Immobilization of Uranium in Contaminated Sediments by Hydroxyapatite Addition

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Batch equilibrations were performed to investigate the ability of hydroxyapatite ($Ca_5(PO_4)_3OH$) to chemically immobilize U in two contaminated sediment samples having different organic carbon contents (123 and 49 g kg^{-1}, respectively). Apatite additions lowered aqueous U to near proposed drinking water standards in batch equilibrations of two distinct sediment strata having total U concentrations of 1703 and 2100 mg kg^{-1}, respectively. Apatite addition of 50 g kg^{-1} reduced the solubility of U to values less than would be expected if autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$) was the controlling solid phase. A comparison of the two sediment types suggests that aqueous phase U may be controlled by both the DOC content through complexation and the equilibrium pH for a given apatite application rate. Sequential chemical extractions demonstrated that apatite amendment transfers U from more chemically labile fractions, including water-soluble, exchangeable, and acid-soluble (pH ≈ 2.55) fractions, to the Mn-occluded fraction (pH ≈ 1.26). This suggests that apatite amendment redirects solid-phase speciation with secondary U phosphates being solubilized due to the lower pH of the Mn-occluded extractant, despite the lack of significant quantities of Mn oxides within these sediments. Energy dispersive X-ray (EDX) analysis conducted in a transmission electron microscope (TEM) confirmed that apatite amendment sequesters some U in secondary Al/Fe phosphate phases.

Introduction

In situ remediation of contaminated soils and aquifer sediments is appealing since it reduces the risk of worker exposure during remediation and is typically less expensive and much less disruptive to ecosystems and hydrology than conventional excavation, treatment, and disposal methods. In situ treatment of uranium-contaminated soils requires an understanding of the chemical and physical relationships of uranium with critical sediment components. In addition, an understanding of both kinetic limitations and reaction product stability over a range of physical and chemical conditions is important in predicting the efficiency of a remediation strategy.

Tims Branch, a second-order stream which drains approximately 16 km^2 within the drainage basin of the Savannah River, was contaminated with U and other metals (e.g., Ni, Al, Cr, Cu, Cd) resulting from fuel fabrication on the Department of Energy's Savannah River Site, near Aiken, SC (*1*). Tims Branch flows directly into Upper Three Runs Creek, which in turn flows into the Savannah River. Approximately 45 000 kg of depleted U were released into Tims Branch from 1954 to 1985, with approximately 70% still remaining in the sediments of Steed Pond, a drainage basin located in the Tims Branch system, primarily as U(VI) (*1–3*). Significant deposition of contaminants and suspended sediments occurred within Steed Pond due to the longer residence times and reduced flow velocities (*1, 4*). The dam ruptured in 1984, exposing the contaminated sediments which are subject to erosion in areas that remain unvegetated.

In situ strategies for remediation of metals frequently involve minimizing the mobility of contaminants by transferring them to nonlabile phases via chemically or biologically induced transformations. Apatite minerals ($Ca_5(PO_4)_3X$ (X = halide, hydroxyl)) are known to react with many transition and heavy metals, metalloids, and radionuclides to rapidly form secondary phosphate precipitates that are stable over a wide range of geochemical conditions (*5–7*). Several studies have shown that Pb reacts with orthophosphate from hydroxyapatite to form highly insoluble Pb phosphates in both model (*8–10*) and contaminated sediment systems (*11–15*).

Complicated redox, mineralogical, and sorptive chemistry makes predicting the behavior of U in the environment difficult. Schoepites ($UO_3 \cdot xH_2O$) and rutherfordine (UO_2CO_3) are generally considered U(VI) solubility controlling phases in the environment (*16–18*). Sowder et al. (*16*), however, found that becquerelite ($Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$) is a weathering product of schoepite in 0.01 M calcium brines. In the presence of 0.01 M calcium and 0.01 M phosphate, schoepite forms becquerelite within days and transforms to autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$) within weeks.

U(VI) solubility is affected by common ligands such as phosphate, carbonate, and sulfate (*19, 20*), and is pH dependent (*20*). Uranyl (UO_2^{2+}) is typically the predominant free aqueous species in natural water systems under aerobic, acidic conditions (pH < 5) (*20*). Under less acidic conditions (pH > 5), various U(VI)−carbonate complexes tend to predominate, enhancing U(VI) solubility (*20*). U(VI) also forms stable complexes with dissolved organic carbon (DOC). Li et al. (*21*) measured stability constants for U(VI) with fulvic acid, humic acid, and tannic acid on the order of 10^7 at "strong" binding sites and 10^5 at "weak" binding sites. The affinity of these organics for U drops dramatically as pH falls below 5, depending on the ligand. U(VI) is also known to bind effectively with Fe and Mn oxides and clays (*22–24*).

Reactive sinks that compete for soil additives such as apatite, however, can significantly reduce the effectiveness of metals precipitation. Thus, amendment remediation methods must be site specifically characterized under a range of field conditions (e.g., metals concentration, organic carbon levels, redox status, sediment mineralogy). Additionally, few studies have characterized the long-term stability (i.e., solubility) or bioavailability of metals in amended sediments, a critical factor in determining the effectiveness of any stabilization method.

