

Geochemical coupling of uranium and phosphorous in soils overlying an unmined uranium deposit: Coles Hill, Virginia

James L. Jerden Jr.^{a,*}, A.K. Sinha^b

^a Argonne National Laboratory, Argonne, IL, United States

^b Virginia Polytechnic Institute and State University, Blacksburg, VA, United States

Received 22 April 2005; accepted 27 December 2005

Available online 3 March 2006

Abstract

The mineralogy and geochemistry of soils developed over the unmined Coles Hill uranium deposit (Virginia) were studied to determine how phosphorous influences the speciation of uranium in oxidizing soil/saprolite systems typical of the eastern US. Results from this study have implications for both uranium remediation (e.g. in situ stabilization) and uranium resource exploration (e.g. near-surface geochemical sampling). The primary uranium ore (coffinite and uraninite hosted in quartzo-feldspathic gneiss) weathers to saprolites containing the same uranium concentration as the underlying ore (approximately 1000 mg U/kg saprolites). In these water saturated (below water table) saprolites the uranium is retained as uranyl phosphates of the meta-autunite group (mainly meta-uranocircite). Above the water table the soils overlying the deposit contain approximately 200 mg uranium per kg soil (20 times higher than uranium concentrations in similar soils formed from unmineralized rocks adjacent to the deposit). In these unsaturated zone soils uranium is retained by two processes: (1) incorporation into barium–strontium–calcium aluminum phosphate minerals of the crandallite group (mainly gorceixite), and (2) sorption of uranium with phosphorous onto iron oxides that coat the surfaces of other soil minerals.

Thermodynamic calculations suggest that the meta-autunite group minerals present in the saprolites below the water table are not stable in the unsaturated zone soils overlying the deposit due to the drop in soil pH from ~6.0 down to ~4.5. Mineralogical observations suggest that, once exposed to the unsaturated environment, the meta-autunite group minerals react to form U(VI)-bearing aluminum phosphates and U(VI) surface complexes or nano-precipitates associated with ferric oxides. These results therefore indicate that models predicting U(VI) speciation in phosphate amended soils must simultaneously account for variations in pH, ion activities (aluminum appears to be particularly important) and surface complexation with iron oxide mineral surfaces.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Uranium mobility; Uranium phosphate; Crandallite; Gorceixite; Autunite

1. Introduction

Geochemical and mineralogical associations of uranium and phosphorous in uranium-rich soils have important implications for both remediation and uranium

resource exploration. Studies of both natural analogues and experimental systems have shown that, under certain geochemical conditions, uranium in contaminated soils may be stabilized by reactions with phosphate amendments (e.g. Murray et al., 1983; Arey et al., 1999; Naftz et al., 1999; Bostic et al., 2000; Fuller et al., 2002, 2003). When uranium concentrations are high enough, this in-situ stabilization process involves

* Corresponding author.

E-mail address: Jerden@cmt.anl.gov (J.L. Jerden).

the precipitation of relatively insoluble U(VI) phosphate minerals that may persist over geologic time scales (e.g. hundreds of thousands of years) (Jerden et al., 2003). This technique therefore represents an effective and potentially cost-saving alternative to soil treatment techniques that involve excavation and removal (e.g. Conca et al., 1999). Furthermore, geochemical and mineralogical studies of soils that have formed within and around uranium mineralized regions can reveal important geochemical markers or signatures that may be used in similar geologic settings to locate uranium resources through surficial sampling.

An excellent natural laboratory for studying geologic associations between uranium and phosphorous is the Coles Hill uranium deposit located in the south-central Virginia Piedmont (Fig. 1). This deposit presents a unique site for study because it was extensively characterized (by bedrock coring), but was never mined. We therefore have extensive knowledge of the mineralogy and geochemistry of the primary deposit as well as access to an undisturbed soil profile developed

from the host rocks. This paper focuses on the unsaturated soil horizons formed from the deposit. Based on the bulk geochemical data and mineralogy (discussed below in Section 3.2) the soils studied are classified as ultisols based on the Comprehensive Soil Classification System (Soil Survey Staff, 1975).

The samples that were characterized for this study were extracted from auger holes drilled adjacent to bedrock wells from which we have continuous core down to approximately 300 m below the surface. In the study area the deposit extends from the top of the bedrock zone (base of the weathering profile) down to depths ranging from 200 to 300 m below the surface. The overlying weathering zone varies from 25 m thick under topographic highs to 10 m thick below surrounding low lying pastures. The weathering zone contains the water table, which also varies in depth as a function of topography. A generalized geologic map showing the deposit and locations of auger holes is shown in Fig. 1.

The Coles Hill deposit is a coffinite/uraninite orebody hosted in quartzo-feldspathic gneiss (Jerden

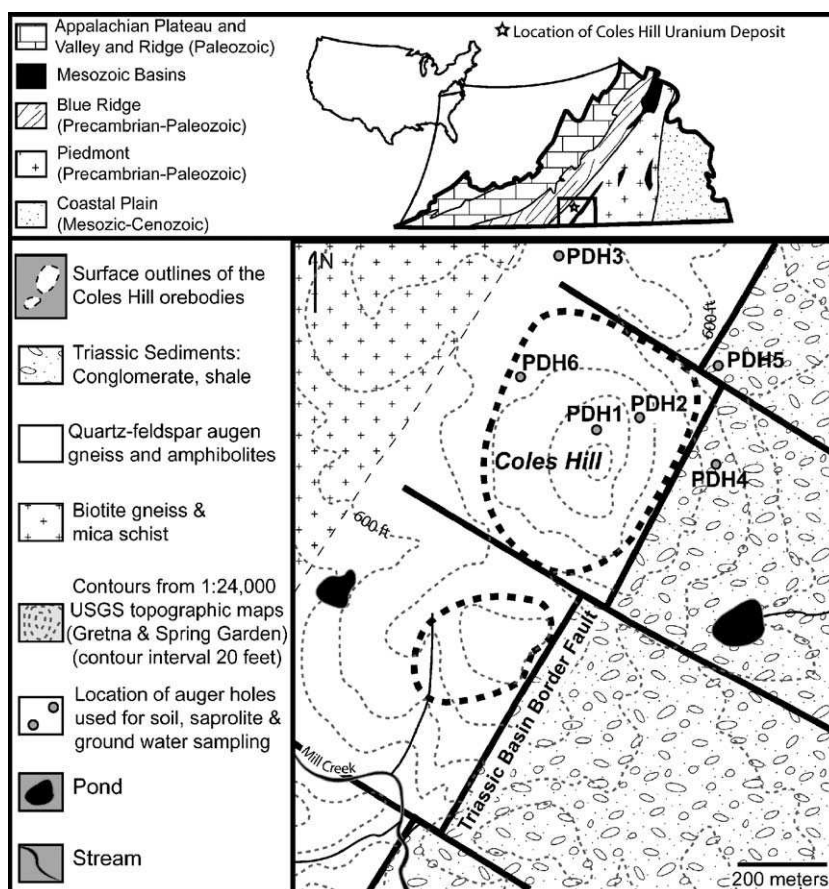


Fig. 1. Location of the Coles Hill Uranium Deposit and drill holes from which soil samples have been extracted (adapted from Jerden et al., 2003).

and Sinha, 2003). The primary coffinite/uraninite ore zones are also enriched in apatite, which can exceed 25 vol.% in some mineralized veins. Studies of the chemical weathering of the Coles Hill deposit by Jerden and Sinha (2003) and Jerden et al. (2003) showed that C-horizon saprolites that formed from the deposit contain as much uranium as the primary ore (800–1400 mg U/kg soil). This indicates that uranium was not leached from the lower (groundwater saturated) portion of the weathering zone during oxidation and weathering of the primary ore. Studies of the geochemistry and mineralogy of the Coles Hill saprolites (Jerden et al., 2003) showed that uranium was naturally immobilized during oxidation and weathering by the precipitation of sparingly soluble U(VI) phosphate minerals of the meta-autunite group. However, the meta-autunite mineral assemblages were found only in samples from below the water table.

Uranium concentrations in soil samples from above the water table are approximately 600 mg/kg lower than those from the saturated zone (Jerden et al., 2003). However, as shown in the present study, the uranium content of these unsaturated (pedogenic) horizons is still approximately 20 times higher than concentrations measured in corresponding horizons off the deposit. The processes by which uranium is retained in these near-surface horizons is not well understood, but has important implications for understanding the long-term speciation of uranium at the geosphere–biosphere interface. The purpose of the present paper is to elucidate these processes by presenting new results from geochemical and mineralogical studies of the unsaturated portion of the Coles Hill weathered zone.

