides, P., Macasek, F., Pinnavaia, T.J., Colella, C., Eds.; Kluwer: Dordrecht, 1999; 193–205.
31. Wersin, P.; Hochella, M.F.; Persson, P.; Redden, G.; Lechie, G.; Harris, D.W. Interaction Between Aqueous Uranium(VI) and Sulfide Minerals: Spectroscopic Evidence for Sorption and Reduction. Geochim. Cosmochim. Acta **1994**, *58*, 2829–2843.
32. Godelitsas, A.; Misaelides, P.; Filippidis, A.; Charistos, D.; Anousis, I. Uranium Sorption from Aqueous Solutions on Sodium Form of HEU-Type Zeolite Crystals. J. Radioanal. Nucl. Chem. Articles **1996**, *208*, 393–402.
33. Bernard, P.; Louer, D.; Dachaux, N.; Brandel, V.; Genet, M. $U(UO_2)(PO_4)_2$, a New Mixed-Valence Uranium Orthophosphate: Ab Initio Structure Determination from Powder Diffraction Data and Optical X-Ray Photoelectron Spectra. Chem. Mater. **1994**, *6*, 1049–1058.
34. Misaelides, P.; Godelitsas, A.; Kossionidis, S.; Manos, G. Investigation of Chemical Processes at Mineral Surfaces Using Accelerator-Based and Surface Analytical Techniques: Heavy Metal Sorption on Zeolite Crystals. Nucl. Instrum. Methods **1996**, *B113*, 296–299.

35. Swanton, S.W.; Baston, G.; Cowper, M.M.; Charnock, J.M. EXAFS Study of Uranium(VI) Sorbed on Hematite. In *Proceedings of the Euroconference and NEA Workshop on the Speciation, Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources*; Paris: NEA-OECD, 1999; 111–118.
36. Keller, C. Binary and Ternary Oxides, Hydroxides and Hydrous Oxides, Peroxides, Phosphates and Arsenates. In *Comprehensive Inorganic Chemistry*; Bailar, J.C., Jr., Emeleus, H.J., Nyholm, Sir R., Trotman-Dickenson, A.F., Eds.; Pergamon: Oxford, 1973; Vol. 5 (Actinides).
37. Sankar, J.; Venkatesvarlu, K.S.; Gopinathan, C. The Chemistry of Protactinium—I: The Nature of Species in HCl Solutions by Solvent Extraction and Paper Electrophoresis. J. Inorg. Nucl. Chem. **1963**, *25*, 57–66.
38. Kirby, H.W. Protactinium. In *The Chemistry of the Actinide Elements*; 2nd Ed.; Katz, J.J., Seaborg, G.T., Morss, L.R., Eds.; Chapman and Hall: New York, 1986; Vol. 1, 102–168.

Received September 2000
Revised July 2001

Downloaded At: 10:35 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS120002244