The objectives of this study were to (1) determine if apatite addition could reduce soluble U to within proposed drinking water standards by redirecting solid-phase speciation to less chemically labile forms; and (2) characterize the effect of varied sediment organic content on the speciation of U and the efficiency of apatite treatment.

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TABLE 1. Physical and Chemical Characteristics of Two U-Contaminated Sediment Strata from Steed Pond

characteristics	sediment zone	
	Z1	Z2
U_{total} (mg kg^{-1})	1703	2100
depth (cm)	2−7	7−22
pH[a]	4.4	4.1
CDB ext. Fe (% by wt)[b]	2.9	3.2
CDB ext. Al (% by wt)[b]	1.3	2.3
organic carbon (g kg^{-1})[c]	123	49
particle size distribution,[d] mineralogy[e]		
sand (%), q ≫ fel	25.7	19.2
silt (%), q > k ≫ fel	35.8	45.2
clay (%), k ≫ HIV > gibb > goe > q	38.5	35.6

[a] Solution/soil ratio (2:1) in deionized water. [b] CDB, citrate−dithionite−bicarbonate extraction (34, 35). [c] Total organic carbon, dry combustion method (36). [d] Micropipet method (37). [e] Mineralogy determined by X-ray diffraction, fel = feldspar; k = kaolinite; HIV = hydroxyinterlayered vermiculite; gibb = gibbsite; q = quartz; goe = goethite.

Materials and Methods

The exposed sediments of Steed Pond are characterized by low pH (4.0−4.5), highly weathered clays such as kaolinite, abundant Fe (ferrihydrite, goethite) and Al oxides and oxyhydroxides, and variable levels of organic carbon (4). Two distinct U-contaminated sediment samples from Steed Pond, hereafter referred to as Z1 and Z2, were taken at depth intervals from 2 to 7 and 7 to 22 cm, respectively, at the same coring site (Table 1). Both sediments have similar properties with respect to mineralogy, pH, and texture, but vary greatly with respect to organic carbon (OC) (4, 25).

Batch Equilibrations. All solutions were prepared with ultrapure DI water and reagent-grade chemicals. All filters were polycarbonate unless otherwise stated. Three replicates of all batch equilibrations were conducted to estimate variability. Five-gram (dry wt) samples of field-moist sediment were placed in 50-mL batch reactors. Four levels of hydroxyapatite were added to each sediment, 0, 0.5, 1.58, and 5.0% by weight, in 25 mL of either a 0.02 M KCl or 0.01 M CaCl₂ background solution. Samples were equilibrated on a reciprocating shaker for 42 h at 25 °C. Supernatant pH and electrical conductivity (EC) readings were taken after sediment suspensions were allowed to settle for at least 2 h. Samples were then centrifuged at 10 000 rpm for 30 min using a Sorvall RC2-B supercentrifuge and passed through a polycarbonate membrane filter (0.22 μm pore size). A fraction of the filtered supernatant was immediately analyzed for DOC using a Shimadzu TOC-500 organic carbon analyzer and soluble orthophosphate using the molybdate ascorbic acid colorimetric method (26). Sulfate, chloride, and nitrate contents in the supernatant were determined by ion chromatography according to EPA Method 300.0. The remaining supernatants were acidified (1% nitric acid) and analyzed for metals by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 6000, Perkin-Elmer Corp., Norwalk, CT) following the QA/QC protocols outlined in EPA Method 200.8 using ²⁰⁹Bi as an internal standard. Following batch equilibration, the sediment samples were split and evaluated using one of the following: (a) toxicity characteristic leaching procedure (TCLP) extraction; (b) sequential extraction; or (c) SEM/TEM spectroscopic microanalysis.

Thermodynamic Modeling. Equilibrium modeling was conducted using the U.S. Environmental Protection Agency's MINTEQA2 geochemical code (v. 3.11) updated with the Nuclear Energy Agency's thermodynamic database for uranium (27, 28). The degree of saturation with respect to a specific solid phase (Ω) is defined as

$$\Omega = IAP/K_{so}$$

where IAP is the ion activity product and K_{so} is the solubility product. To readily compare the degree of saturation for a set of potential solid phases, the saturation index (SI) is then defined as the log Ω. A SI of < 0 (i.e., negative value) indicates that the solution is undersaturated while a SI > 0 indicates the solution is supersaturated with respect to a given solid phase. A SI of 0 indicates that the solution is in equilibrium with a given solid. To calculate the saturation indices for various autunites, modeling was performed using hydroxyapatite as an infinite solid without allowing secondary phases to precipitate that would alter the solution chemistry. The solution composition (i.e., U and PO₄) and pH were based on results from the initial apatite/soil equilibrations for the 5% amendment treatment level in each of the background equilibrating solutions, 0.01 M CaCl₂ or 0.02 M KCl.