2. Materials and methods

Bulk soil samples from the area overlying the Coles Hill uranium deposit, and control samples from off the deposit were obtained by auger drilling. Approximately 1 kg soil was extracted from each sample interval. All samples were dried immediately after collection within a laminar flow, clean air (+100) environment. Intact (i.e., coherent) soil fragments that retain soil structures and mineral reaction textures from each sample interval were vacuum impregnated with epoxy and polished for characterization and analyses by scanning electron microscopy (SEM), energy dispersive X-ray analyses (EDS) and electron microprobe microanalyses (EMP). The remainder of each sample were well mixed and divided into three subsamples. One subsample was pulverized using a tungsten carbide shatter box and digested for ICP-MS analyses. The ICP-MS analyses

were performed by an accredited commercial analytical chemistry laboratory.

Another subsample was disaggregated to grain-size using mortar–pestle and mineralogically fractionated using a heavy liquid density separation technique. This separation procedure involved mixing the granular samples with bromoform (CHBr_3) (specific gravity 8.9) in a separatory funnel and collecting the dense mineral fraction. These dense separates were dominated by phases with specific gravities >2.9 ; however, the separation technique was not quantitative as evidenced by minor quartz and kaolinite in the heavy mineral fraction. The mineral fractions were analyzed by powder X-ray diffraction (XRD).

Operating conditions for EMP analyses were: 15 kV acceleration voltage, 20 nA beam current. For EMP imaging the beam current was increased to 50 nA. All SEM, EDS and EMP analyses were performed at the Virginia Tech, Department of Geological Sciences, electron microbeam facilities using a CAM-ScanII electron microscope and Cameca SX-50 electron microprobe. For the XRD analyses samples were ground under ethanol and transferred to a “zero-background” sample holder (single crystal oriented silicon). Diffraction patterns were obtained using Ni-filtered, Cu K-alpha radiation (30 kV, 15 mA).

The pH of each soil sample was measured using the method of Hendershot et al. (1993). Ten grams of dried soil (room temperature) was placed in a beaker, 20 mL of distilled water was added and stirred for 30 min. The mixture was allowed to stand for 1 h prior to measuring the pH of the supernatant with a standard pH probe. Replicates of each sample were within ± 0.1 pH unit.

3. Results and discussion

3.1. Bulk geochemistry

Concentrations of key elements in soil samples from auger holes PDH1 and PDH2 were used to elucidate the processes that control the distributions of uranium and phosphorous in the Coles Hill weathered zone. The measured concentrations of key elements were corrected for changes in the bulk mass (volume change) caused by chemical weathering of primary minerals and leaching soluble ions such as Ca^{2+} , Na^+ , $\text{SiO}_2(\text{aq})$ from the pedogenic profile. The raw (uncorrected) data for auger holes PDH1, PDH2 and the control profile PDH3 are shown in the Appendix. The correction was done by assuming that the element titanium is conserved during the weathering process (i.e., is not leached by infiltrating

fluids). This type of normalization has been used in a number of other studies of soil profiles (e.g. Goldich, 1938; Krauskopf, 1967; Nesbitt and Wilson, 1992; Langmuir, 1997; Nesbitt and Markovics, 1992) and is justified in the present case due to the persistence of primary titanium minerals from lower parts of the profile in the upper horizons. These corrected concentration profiles are shown in Fig. 2.

The normalization was done by multiplying the concentration of uranium and other key elements in the weathered sample by the normalizing ratio: $C_{\text{Sap}}/C_{\text{Ped}}$, where C_{Sap} is the concentration (g/g) of titanium in the saprolite sample from which the pedogenic horizons formed and C_{Ped} is the concentration (g/g) of titanium in the pedogenic horizons under investigation. The saprolite samples (i.e., protoliths or starting material) used for the normalization are from 18.3 m depth (from ground surface) in auger hole PDH1 and 5.5 m depth in PDH2. The raw chemical data used for the normalization are presented in the Appendix. The variation in depth to the protoliths reflects variations in the thickness of the weathered zone in the study area. The primary evidence that the samples chosen for normalization represent protoliths for the pedogenic samples is that they share the same type of textural and compositional anisotropy (i.e., relict foliation and mineral layering).

The gradient in uranium concentrations within the profiles PDH1 and PDH2 has been established by hundreds of thousands of years of leaching and chemical weathering of the underlying uranium source (the Coles Hill uranium deposit). The age of the column was estimated using a weathering rate of 20 m per million years. This rate is from the work of Pavich et al. (1985) and Pavich (1986, 1989) and represents the maximum rate of saprolite (weathered rock) production for weathering zones in the physiographic region of interest. Using this weathering rate we estimate that the Coles Hill soil column is approximately 900,000 years old (give the average thickness of 18 m). Based on its advanced age, this soil system is interpreted to have reached a steady state with respect to its uranium retardation capacity. Results from this site can therefore yield important insights into the long-term behavior of uranium in well-developed soil profiles.

Uranium concentrations in profiles PDH1 and PDH2 can be divided into three zones (Fig. 2A and B, respectively): (1) near surface (<0.5 m depth) where the concentration is <100 mg/kg, (2) unsaturated zone where (0.5–10 m in PDH1 and 1–3.5 m in PDH2) uranium concentrations vary from 127 to 338 mg/kg (generally increases with depth), (3) top portion of the

zone of water table fluctuation (>10 m depth in PDH1 and >3.5 m depth in PDH2) where uranium concentrations increase abruptly to >700 mg/kg. Uranium concentrations in the near-by auger hole PDH3, from off the deposit, are all less than 13 mg/kg (Appendix).

Another important pattern recorded in the bulk chemical data is the existence of a zone of relatively low soil pH (<5.0) extending from 1.0 to 5.0 m depth in PDH1 and from 0.5 to 3.3 m depth in PDH2. These low pH zones corresponds to intervals depleted in calcium, sodium and silica.

The upper part of the PDH1 profile is enriched in phosphorous, strontium, barium, and cerium. The two samples most highly enriched in these elements (samples from 0.6 and 2.1 m depth) are also enriched in uranium (relative to surrounding samples). As discussed in the next section, these enrichments are caused by a relatively high volume percent of aluminum phosphate minerals that formed during chemical weathering of primary and secondary phosphate minerals. In profile PDH2 there is a dramatic enrichment in phosphorous, calcium, strontium, barium and cerium at 3.4 m depth. This enrichment is also associated with a relatively high volume percent of aluminum phosphate minerals. The influence of agricultural lime amendments is evident in PDH1 (Fig. 2A) where the pH profile shows an abrupt decrease in soil acidity in the upper 0.6 m.

3.2. Mineralogy of uranium stabilization

X-ray diffraction and thermal gravimetric analyses were used to determine the dominant soil minerals in these unsaturated horizons (Jerden, 2001). The most abundant mineral in all samples is kaolinite, however its abundance decreases in shallower samples in which gibbsite is present. The shallowest soils (<0.5 m below surface) contain up to 5% gibbsite, 60% kaolinite and an abundance of relict quartz grains concentrated at the within the upper 10 cm. Soils from 0.5 to 5 m depth are dominantly kaolinite (~80%) and montmorillonite (~20%) with minor (<1%) gibbsite, vermiculite and quartz. Soils from 5 down to 10 m depth (near water table) are also dominantly kaolinite (~70%), but also contain abundant rock fragments of partially weathered quartz-feldspar gneiss. Nearly all soil minerals are coated with a 0.5–5 μm thick multi-granular armoring of iron oxides. The dominant iron oxides present in these mineral coatings are goethite and hydrous ferric oxide (ferrihydrite). The goethite was identified by its optical characteristics and morphology (e.g. presence of pleochroic acicular crystals) and by X-ray diffraction peaks. The ferrihydrite was distinguished from the

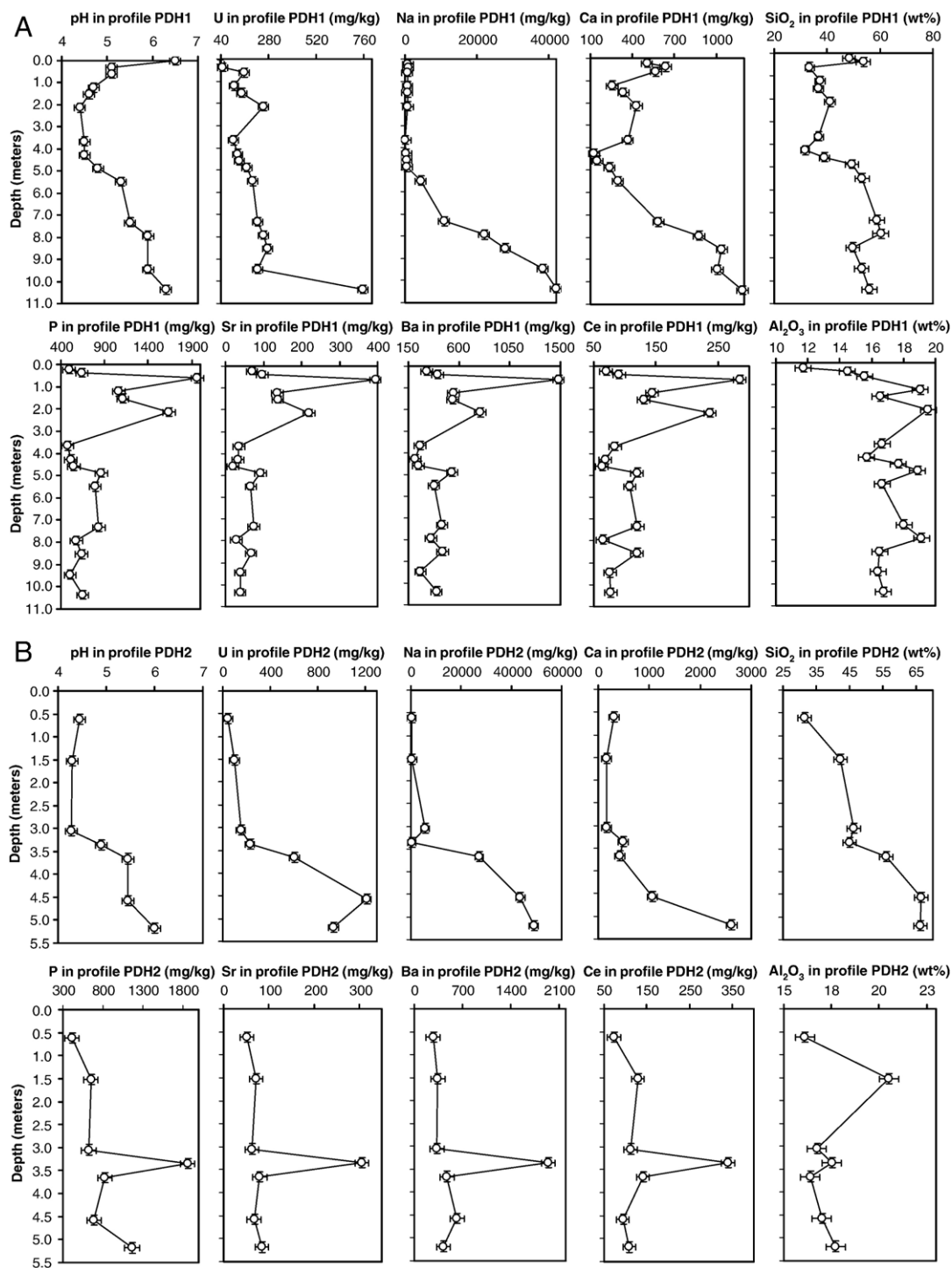


Fig. 2. (A) Soil pH and bulk soil chemistry depth profiles for key elements in the Coles Hill unsaturated zone. These data are for auger hole PDH1. (B) Soil pH and bulk soil chemistry depth profiles for key elements in the Coles Hill unsaturated zone. These data are for auger hole PDH2.

goethite by its colloidal (sub-micrometer) grain size, color (goethite is yellow, ferrihydrite is black to dark red) and amorphous nature (broad X-ray diffraction peaks).

Based on SEM characterization, Jerden et al. (2003) suggest that uranium retention within the unsaturated zone is due to the incorporation of uranium into an aluminum phosphate mineral and surface complexation

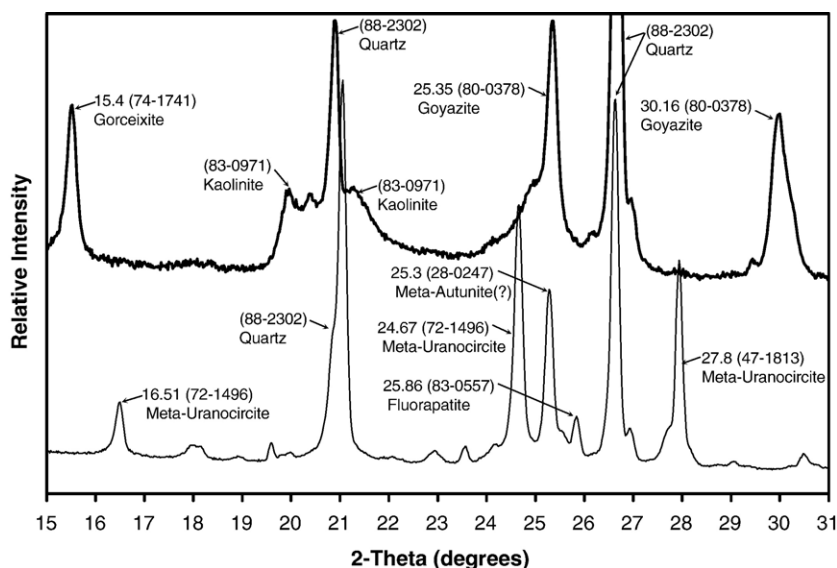


Fig. 3. Powder X-ray diffraction patterns for samples from the Coles Hill unsaturated zone (top scan) and underlying saturated zone (bottom scan). The samples are from the same profile (top: PDH1, 1.5 meters depth, bottom: PDH1, 16.8 m depth) and are representative of other XRD patterns. The 2-Theta range shown was chosen to clearly demonstrate the presence of crandallite group peaks and the lack of meta-autunite group peaks in the unsaturated soil sample.

with iron oxide and oxy-hydroxide mineral coatings. These uranium uptake processes are confirmed and quantified in the current study using XRD and EMP analyses.

Microscopic characterization of all representative samples from the unsaturated sample profiles (PDH1 and PDH2) indicate that the main sink for uranium in these samples are the aluminum phosphate minerals, which range in size from 20 to 300 μm in diameter.

Fig. 3 shows a typical XRD scan from a heavy mineral separate from the pedogenic soil profile (PDH1, 1.5 m depth) and one from the saturated zone for

comparison (PDH1, 16.8 m depth). These results indicate that the unsaturated zone contains abundant strontium, and barium bearing aluminum phosphates of the crandallite group. The XRD scan shows strong peaks for the minerals goyazite ($\text{SrAl}_3(\text{PO}_4)_2(\text{OH})_6\cdot\text{H}$), and gorceixite ($\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_6\cdot\text{H}$). However, EMP results (discussed below) suggest that these peaks may be from the same mineral, which is a compositional solid solution of goyazite and gorceixite (closer to the gorceixite end member).

The phosphate mineralogy of the pedogenic soil samples are distinct from samples from the saturated

Table 1

Electron microprobe analyses (concentrations in wt.%) of crandallite group minerals with inclusions of manganese oxide, quartz and kaolinite

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Al_2O_3	31.21	31.18	31.14	30.83	30.59	30.54	30.41	30.19	27.93	29.19	30.3 (± 1.0)
P_2O_5	22.85	26.51	26.11	26.01	25.95	26.47	25.65	25.90	23.27	16.62	24.5 (± 3.1)
MnO	<0.10	<0.10	<0.10	0.11	0.37	<0.10	<0.10	0.36	2.21	<0.10	0.8 (± 1.0)
SiO_2	9.83	5.12	5.83	5.38	5.10	5.18	5.15	5.31	3.86	16.61	6.7 (± 3.8)
CaO	2.12	2.30	2.33	2.26	2.26	2.37	2.23	2.32	2.30	1.57	2.2 (± 2.0)
Fe_2O_3	0.88	0.96	1.00	0.84	0.95	1.04	1.01	0.85	0.97	1.28	1.0 (± 0.1)
SrO	3.25	2.49	2.37	2.54	2.25	2.56	2.51	2.36	2.97	2.52	2.6 (± 0.3)
BaO	12.18	15.85	15.41	15.07	16.00	15.93	15.72	15.33	13.31	8.05	14.3 (± 2.5)
UO_3	1.03	1.36	1.29	1.32	1.34	1.23	1.19	1.25	1.08	0.72	1.2 (± 0.2)
Total	83.33	85.76	85.48	84.37	84.81	85.32	83.87	83.86	77.89	76.54	83.1

PbO , K_2O are below detection limit of 0.1 wt.%. Totals do not equal 100% due to H_2O in mineral structure (gorceixite may contain up to 15.0 wt.% H_2O). SiO_2 values and high Al_2O_3 values are from quartz and kaolinite contamination of analyses. (1)–(4) are from DH1, 0.6 m depth; (5)–(10) are from DH1, 2.1 m depth. Relative standard deviations of raw data (calculated from counting statistics) are 5% or less. Data in column 11 are the average compositions and associated standard deviations ($n=10$) for analyses (1)–(10).

zone such as the typical sample from PDH1 (16.8 m depth) shown in Fig. 3. Saturated zone samples contain abundant uranyl phosphates of the meta-autunite group including meta-uranocircite $[\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2(\text{H}_2\text{O})_7]$ and meta-autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2(\text{H}_2\text{O})_6]$. The discontinuity in phosphate mineralogy within the study area indicates that meta-autunite group minerals are not stable in the unsaturated zone of this type of soil profile.