TCLP Extraction. Two replicates of each sample type were extracted using the EPA-standardized TCLP method (40 CFR, Chapter 1, Part 268, Appendix 1). The TCLP leaching solution is 0.1 M glacial acetic acid, 0.0643 M NaOH, and has a pH of 4.93. Fifty grams of leaching solution was added to 2.5 g of treated sediment, and the mixture was agitated on a reciprocating shaker for 18 h at 25 °C, and then centrifuged as described above. After centrifugation, supernatants were filtered through 0.22 μm pore-size polycarbonate filters, acidified (2% HNO₃), and analyzed for metals using ICP-MS.

Sequential Extraction. Sequential extraction was performed in triplicate for each of the sediment treatments using the modified procedure from Miller et al. (29). Each extraction step and the target phase is listed in procedural order from least to most chemically aggressive: (1) deionized water = water soluble; (2) 0.5 M Ca(NO₃)₂ = exchangeable; (3) 0.44 M glacial acetic acid + 0.1 M Ca(NO₃)₂ = acid soluble; (4) 0.01 M NH₂OH·HCl + 0.1 M HNO₃ = Mn occluded; (5) 0.1 M Na₄P₂O₇·10H₂O = organically bound; (6) 0.175 M (NH₄)₂-C₂O₄·H₂O, 0.1 M H₂C₂O₄ = amorphous Fe oxides; (7) reduction with 0.5 g Na dithionite in 0.15 M Na₃H₅C₆O₇ + 0.05 M H₈C₆O₇ (sodium citrate buffer) = crystalline Fe oxides; and (8) 6 mL of HF and 5 mL of HNO₃ and heated at 120 psi in a digestion microwave for 30 min intervals until digestion was complete = residual fraction. Uranium in sequential extractions was quantified by ICP-MS. DOC was measured in the H₂O soluble extraction using a Shimadzu TOC analyzer. Orthophosphate in the acid soluble fraction was quantified using the colorimetric method cited above (26).

Electron Microscopy Analysis. Electron microscopy was used to identify U-rich solid phases that may influence U solubility in control and apatite-treated sediments. Sediments were homogenized using a mortar and pestle, uniformly dispersed and fixed to an SEM stub using carbon tape, and then coated with evaporated carbon to reduce particle charging prior to analysis. Samples were randomly surveyed using a JEOL 6400 SEM equipped with a thin-window energy dispersive X-ray (EDX) system for compositional analysis. Random field surveys were conducted to locate U-rich particles for EDX analysis based on backscattered electron contrast. Using this technique, particles rich in heavy elements such as U appear as bright patches against the dark background. For transmission electron microscopy (TEM), a small fraction of each soil treatment including the control samples without apatite was deposited on a thin carbon film and analyzed using a JEOL 2010 electron microscope equipped with a thin-window detector for EDX analysis of lighter elements ($Z \geq 6$).

Results and Discussion

Batch Equilibrations. Previous studies (4, 20, 21, 25) suggest that organic matter may be an important sorbent for U(VI)
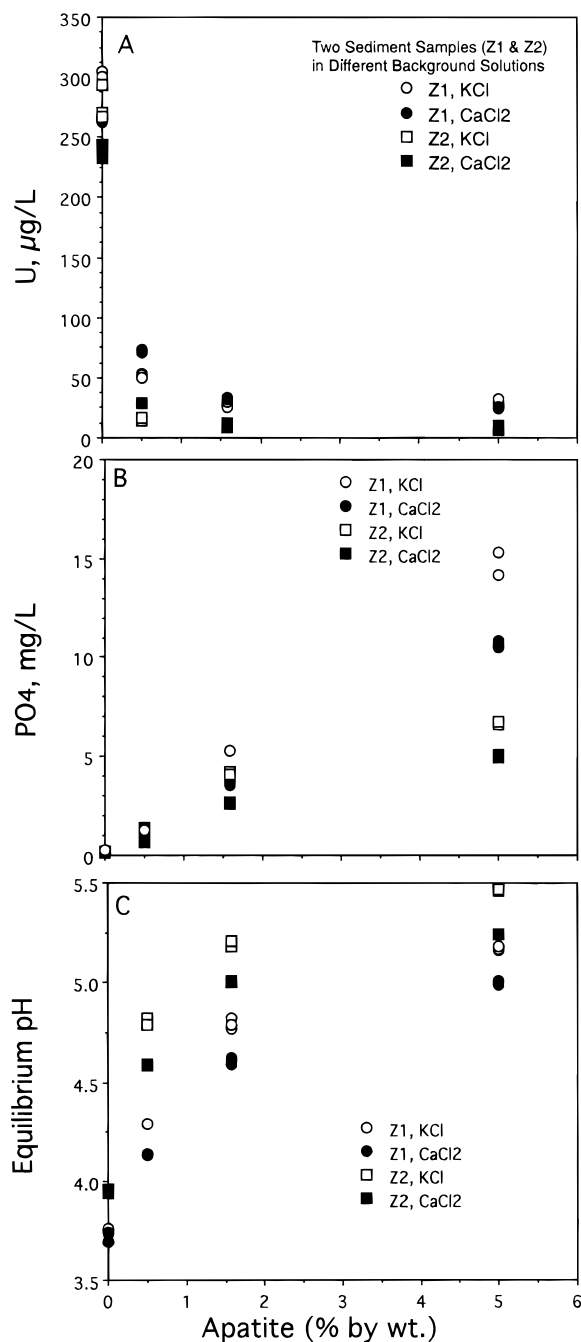
FIGURE 1. Effect of apatite amendment on equilibrated U concentration (A), PO₄ concentration (B), and suspension pH (C) for two sediments equilibrated in either a 0.02 M KCl solution or 0.01 M CaCl₂ solution.

in high OC sediments such as these. Two distinct sediment strata differing in organic carbon content were intentionally studied to test this hypothesis. In batch experiments, aqueous U concentrations decreased substantially with apatite addition (Figure 1A). Several possible mechanisms can explain the loss of aqueous U by addition of apatite. Soluble phosphate increased almost linearly as a function of apatite addition in sediment-free background solutions, suggesting that apatite dissolution is kinetically controlled (data not shown), and displays similar but less dramatic behavior in the presence of sediments (Figure 1B). For both sediment-free background solutions and equilibrated sediments, the equilibrium phosphate concentration and pH are consistently lower when CaCl₂ is used as the background electrolyte, perhaps the result of the common ion effect of calcium on
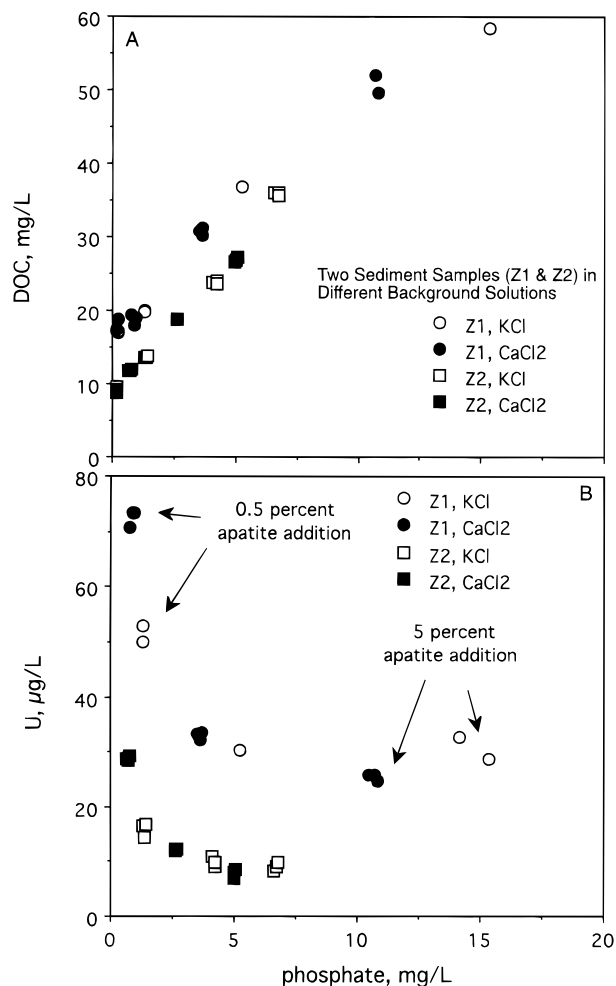

FIGURE 2. Equilibrated aqueous PO₄ as related to DOC concentration (A) and U concentration (B) in apatite amended sediments.
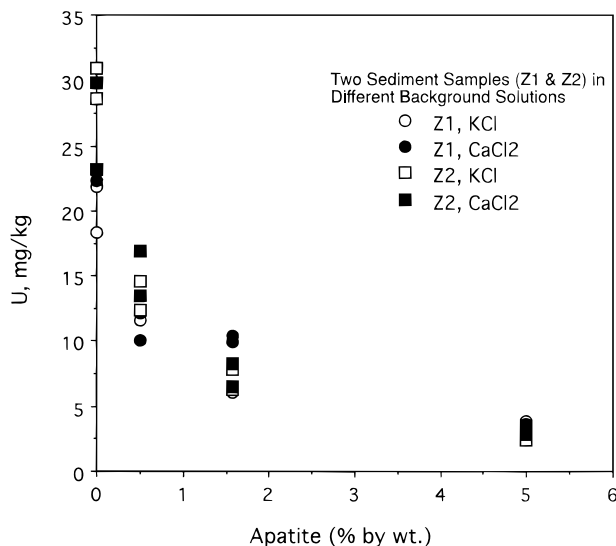

FIGURE 3. TCLP (toxicity characteristic leaching procedure) extractable U in apatite amended sediments.