The mineral compositions of phosphates from the unsaturated zone were characterized by EMP to determine the amount of uranium associated with these minerals (Table 1). Uranium rich iron oxide mineral coatings in the unsaturated zone (identified by SEM-EDS) were also characterized by EMP analyses to determine uranium content (Table 2). The crandallite group mineral grains analyzed by EMP are from different depths with in PDH1 (Table 1). This mineral is thus identified as strontium–calcium–uranium-bearing gorceixite. Silica, iron and manganese are also recorded in these analyses due to the presence of quartz and manganese/iron oxides that are intermixed with the gorceixite.

The gorceixite analyses (EMP spots) with the highest uranium concentrations (1.2–1.4 wt.% as UO_3) have Al_2O_3 and P_2O_5 contents that most closely approach those of an ideal gorceixite formula (29.9 and 27.7 wt. %, respectively) (Fig. 4). These uranium concentrations are thus interpreted as representative of the gorceixite-type (i.e., Sr, Ca, U bearing) phase present in these soils. The uranium concentrations for spot analyses with lower than ideal Al_2O_3 and P_2O_5 concentrations are lower than the representative values of 1.2–1.4 wt.% (reported as UO_3) due to “contamination” of the analyses by other soil minerals (e.g. iron and manganese oxides and kaolinite). These results indicate that the aluminum phosphate gorceixite plays an important role

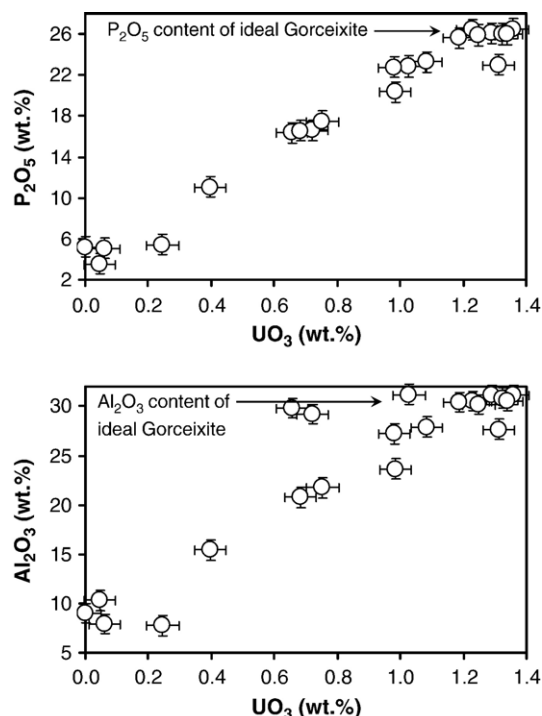


Fig. 4. Electron microprobe data for uranium-bearing gorceixite from the Coles Hill unsaturated zone. Note that the highest UO_3 concentrations are found in the purest gorceixite. Error bars reflect X-ray counting statistics.

in the retention of uranium within the unsaturated soils over the Coles Hill deposit.

The observation of uranium being sequestered by an aluminum phosphate mineral is consistent with the results of Arey et al. (1999). Their experiments, which involved batch reactions of hydroxyapatite with uranium-rich sediments, showed that apatite amendment leads to the re-speciation of uranium from a labile form

Table 2

Electron microprobe analyses (concentrations in wt.%) of manganese-rich inclusions within crandallite group minerals

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Al_2O_3	27.67	27.20	23.66	21.75	20.78	15.41	10.30	8.99	7.90	7.75
P_2O_5	22.99	22.76	20.35	17.49	16.58	11.04	3.58	5.18	5.08	5.45
MnO	2.80	4.24	9.06	12.74	11.84	20.04	29.48	25.20	19.90	24.42
SiO_2	3.49	3.36	3.29	3.47	2.36	1.76	0.97	1.11	38.94	1.07
PbO	<0.10	<0.10	<0.10	<0.10	0.14	0.21	0.13	0.19	<0.10	0.13
CaO	2.30	1.86	1.95	1.59	1.31	0.95	0.33	0.48	0.59	0.51
Fe_2O_3	1.25	1.60	2.22	3.31	3.51	4.30	4.18	6.44	4.70	5.49
SrO	2.94	2.65	2.75	2.28	1.62	1.14	0.31	0.54	0.16	0.48
BaO	13.85	13.03	12.75	11.64	11.60	10.31	6.52	8.72	6.88	8.21
UO_3	1.31	0.98	0.98	0.75	0.68	0.40	<0.10	<0.10	<0.10	0.25
Total	78.59	77.68	77.01	75.01	70.41	65.55	55.80	56.85	84.15	53.75

K_2O was below detection limit of 0.1 wt.%. (1)–(8) are from PDH1, 0.6 m depth; (9) and (10) are from PDH1, 2.1 m depth. Relative standard deviations of raw data (calculated from counting statistics) are 5% or less.

(i.e., readily extractable) to a residual form (i.e., associated with an aluminum/iron phosphate). Our field study results suggest a similar process and thus underscore the potential importance of aluminum phosphates in uranium speciation in relatively low pH (4–6) soil/sediment environments.

The analyses of manganese-rich inclusions that occur within the uranium bearing gorceixite grains are shown in Table 2. Average compositions for these analyses are not given because of the significant variation. This compositional variation is caused by the fine-scale (sub-micrometer) mineralogical heterogeneity of these phases. The MnO content of these inclusions vary from 2.8 to 29.5 wt.% depending on how much gorceixite (or other surrounding soil minerals) was also present in the microprobe interaction volume. The uranium content (as UO_3) of inclusions containing >10.0 wt.% MnO varies from below detection (<0.1 wt.%) to 0.75 wt.%. This indicates that, for this mineral assemblage, uranium is more strongly partitioned into the aluminum phosphate gorceixite relative to the intermixed manganese oxides.

Table 3 shows electron microprobe analyses of iron oxide minerals that form coatings on other minerals in the soil. Both uranium and phosphorous are present in these iron oxide coatings in significant amounts (up to 7.5 wt.% UO_3 and 7.7 wt.% P_2O_5); however, their concentrations vary spatially. Despite the spatial variations there is a general positive correlation between uranium and phosphorous. The EMP and SEM characterization of these samples can not distinguish whether the uranium and phosphorous associated with these iron coatings are present as surface complexes or surface precipitates, but in either case this association appears to have played an important role in retaining uranium within this zone for hundreds of thousands of years.

Sato et al. (1997) found that the long-term retention of uranium in the iron oxide rich soils overlying the Koongarra uranium deposit in Australia involved an initial adsorption stage (i.e., uranium surface complexation with iron oxides) followed by a precipitation stage (i.e., the formation of uranyl phosphate minerals). Our results suggest a similar process involving the uptake of uranium on iron oxides and the precipitation of thermodynamically stable uranium bearing phosphate minerals (crandallite group). Our results therefore, reiterate the importance of both mineral precipitation and surface complexation in the long-term retardation of uranium in iron oxide rich soils.

3.3. Activity and reaction path modeling

The mineralogical observations described above allow us to model the solid and aqueous phase speciation of key elements in the Coles Hill unsaturated zone. We have taken an equilibrium thermodynamic approach to this problem using the software “Geochemist’s Workbench” (Bethke, 1998). Although the system we are studying does not maintain chemical equilibrium, and kinetic effects are not accounted for (e.g. microbial activity), we deem this modeling approach instructive because it allows us to quantify the thermodynamic driving forces influencing the system. That is, it indicates the directions of key reactions through Gibbs free energy minimization and allows us to predict how the system would respond (e.g. mineral dissolution/precipitation) to changes in chemical conditions.