apatite dissolution. Soluble phosphate levels in sediment-free CaCl₂ solution with apatite are comparable to those observed in the presence of apatite-treated sediments. Soluble phosphate in sediment-free KCl solutions are roughly an order of magnitude higher than in supernatants from sediment equilibrations, demonstrating the impact of sediment components on phosphate solubility.
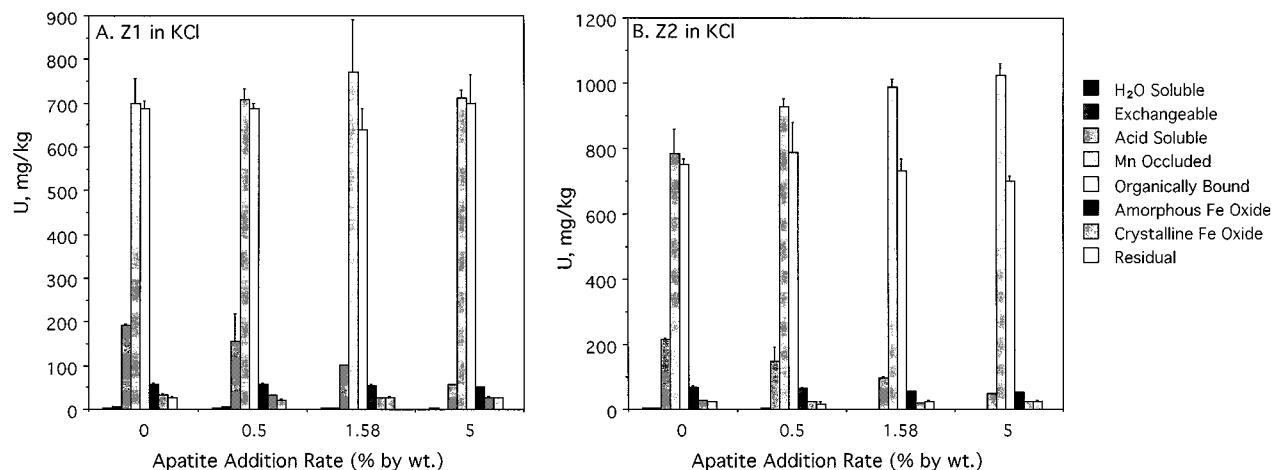
FIGURE 4. Sequential extraction results for sediment Z1 (A) and Z2 (B) amended with various apatite treatment levels and equilibrated in a 0.02 M KCl background solution.

TABLE 2. MinteqA2 Input Parameters and Calculated Saturation Indices for Select Uranyl Mineral Phases Based on the Average Equilibration Data for Three Replicates of Sediments Z1 and Z2 Amended with 5% Hydroxyapatite in Either a 0.01 M $CaCl_2$ or 0.02 M KCl Background Solution

							sat. indices (log Ω)		
sediment	pH	Ca (mg/L)	K (mg/L)	Cl (mg/L)	PO_4 (mg/L)	U (μg/L)	autunite	H$-$autunite	K$-$autunite
					Z1				
KCl	5.17		782	709	14.8	29.83	−4.78	−6.35	−1.288
$CaCl_2$	5.00	401		709	10.7	25.33	−4.77	−6.48	
					Z2				
KCl	5.46		782	709	6.7	9.02	−5.33	−7.44	−1.78
$CaCl_2$	5.24	401		709	5.0	7.76	−5.37	−7.53	

Apatite addition increased pH in both sediments due to the buffering capacity of the phosphate anion (Figure 1C). In addition, hydroxyl release during solubilization and ligand exchange of phosphate for hydroxyls on amphoteric oxy−hydroxide mineral surfaces such as goethite and gibbsite may contribute to the pH shift. DOC increased almost linearly with increasing phosphate in apatite-amended sediments (Figure 2A). Increased solubilization of organic matter is possibly the result of enhanced solubility of humic substances with increased pH and competition of anionic organic acids with phosphate for sorption sites (30−32). Note that DOC was consistently higher in the high organic sediment, Z1.

A plot of [U] with regard to soluble phosphate shows that apatite-related removal of U differs considerably for the two sediment strata for a given level of phosphate (Figure 2B). At the lowest apatite amendment level (i.e., 0.5%), less U is removed by apatite in sediments equilibrated in a $CaCl_2$ background solution, suggesting a dependence on phosphate concentrations and apatite solubility. Phosphate minerals should be less soluble for a given treatment in sediment Z2 than in sediment Z1 due to the consistently higher pH observed in Z2. Sediment Z1 has consistently higher levels of both dissolved phosphate and dissolved U for a given apatite treatment, irrespective of background solution treatment (Figure 2B). The higher soluble U may result from the lower pH observed for Z1, and thus increased solubility of U phosphates. In addition, the higher DOC observed for sediment Z1 suggests that complexation may also enhance U solubility since U(VI) forms strong complexes with various soil organic acids (21). In both sediments, soluble U did not decrease significantly between the highest two apatite addition rates (1.58% and 5.0%) which increased solution PO_4, suggesting that U activity in solution was lowered as a result of complexation with organics.

Thermodynamic Modeling. Input values and calculated saturation indices for the two sediments equilibrated with 5% apatite are presented in Table 2. Apatite was entered as an infinite solid since residual grains were identified in amended samples during SEM/TEM analysis. The levels of U were well below the predicted saturation point (i.e., SI < 0) for all of the autunite minerals without including complexation by DOC which would further reduce the free-ion activity product for uranyl despite the fact that the total solution concentration is constrained by the analytical data, thereby increasing the degree of undersaturation. This suggests that alternate sorption reactions and solid phases control U solubility in the amended soils.

Extractability of Solid-Phase U. The TCLP extraction is used by EPA as an operation measure of the leachability of sediment contaminants in response to mildly acidic (pH ≈ 4.93), weak ligand extraction (acetate) conditions thought to be analogous to the leaching environment of municipal landfills. TCLP extractable U (Figure 3) is substantially diminished in sediments equilibrated with apatite. Significantly more U is extracted from Z2 than Z1 in untreated sediments, but sediment type appears to have less of an effect in apatite-amended sediments. TCLP extracts roughly 20 times more U from unamended sediments compared to initial batch equilibrations, suggesting that extensive U phase redistribution is induced by apatite addition and continued PO_4 release during the TCLP and sequential extractions than is reflected in the changes in U solubility during the initial batch equilibrations.

Sequential extractions provide a more refined operational assessment of phase associations of contaminants in sediments. The procedure generally liberates successively less chemically labile phases and, ideally, their associated contaminants. The total mass of sequentially extracted U
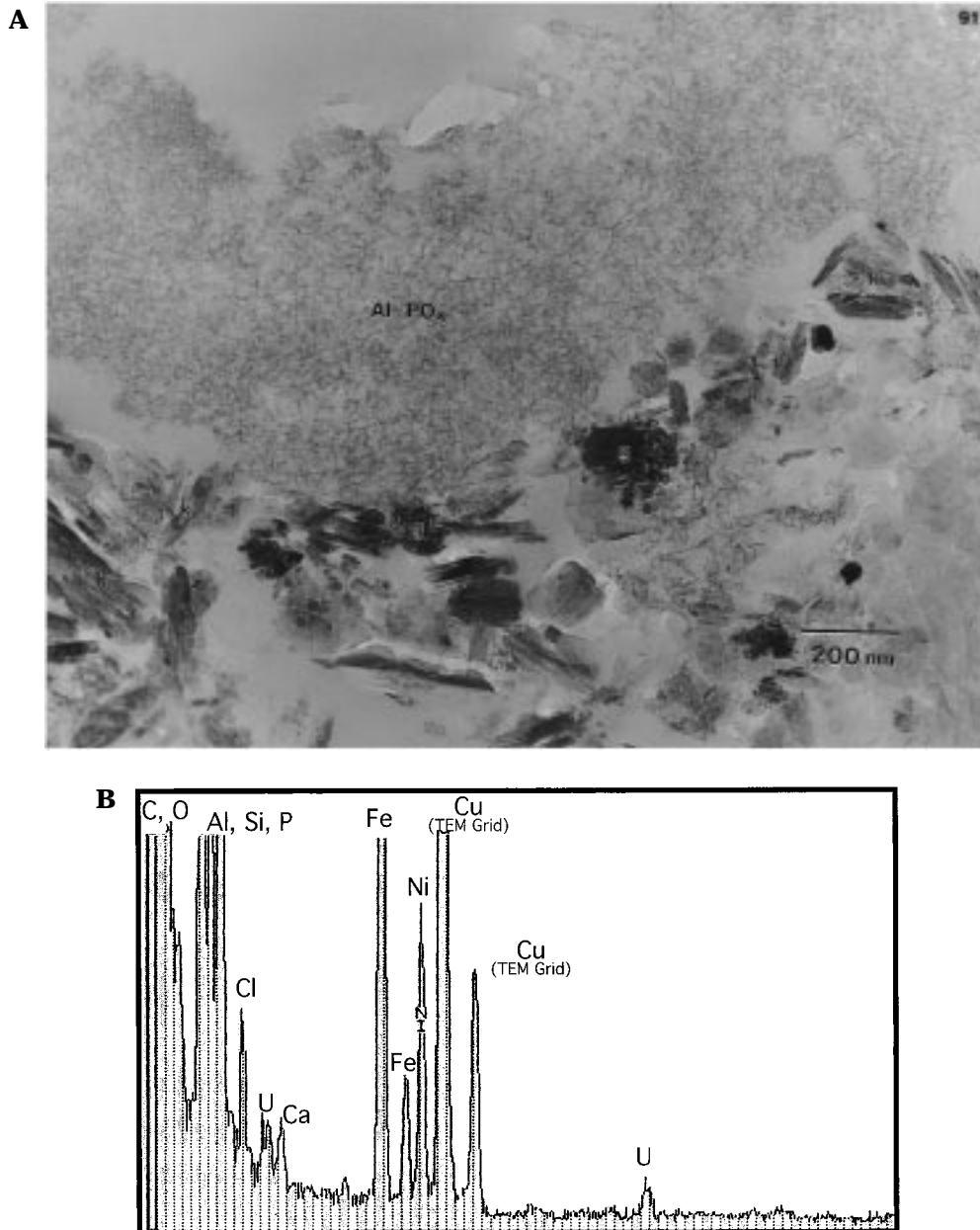
FIGURE 5. TEM micrograph of U bearing Al/Fe phosphate phases in sediment Z1 amended with 5% (w/w) apatite (A), and typical EDXA spectrum of these U-rich phases (B). The letters k and g refer to kaolinite and goethite, respectively.

accounts for 92.6% of U measured using single complete digestion, on average, with a standard deviation of 6.0%. Regardless of apatite treatment, U was primarily associated with the Mn oxide and organic fractions in both sediments, as defined by the sequential extraction procedure (Figure 4A,B). This illustrates the operational nature of such procedures in that Mn oxides represent a minor fraction in these sediments. A greater amount of U than Mn ($\approx 3\times$) was actually released in the "Mn-occluded" extraction, suggesting the dissolution of alternate U-bearing phases.