Key assumptions for the modeling are as follows: the activities of aluminum and iron are set by gibbsite and ferrihydrite. Gibbsite is chosen as it appears to be the most stable aluminum phase in the most highly weathered samples. Although ferrihydrite is probably

Table 3

Electron microprobe analyses (concentrations in wt.%) of uranium and phosphorous rich iron oxides that coat other soil minerals (mainly kaolinite and quartz)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Al_2O_3	4.77	4.50	2.90	6.73	4.21	4.22	6.53	12.59	18.44	14.19
P_2O_5	6.07	7.69	4.20	5.74	5.00	4.79	4.60	2.12	0.55	0.33
K_2O	<0.10	<0.10	<0.10	0.11	<0.10	<0.10	0.11	0.27	0.27	0.18
SiO_2	20.47	10.24	33.02	16.33	10.54	13.17	16.26	32.78	34.36	22.38
CaO	0.42	0.41	0.38	0.32	0.25	0.29	0.27	0.25	0.24	0.04
Fe_2O_3	31.88	42.31	26.52	36.10	43.75	35.88	35.56	29.49	10.91	4.89
UO_3	7.55	6.22	5.44	3.26	2.56	2.47	2.37	0.32	<0.10	<0.10
Total	71.15	71.36	72.45	68.58	66.31	60.82	65.70	77.82	64.77	42.00

SrO , BaO , PbO are below detection limit of 0.10 wt.%. Totals do not equal 100% due to H_2O in mineral structure. All analyses are from auger hole PDH1, 2.1 m depth. Relative standard deviations of raw data (calculated from counting statistics) are 5% or less.

not the most stable iron mineral, it was chosen to control the iron activity because it has the highest reactive surface area of the iron minerals present and thus likely dominates surface complexation reactions. The concentrations of calcium and sodium are set by assuming concentrations of 1×10^{-3} M. This assumption, which was also used by Lindsay et al. (1989) in their assessment of phosphate speciation in soils, is based on the indication that these elements are being leached from the soil profile (i.e., their activities are not solubility controlled). The activities of phosphorous, barium and uranium are controlled by mineral precipitation and surface complexation. To test the model sensitivity to lower sodium and calcium concentrations we also ran the model using a 10^{-4} M concentration for these elements. The results of this alternative model run were found to have no effect on uranium speciation and are therefore not discussed in detail.

The thermodynamic data used for our modeling was as follows: the equilibrium constant for gorceixite was calculated from the standard free-energy of formation data of Schwab et al. (1989, 1993). This calculation results in a standard free energy value of -5628.7 kJ/mol for gorceixite. This standard free energy yields a $\log K$ (solubility product) of -0.693 for the reaction: $\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_6 \cdot \text{H} + 7\text{H}^+ = 3\text{Al}^{3+} + 2\text{HPO}_4^{2-} + \text{Ba}^{2+} + 6\text{H}_2\text{O}$. The solubility data for the barium uranium phosphate meta-uranocircite is from Vochten et al. (1992). These data yield a $\log K$ of -27.088 for the reaction $\text{Ba}[(\text{UO}_2)(\text{PO}_4)_2]_2 \cdot 6(\text{H}_2\text{O}) + 2\text{H}^+ = \text{Ba}^{2+} + 2(\text{UO}_2)^{2+} + 2(\text{HPO}_4)^{2-} + 6(\text{H}_2\text{O})$. The solubility data used for gibbsite and verisizite are from Vieillard et al. (1979), the data for hydroxyapatite, goethite and strengite are from Robie et al. (1979), and the data for ferrihydrite are from Wagman et al. (1982). The thermodynamic data for auxiliary species (including uranium) are from the Nuclear Energy Agency data bank (Grenthe et al., 1992; Guillaumont et al., 2003).

All thermodynamic calculations were performed using the software package “Geochemist’s Workbench” (Bethke, 1998) employing an extended form of the Debye-Huckel equation (the “B-dot” equation) for the calculation of activity coefficients (Helgeson, 1969). Surface complexation reactions were modeled using a double layer theory (diffuse layer theory) approach employed by “Geochemist’s Workbench” (Bethke, 1996, 1998). We used the surface complexation data base of Dzombak and Morel (1990) which assumes a surface area of $600 \text{ m}^2/\text{g}$ for the surface reactive species (ferrihydrite) and site densities of 0.005 and 0.200 mol of surface sites per mole of ferrihydrite for the strongly and weakly binding

surface sites, respectively ($\equiv(\text{s})\text{FeOH}$ and $\equiv(\text{w})\text{FeOH}$). The use of ferrihydrite for the surface reactive species is justified by the observation that it has the highest reactive surface area of any mineral in these soils (due to its pervasiveness in mineral coatings and colloidal grain size).

Activity diagrams plotting phosphate activity as a function of pH for the system P–Al–Ca–Ba–Fe are shown in Fig. 5. For this plot the activities of both calcium and barium are set at 1×10^{-3} and aluminum and iron concentrations controlled by gibbsite and goethite, respectively. This calculation predicts that gorceixite is the most stable phase from pH 4.0 to 6.8. Above this pH range hydroxyapatite becomes most stable. If a more soluble mineral is used to control the iron activity (e.g. amorphous hydrous ferric oxide) the low pH portion (pH 4–5.3) of the gorceixite field is replaced by the iron phosphate strengite (Fig. 5b). The plot showing the gorceixite field extending to lower pH (Fig. 5a) is more consistent with mineralogical observations from the Coles Hill soil samples. The speciation of uranium in the P–Al–Ca–Ba system was studied by reaction path modeling.

The reaction models shown in Figs. 6 and 7 were calculated by assuming controls on the concentrations of key elements and varying the pH from 4 to 7. The model accounts for activity coefficients, mineral precipitation, dissolution of atmospheric gasses and aqueous speciation. Fig. 6 shows the solid and aqueous phase speciation of uranium and phosphorous in the P–Al–Ca–Ba–Fe–U system when no surface reactive minerals (e.g. no iron oxide surface complexes) are present. Fig. 7 shows how the model results change when surface

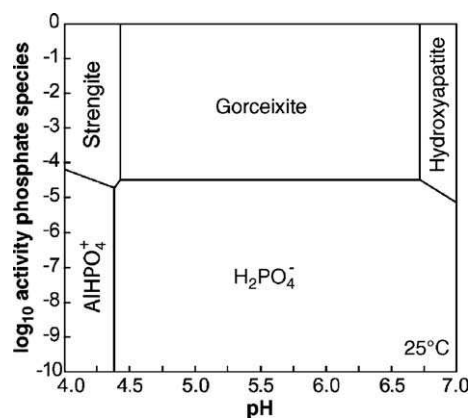


Fig. 5. Activity diagrams for the P–Al–Ca–Ba–Fe system assuming that $\text{O}_2(\text{g})$ and $\text{CO}_2(\text{g})$ fugacities are 0.2 and 0.01, respectively, Ca^{2+} and Ba^{2+} activities = 10^{-3} and Al^{3+} and Fe^{3+} are controlled by gibbsite and ferrihydrite, respectively.

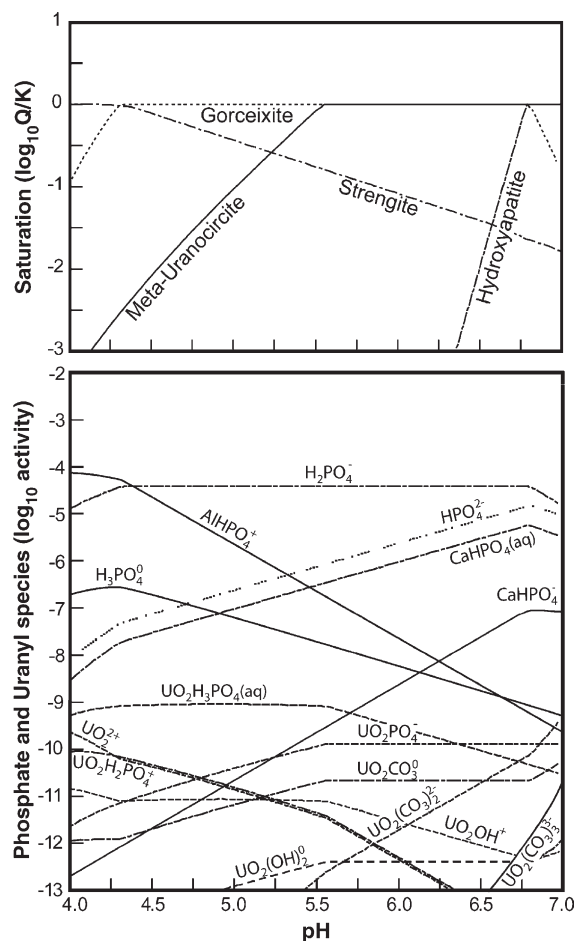


Fig. 6. Speciation plots for the P–Al–Ca–Ba–Fe–U system assuming that $O_2(g)$ and $CO_2(g)$ fugacities are 0.2 and 0.01, respectively, Ca^{2+} and Ba^{2+} activities = 10^{-3} and Al^{3+} and Fe^{3+} are controlled by gibbsite and ferrihydrite, respectively. The top diagram shows saturation indices ($\log Q/K$) as a function of pH (Q =the reaction quotient and K =the equilibrium constant). The lower plot shows the corresponding aqueous speciation of phosphorous and uranium.

complexation is accounted for. That is, for the model shown in Fig. 7, ferrihydrite is present as a surface reactive phase that adsorbs both phosphate and uranium species. The model inputs are as follows: aluminum and iron concentrations were set by gibbsite and ferrihydrite, oxygen fugacity was fixed at 0.2, $CO_2(g)$ fugacity was fixed at 0.01 (assumed higher than atmospheric due to $CO_2(g)$ production in soils e.g. Langmuir, 1997), barium and calcium set at 1×10^{-3} m, total uranyl set at 1×10^{-9} m and total phosphate set as 1×10^{-4} m.