The high concentration of U in the Mn-occluded fraction makes it difficult to experimentally observe a transfer from the less abundant, more labile fractions, such as water-soluble and exchangeable fractions, to the Mn-occluded fraction based solely on the Mn extraction. However, the redistribution of U is evident from both the exchangeable and acid-soluble fractions which represent a significant portion of the total initial U (10−15%) (Figure 4A,B). For example, clear decreases in exchangeable and acid soluble U are observed with increasing apatite addition, but Mn-occluded U in-

creases only marginally for sediment Z2 and does not appear to increase for Z1. Sediment Z1 has higher exchangeable U in both amended and unamended sediments, suggesting that organic carbon may be responsible for some UO_2^{2+} exchange. In amended sediments, samples originally equilibrated with $CaCl_2$ consistently have significantly more exchangeable U, suggesting that the apatite-related removal of U depends on initial soluble phosphate levels.

The 0.01 M $NH_2OH\cdot HCl$/0.1 M HNO_3 extractant (Mn-occluded fraction) likely solubilizes U phosphates or U associated with other secondary phosphate phases due to its pH (measured extractant pH ≈ 1.26) which is initially lower than the acid-soluble extractant (pH ≈ 2.55). Uranium associated with both amorphous and crystalline Fe oxides decreased marginally, suggesting possible transfer from these phases. For other extractions (organically bound, residual), U data show increased variability, and apatite amendments do not significantly affect U leachability. Sequential extraction data suggest that significant amounts of U are transferred from highly labile phases (water soluble, exchangeable, and

mild acid soluble) to less labile phases. Affected U is presumably being sequestered with phosphate phases and consequently solubilized during Mn oxide extraction, due to the low pH of the extractant.

SEM/TEM. Electron microscopic analysis suggests that U is widely dispersed as sorbed and possibly microcrystalline mineral phases, since discrete U-bearing phases were not identified in untreated sediments using either SEM-EDX or TEM-EDX analysis. This indicates that despite relatively high levels (0.15% to 0.2% by wt), U is relatively homogeneously distributed in this system (e.g., sorbed, microcrystalline), rather than concentrated in distinct, secondary U-rich phases. TEM-EDX analysis showed that U (1–2% by wt) was associated with poorly ordered, secondary Al phosphate or Al/Fe phosphate and goethite (identified by electron diffraction) phases in apatite-amended sediments that were not observed in control samples (Figure 5A,B). In fact, sorption of U and phosphate to crystalline Fe oxides can act as a precursor to eventual precipitation of secondary U phosphates under conditions below the solubility threshold (33) which may account for the negative saturation indices (i.e., undersaturated) with respect to autunite. Detectable levels of U were not observed to be associated with residual apatite grains in amended treatments, suggesting that U precipitation, rather than sorption to apatite or other phosphate phases, is primarily responsible for the removal of U observed during initial equilibration and sequential extractions.

Apatite addition dramatically lowered U solubility in batch experiments to values below the predicted solubility of autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$), a uranyl phosphate mineral thought to control U solubility in phosphate-rich systems. However, U concentrations remained higher for the organic-rich sediment, presumably related to the lower equilibrium pH and U complexation with DOC. Sequential extraction suggests that apatite addition transfers significant amounts of highly labile U to less labile phases with U removal controlled by phosphate levels during batch equilibrations and subsequent extractions. Uranium immobilization appears to be controlled by the precipitation of secondary phosphate phases which can be extracted, however, under acidic conditions that favor phosphate dissolution.

Acknowledgments

Literature Cited

(1) Evans, A. G.; Bauer, L. R.; Haslow, J. S.; Hayes, D. W.; Martin, H. L.; McDowell, W. L.; Pickett, J. B. Westinghouse Savannah River Company, 1992; report no. WSRC-RP-92-315.

(2) Pickett, J. B. Westinghouse Savannah River Company, Aiken, SC, 1990; report no. OPS-RMT-900200.

(3) Bertsch, P. M.; Hunter, D. B.; Sutton, S. R.; Bajt, S.; Rivers, M. L. *Environ. Sci. Technol.* **1994**, *28*, 980–984.

(4) Batson, V. M.S. Thesis Texas A&M University, 1994.

(5) Nriagu, J. O. *Geochim. Cosmochim. Acta* **1974**, *38*, 887–898.

(6) Wright, J. In *Skeletal Biomineralization: Pattern, Processes, and Evolutionary Trends*; Carter, J., Ed.; Van Nortsrand Reinhold: New York, 1990; pp 445–459.

(7) Wright, J.; Schrader, H.; Holser, W. T. *Geochim. Cosmochim. Acta* **1987**, *51*, 631–644.

(8) Ma, Q. Y.; Traina, S. J.; Logan, T. J.; Ryan, J. A. *Environ. Sci. Technol.* **1994**, *28*, 1219–1228.

(9) Ma, Q. Y.; Logan, T. J.; Traina, S. J.; Ryan, J. A. *Environ. Sci. Technol.* **1994**, *28*, 408–418.

(10) Zhang, P.; Ryan, J. A.; Bryndzia, L. T. *Environ. Sci. Technol.* **1997**, *31*, 2673–2678.

(11) Chen, X.; Peurrung, L. M.; Wright, J. V.; Conca, J. L. Proceedings of Spectrum 96 International Conference on Nuclear and Hazardous Waste Management, 1996; pp 1–8.

(12) Ruby, M. V.; Davis, A.; Nicholson, A. *Environ. Sci. Technol.* **1994**, *28*, 646–654.

(13) Ma, Q. Y.; Traina, S. J.; Logan, T. J. *Environ. Sci. Technol.* **1993**, *27*, 1803–1810.

(14) Laperche, V.; Logan, T. J.; Gaddan, P.; Traina, S. J. *Environ. Sci. Techol.* **1997**, *31*, 2745–2753.

(15) Berti, W. R.; Cunningham, S. D. *Environ. Sci. Technol.* **1997**, *31*, 1359–1364.

(16) Sowder, A. G.; Clark, S. B.; Fjeld, R. A. *Radiochim. Acta* **1996**, *74*, 45–49.

(17) Bruno, J.; Sardino, A. *Mater. Res. Soc. Symp. Proc.* **1989**, *127*, 871–878.

(18) Choppin, G. R. *Mater. Res. Soc. Symp. Proc.* **1990**, *176*, 449–456.

(19) Sandino, A.; Bruno, J. *Geochim. Cosmochim. Acta* **1992**, *56*, 4135–4145.

(20) Langmuir, D. *Aqueous Environmental Geochemistry*; Prentice Hall: Upper Saddle River, NJ, 1997.

(21) Li, W. C.; Victor, D. M.; Chakrabarti, C. L. *Anal. Chem.* **1980**, *52*, 520–523.

(22) Langmuir, D. *Geochim. Cosmochim. Acta* **1978**, *42*, 547–569.

(23) Barnes, C. E.; Cochran, J. K. *Geochim. Cosmochim. Acta* **1993**, *57*, 555–569.

(24) Turner, G. D.; Zachara, J. M.; McKinley, J. P.; Smith, S. C. *Geochim. Cosmochim. Acta* **1996**, *60*, 3399–3414.

(25) Batson, V. L.; Bertsch, P. M.; Herbert, B. E. *J. Environ. Qual.* **1996**, *25*, 1129–1137.

(26) Olsen, S. R.; Sommers, L. E. In *Methods of Soil Analysis: Part 2-Chemical and Microbiological Properties*; Page, A. L., Miller, R. H., Keeney, D. R., Eds.; ASA: Madison, WI, 1982; pp 403–430.

(27) Turner, D. R.; Griffin, T.; Dietrich, T. B. *Scientific Basis for Nuclear Waste Management-XVI*; Materials Research Society: Pittsburgh, PA 1993; 783–789.

(28) USEPA. *MINTEQA2/PRODEFA2 Geochemical Code (V. 3.H)*; U.S. Environmental Protection Agency, Environmental Research Laboratory: Athens, GA, 1997.

(29) Miller, W. P.; Martens, D. C.; Zelazny, L. W. *Soil Sci. Soc. Am. J.* **1986**, *50*, 598–601.

(30) Lopez-Hernandez, D.; Siegert, G.; Rodriguez, J. V. *Soil Sci. Soc. Am. J.* **1986**, *50*, 1460–1462.

(31) Violante, A.; Colombo, C.; Buondonno, A. *Soil Sci. Soc. Am. J.* **1991**, *55*, 65–70.

(32) Yuan, T. L. *Soil. Sci. Soc. Am. J.* **1980**, *44*, 951–955.

(33) Sato, T.; Murakami, T.; Yanase, N.; Isobe, H.; Payne, T. E.; Airey, P. L. *Environ. Sci. Technol.* **1997**, *31*, 2854–2858.

(34) Mehra, O. P.; Jackson, M. L. *7th National Conference on Clays and Clay Mineralogy*, 1960; pp 317–327.

(35) Jackson, M. L.; Lin, C. H.; Zelazny, L. W. In *Methods of Soil Analysis: Part 1–Physical and Mineralogical Methods*; Klute, A., Ed.; American Society of Agronomy, Inc.: Madison, WI, 1986; pp 101–150.

(36) Nelson, D. W.; Sommers, L. E. In *Methods of Soil Analysis*; Page, A. L., Miller, R. H., Keeney, D. R., Eds.; American Society of Agronomy: Madison, WI, 1982; Vol. 2. Nelson, D. W.; Sommers, L. E. In *Methods of Soil Analysis*; *Part 2–Chemical and Microbiological Properties*; Page, A. L., Miller, R. H., Keeney, D. R., Eds.; ASA: Madison, WI, 1982; pp 539–579.

(37) Miller, W. P.; Miller, D. M. *Commun. Soil Plant Anal.* **1987**, *18*, 1–15.