The model that does not include surface complexation on ferrihydrite (Fig. 6) predicts a solution saturated with respect to meta-uranocircite from pH > 7 down to 5.5. Below pH 5.5 gorceixite becomes the dominant barium phase. For our model system the dominant

aqueous phosphate species at high pH (~ 6.5) are $H_2PO_4^-$, HPO_4^{2-} and $CaHPO_4(aq)$ and at low pH (~ 4.0) are $AlHPO_4^+$ and $H_2PO_4^0$. Uranium speciation at high pH (~ 6.5) is dominated by $UO_2(CO_3)_2^{2-}$, $UO_2PO_4^-$, $UO_2CO_3^0$, $UO_2HPO_4^0$ and at lower pH (~ 4.0) by $UO_2HPO_4^0$, UO_2^{2+} , $UO_2H_2PO_4^+$.

Our uranium and phosphate speciation calculations agree with the results of Sandino and Bruno (1992) showing that phosphate complexation of uranium is more important than carbonate complexation when the

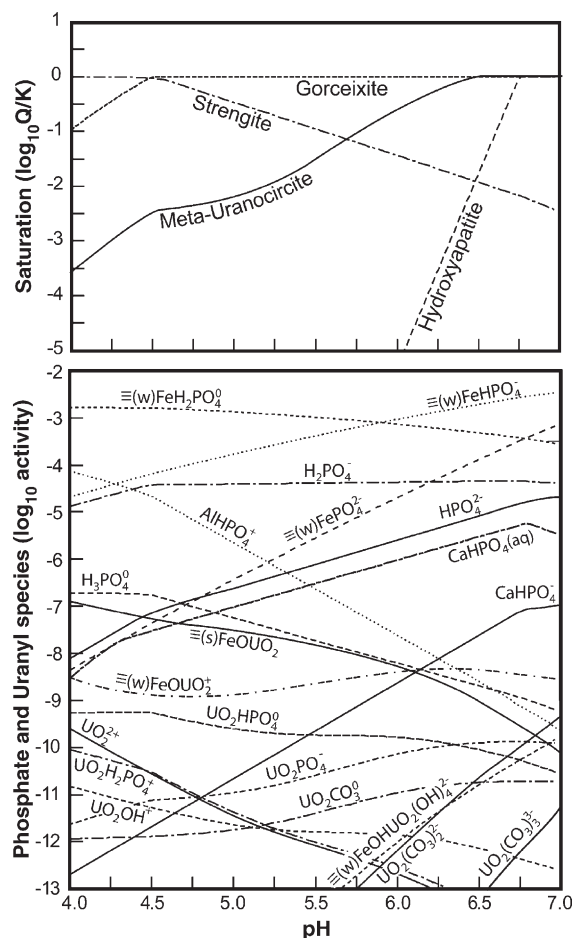


Fig. 7. Speciation plots for the P–Al–Ca–Ba–Fe–U system in which ferrihydrite is included as a surface reactive species (i.e. is available for surface complexation). The model assumes 1 g ferrihydrite/L of solution, a ferrihydrite surface area of 600 m²/g and site densities of 0.005 and 0.200 mol surface site per mol ferrihydrite for strong and weak binding sites, respectively. The model also assumes that the $O_2(g)$ and $CO_2(g)$ fugacities are 0.2 and 0.01, respectively, Ca^{2+} and Ba^{2+} activities = 10^{-3} and Al^{3+} and Fe^{3+} are controlled by gibbsite and ferrihydrite, respectively. The top plot shows saturation indices ($\log Q/K$) as a function of pH (Q =the reaction quotient and K =the equilibrium constant). The lower plot shows the corresponding aqueous speciation of phosphorous (include surface complexes) and uranium (include surface complexes).

ratio of phosphate_(total)/carbonate_(total) exceeds ~ 1.0 . This observation is also supported by the field results of Yanase et al., 1995 who found that the most significant uranium mobilization in the weathered zone overlying the Koongara uranium deposit in Australia occurred where groundwaters contained relatively low concentrations of phosphate (e.g. 0.1 mg/L) relative to bicarbonate (e.g. 180 mg/L).

When ferrihydrite is present as a surface reactive phase (Fig. 7) the pH stability field of meta-uranocircite is compressed to a range of >7 –6.5. This is caused by the lowering of the activities of aqueous uranyl species due to uranium uptake onto the ferrihydrite sorbent. Thus, this model predicts that gorceixite is the dominant barium mineral over the pH range 6.5 down to 4.5. This prediction is consistent with the mineralogical observation that, as the soil pH drops below 6.5, meta-uranocircite is unstable and gorceixite and ferrihydrite mineral coatings become the dominant uranium sinks.

For the surface complexation model the ferrihydrite surface charge of varies from $2.1 \mu\text{C}/\text{cm}^2$ at pH 4.0 to $-0.5 \mu\text{C}/\text{cm}^2$ at pH 7.0 with a charge of zero $\mu\text{C}/\text{cm}^2$ at around pH 6.0. The dominant phosphate species predicted when the ferrihydrite sorbent is present are $\equiv(\text{w})\text{FeHPO}_4^- \equiv (\text{w})\text{FePO}_4^{2-}$ at high pH (~ 6.5) and $\equiv(\text{w})\text{FeH}_2\text{PO}_4^+$ and AlHPO_4^+ at low pH (~ 4.0). For uranium, the dominant model species at high pH (~ 6.5) are $\equiv(\text{w})\text{FeOUO}_2^+$ and $\equiv(\text{w})\text{FeOHUO}_2(\text{OH})_2^{2-}$ and at low pH (~ 4.0) is $\equiv(\text{s})\text{FeOUO}_2^+$. For this model, (w) and (s) refer to weaker and stronger binding sites (stronger site has higher affinity for sorbate) the strength of which are quantified by equilibrium constants ($\log K$ values) that account for surface charge density and surface potentials. For example, for the reaction $\equiv(\text{s})\text{FeOUO}_2^+ + \text{H}^+ \rightleftharpoons \equiv(\text{s})\text{FeOH} + \text{UO}_2^{2+}$, the equilibrium constant K is calculated by: $K \exp[\Psi F/RT_K] = m[\equiv(\text{s})\text{FeOUO}_2^+]a[\text{H}^+]/m[\equiv(\text{s})\text{FeOH}]a[\text{UO}_2^{2+}]$, where Ψ is the surface potential of the sorbent, F is the faraday constant, R is the universal gas constant and T_K is absolute temperature (Dzombak and Morel, 1990; Bethke, 1996).

The stronger binding sites dominate at lower pH because at low pH the most abundant surface site is protonated [$\equiv(\text{w})\text{FeOH} + \text{H}^+ \rightarrow \equiv(\text{w})\text{FeOH}_2^+$] and thus unavailable for complexation with the positively charged uranyl ion. However, a fraction of the stronger surface sites remain unprotonated at the lower pH values and are thus available for complexation [$\equiv(\text{s})\text{FeOH} + \text{H}^+ + \text{UO}_2^{2+} \rightarrow \equiv(\text{s})\text{FeOUO}_2^+$]. Correspondingly at the higher pH the weaker (and more abundant) surface sites are unprotonated and are thus available for complexation [$\equiv(\text{w})\text{FeOH} + \text{H}^+ + \text{UO}_2^{2+} \rightarrow \equiv(\text{w})\text{FeOUO}_2^+$].

Phosphate adsorption is distinct from uranium because of its anionic nature. The key surface reactions predicted by the surface complexation calculations are shown in Table 4.

Our surface complexation modeling has relatively large uncertainties due to lacking thermodynamic data; however, the results are believed to be useful in a semi-quantitative way because they show how the presence of surface species will strongly influence uranium and phosphate speciation in soils containing abundant (from a surface area stand point) ferric oxides.

Results from our mineralogical characterizations of Coles Hill soils suggest that a potentially important type of surface complex that is not accounted for in our modeling are uranyl-phosphato complexes (Payne et al., 1996). It is possible that aqueous complexes UO_2PO_4^- or $\text{UO}_2\text{H}_2\text{PO}_4^+$ may interact with the iron oxide substrate to form a stable uranyl-phosphate surface species that may contribute to the retention of uranium in the unsaturated zone. The formation of uranyl-phosphato ternary surface complexes as a process that enhances uranium sorption onto iron oxides is supported by the work of Payne and Waite (2001).

It is also possible that the association of uranium and phosphorous with iron oxide mineral surfaces is caused by the presence of nano-scale uranyl phosphate precipitates. This process plays an important role in uranium retention in the weathered zone associated with the Koongara uranium deposit (Sato et al., 1997; Murakami et al., 1997). With in Koongara soils, 2–50 nm uranyl phosphate crystals were found within layers and nodules of goethite, hematite and ferrihydrite (Sato et al., 1997; Murakami et al., 1997).

This similarity between our results and those from the mineralogical studies of the soils overlying the

Table 4

Reactions of the phosphate and uranyl species with the goethite mineral surfaces

Surface reactions	$\log K^a$
pH ~ 4	
$\equiv(\text{w})\text{FeH}_2\text{PO}_4^+ + \text{H}_2\text{O} \rightleftharpoons \equiv(\text{w})\text{FeOH} + \text{H}_2\text{PO}_4^- + \text{H}^+$	-11.76
$\equiv(\text{s})\text{FeOUO}_2^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{UO}_2\text{HPO}_4(\text{aq}) + \equiv(\text{s})\text{FeOH}$	-3.97
$\equiv(\text{s})\text{FeOUO}_2^+ + \text{H}^+ \rightleftharpoons \equiv(\text{s})\text{FeOH} + \text{UO}_2^{2+}$	-5.20
pH ~ 7	
$\equiv(\text{w})\text{FeHPO}_4^- + \text{H}_2\text{O} \rightleftharpoons \equiv(\text{w})\text{FeOH} + \text{H}_2\text{PO}_4^-$	-5.86
$\equiv(\text{w})\text{FePO}_4^{2-} + \text{H}_2\text{O} + \text{H}^+ \rightleftharpoons \equiv(\text{w})\text{FeOH} + \text{H}_2\text{PO}_4^-$	1.81
$\equiv(\text{w})\text{FeOUO}_2^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \equiv(\text{w})\text{FeOH} + \text{H}^+ + \text{UO}_2\text{PO}_4^-$	-7.93
$\equiv(\text{w})\text{FeOHUO}_2(\text{OH})_2^{2-} + 2\text{H}^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \equiv(\text{w})\text{FeOH} + \text{UO}_2\text{PO}_4^- + 4\text{H}_2\text{O}$	13.87

^a $\log K$ calculated from the relationship: $K \exp[\Psi F/RT_K] = m[\equiv(\text{s})\text{FeOUO}_2^+] a[\text{H}^+]/m[\equiv(\text{s})\text{FeOH}] a[\text{UO}_2^{2+}]$, where Ψ is the surface potential of the sorbent, F is the faraday constant, R is the universal gas constant and T_K is absolute temperature.

Koongara deposit indicate that uranium distribution in iron oxide rich soils containing abundant phosphate will likely involve both surface complexation (i.e., uptake on iron oxide minerals) as well as mineral precipitation processes (i.e., formation of sparingly soluble uranyl phosphates or uranium-bearing aluminum phosphates). This has important implications for uranium transport studies and uranium exploration by near-surface sampling in potentially mineralized regions.

4. Conclusions

Soils developed from the unmined Coles Hill uranium deposit (hosted in quartzo-feldspathic gneiss) are enriched in uranium relative to soil profiles developed from unmineralized bedrock adjacent to the deposit (200–1000 mg/kg U in soils overlying the deposit vs. 5–15 mg/kg U in adjacent soil profiles). Uranium enrichment is greatest in the saturated zone saprolites where uranium concentrations are equal to, or higher than, the average concentration in the primary ore (~1000mg/kg U in the saturated saprolite vs. 960 U mg/kg in primary ore). Uranium in the primary ore is present as coffinite and uraninite (Jerden and Sinha, 2003) and in the saturated saprolites, as meta-autunite group mineral (Jerden et al., 2003). The present paper focused on the unsaturated soil horizons developed from the uranium rich saprolites.

Bulk chemical analyses show that the unsaturated zone soils overlying the Coles Hill deposit are also enriched in uranium relative to surrounding soil profiles, however, the level of enrichment is lower than in the underlying saprolites (~200 mg/kg U in the unsaturated soils vs. ~1000 mg/kg U in the saturated saprolites). This discontinuity in uranium concentration corresponds to an abrupt change in uranium mineralogy at the water table. In soils above the water table uranyl phosphates are absent; however, uranium is still closely associated with phosphate. The two main uranium sinks in the unsaturated zone soils are: (1) a barium–strontium–calcium aluminum phosphate of the crandallite group (composition and XRD patterns most closely match that of gorceixite), which contains 1.1 wt.% uranium and (2) phosphate-rich iron oxide mineral coatings which contain up to 6.3 wt.% uranium (uranium concentrations determined by EMP). In the iron oxide mineral coatings uranium is positively correlated with phosphorous. Electron microprobe analyses of manganese oxide inclusions within the uranium-bearing

gorceixite show that uranium is preferentially partitioned into the aluminum phosphate relative to the intermixed manganese oxides.

Thermodynamic calculations suggest that the absence of meta-autunite group minerals in the unsaturated soil horizons is primarily due to a drop in pH of the pore fluids (soil pH in unsaturated zone is <6.0, pH of saprolites ground waters in saprolites ≥6.0). One indication of this is that the modeled pore water solutions become under-saturated with respect to meta-uranocircite at a pH of approximately 6.5 (Fig. 7).

Results from our mineralogical characterizations of Coles Hill soils suggest that a potentially important type of surface complex that is not accounted for in our modeling are uranyl-phosphato complexes. It is possible that aqueous complexes UO_2PO_4^- or $\text{UO}_2\text{H}_2\text{PO}_4^+$ may interact with the iron oxide substrate to form a stable uranyl-phosphate surface species that may contribute to the retention of uranium in the unsaturated zone.

Overall our thermodynamic modeling supports the field observations showing that, in well developed saprolites/soil profiles typical of the mid-Atlantic and south eastern US, the presence of phosphorous will strongly influence both the solid and aqueous phase speciation of uranium. The results of this study therefore have important implications for uranium stabilization strategies involving phosphate amendments and for geochemical exploration for uranium resources in phosphate-rich weathered regions.

The primary implications of this work are: (1) secondary uranyl phosphates (e.g. autunite or meta-autunite group minerals) may not be stable in unsaturated soils with relatively low pH, and (2) even if uranyl phosphates are not stable uranium may be retained in relatively low pH soils (e.g. pH 4–6) through incorporation into aluminum phosphates and the formation of uranium–phosphate surface complexes (or nano-precipitates) associated with iron oxides.

Acknowledgements

This work was supported in part by a Virginia Museum of Natural History Research Fellowship (to JLJ) and a Society of Economic Geologists Research Fellowship-Hugh E. McKinstry Fund (to JLJ). The authors are grateful to Mr. Walter Coles for logistic support and access to his property through out this study. We thank Dr. Robert Finch of Argonne National Laboratory for X-ray diffraction data collection and evaluation.

Appendix A

(A) Raw chemical data for PDH1. Concentrations of Al₂O₃ and SiO₂ are in wt.%, all others are in mg/k

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
Depth (m)	0.2	0.4	0.6	1.2	1.5	2.1	3.7	4.3	4.6	4.9	5.5	7.3	7.9	8.5	9.5	10.4	18.3
Al ₂ O ₃	16.6	17.9	23.5	26.6	24.7	26.0	26.0	26.8	25.4	22.9	20.2	19.8	20.2	20.4	19.8	19.1	18.7
SiO ₂	68.6	66.2	50.4	52.1	55.0	54.7	57.4	54.0	56.0	59.9	64.6	64.5	63.8	61.5	63.9	64.0	65.5
Na	1112.8	1038.6	1038.6	964.4	964.4	964.4	148.4	445.1	593.5	593.5	5267.2	11,869.7	23,294.3	34,422.2	46,143.5	47,998.1	53,191.1
P	698.2	785.5	2967.5	1483.8	1658.3	2182.0	741.9	872.8	785.5	1047.4	960.1	916.4	611.0	785.5	611.0	741.9	3054.8
Ca	714.7	786.2	857.6	357.4	500.3	571.8	571.8	214.4	214.4	285.9	357.4	643.2	929.1	1286.5	1215.0	1357.9	7289.9
Ti	4220.5	3662.9	4490.3	4148.5	4442.3	3956.7	4628.1	5065.8	4274.4	3603.0	3609.0	3261.3	3147.4	3674.9	3585.0	3399.2	2973.5
Sr	98.7	119.0	596.1	190.8	205.4	291.9	54.5	56.1	28.2	112.6	81.2	82.0	30.9	83.0	46.8	44.0	103.6
Ba	446.8	502.7	2240.0	765.7	808.8	1050.0	393.1	354.5	344.5	652.2	458.2	492.6	370.2	561.5	308.4	456.9	579.1
Ce	99.4	111.9	430.4	200.5	194.9	315.2	130.7	117.0	90.9	144.5	130.9	132.1	68.5	147.6	91.4	88.5	87.1
U	48.1	61.5	237.3	146.8	217.2	337.5	162.7	213.2	192.0	207.5	242.5	247.1	268.2	338.4	272.9	862.6	1060.0

(B) Raw chemical data for PDH2 [(1)–(6)] and PDH3 [(7)–(12)]. Concentrations of Al₂O₃ and SiO₂ are in wt.%, all others are in mg/kg

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Depth (m)	0.6	1.5	3.0	3.4	3.7	5.5	0.3	1.5	4.6	5.5	7.0	8.5
Al ₂ O ₃	25.6	26.2	22.3	23.0	19.1	17.5	27.7	25.9	24.5	27.5	22.7	21.4
SiO ₂	50.1	53.9	61.4	59.3	65.3	66.9	44.9	49.9	50.7	47.7	53.3	56.3
Na	296.7	593.5	7492.8	519.3	31,751.5	49,704.4	519.3	445.1	667.7	1187.0	741.9	1112.8
P	654.6	829.2	829.2	2443.8	960.1	741.9	567.3	741.9	872.8	872.8	872.8	829.2
Ca	500.3	214.4	214.4	643.2	500.3	1786.8	500.3	142.9	71.5	214.4	142.9	214.4
Ti	4340.4	3489.1	3633.0	3591.0	3189.3	2733.7	6168.9	8003.3	8447.0	6846.3	7673.6	7625.6
Sr	81.2	92.1	83.3	401.2	93.4	66.0	36.0	43.5	73.5	65.0	125.7	116.5
Ba	436.7	437.8	441.2	2560.0	554.7	366.0	394.1	1000.0	1880.0	1700.0	2410.0	2610.0
Ce	116.2	164.6	148.7	446.7	163.9	76.0	216.0	397.0	376.9	124.0	309.3	269.1
U	69.4	127.1	202.0	301.1	706.0	953.0	9.6	10.0	8.8	11.1	7.8	6.6

References

- Arey, J.S., Seaman, J.C., Bertsch, P.M., 1999. Immobilization of uranium in contaminated sediments by hydroxyapatite addition. *Environmental Science and Technology* 33 (2), 337–342.
- Bethke, C.M., 1996. *Geochemical Reaction Modeling: Concepts and Applications*. Oxford University Press, New York. 397 pp.
- Bethke, C.M., 1998. The Geochemist's Workbench™, Version 3.0, A Users Guide to Rxn, Act2, Tact, React, and Gtplot. Hydrogeology Program, University of Illinois. 184 pp.
- Bostic, W.D., Stevenson, R.J., Jarabek, R.J., Conca, J.L., 2000. Use of apatite and bone char for the removal of soluble radionuclides in authentic and simulated DOE groundwater. *Advances in Environmental Research* 3, 488–498.
- Conca, J.L., Parker, G., Ningping, L., Wright, J., Heller, P., 1999. Phosphate-induced metal stabilization for remediation of uranium contaminated waters and soils. Geological Society of America, Abstracts with Programs, National Meeting, vol. 31 (7), p. 67.
- Dzombak, Morel, 1990. *Surface Complexation Modeling: Hydrrous Ferric Oxide*. John Wiley and Sons, New York. 393 pp.
- Fuller, C.C., Bargar, J.R., Davis, J.A., Piana, M.J., 2002. Mechanisms of uranium interactions with hydroxyapatite: implications for ground water remediation. *Environmental Science and Technology* 36 (2), 158–165.
- Fuller, C.C., Bargar, J.R., Davis, J.A., 2003. Molecular-scale characterization of uranium sorption by bone apatite materials for a permeable reactive barrier demonstration. *Environmental Science and Technology* 37 (20), 4642–4649.
- Goldich, S.S., 1938. A study in rock weathering. *Geology* 46, 17–58.
- Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung Cregu, C., Wanner, H., 1992. Chemical thermodynamics of uranium. In: Wanner, H., Forest, I. (Eds.), *Chemical Thermodynamics Series*, vol. 1. Elsevier, Amsterdam.
- Guillaumont, R., Fanghanel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D.A., Rand, M.H., 2003. Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. In: Mompean, F.J., Illemassene, M., Domenech-Orti, C., Ben-Said, K. (Eds.), *Chemical Thermodynamic Series*, vol. 5. Elsevier, Amsterdam.
- Hendershot, W.H., Lalonde, H., Duquette, M., 1993. Soil reaction and exchangeable acidity. In: Carter, M.R., (Ed.), *Soil Sampling and Methods of Analysis*. Canadian Society of Soil Science, Lewis Publishers.
- Helgeson, H.C., 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *American Journal of Science* 267, 729–804.
- Jerden J.L., Jr., 2001. Origin of Uranium Mineralization at Coles Hill Virginia (USA) and its Natural Attenuation within an Oxidizing Rock-Soil-Ground Water System, Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg Virginia. 157 pp.
- Jerden Jr., J.L., Sinha, A.K., 2003. Phosphate based immobilization of uranium in an oxidizing bedrock aquifer. *Applied Geochemistry* 18, 823–843.
- Jerden Jr., J.L., Sinha, A.K., Zelazny, L., 2003. Natural immobilization of uranium by phosphate mineralization in an oxidizing saprolite-soil profile: chemical weathering of the Coles Hill Uranium deposit, Virginia. *Chemical Geology* 199, 129–157.
- Krauskopf, K.B., 1967. *Introduction to Geochemistry*. McGraw-Hill, New York.
- Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice-Hall Incorporated, Upper Saddle River, New Jersey. 600 pp.
- Lindsay, W.L., Vlek, P.L.G., Chien, S.H., 1989. Phosphate minerals, In: Dixon, J.B., Weed, S.B. (Eds.), *Minerals In Soil Environments*, 2nd Edition. Soil Science Society of America, Madison Wisconsin, pp. 1089–1130.
- Murakami, T., Ohnuki, T., Isobe, H., Sato, T., 1997. Mobility of uranium during weathering. *American Mineralogist* 82, 888–899.
- Murray, F.H., Brown, J.R., Fyfe, W.S., Kronberg, B.I., 1983. Immobilization of U–Th–Ra in mine wastes by phosphate mineralization. *Canadian Mineralogist* 21, 607–610.
- Naftz, D.L., Davis, J.A., Fuller, C.C., Morrison, S.J., Freethey, G.W., Feltcorn, E.M., Wilhelm, R.G., Piana, M.J., Joye, J., Rowland, R. C., 1999. Field demonstration of permeable reactive barriers to control radionuclide and trace-element contamination in ground water from abandoned mine lands. In: Morganwalp, D.W., Buxton, H.T. (Eds.), *U. S. Geological Survey, Water-Resources Investigations*, WRI-99-4018-A.
- Nesbitt, H.W., Markovics, G., 1992. Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments. *Geochimica et Cosmochimica Acta* 61, 1653–1670.
- Nesbitt, H.W., Wilson, R.E., 1992. Recent chemical weathering of basalts. *American Journal of Science* 292, 740–777.
- Pavich, M.J., 1986. Processes and rates of saprolite production and erosion on a foliated granitic rock of the Virginia piedmont. In: Colman, S.M., Dethier, D.P. (Eds.), *Rates of Chemical Weathering of Rocks and Minerals*. Academic Press, New York, pp. 552–590.
- Pavich, M.J., 1989. Regolith residence time and the concept of surface age of the Piedmont “peneplain”. *Geomorphology* 2, 181–196.
- Pavich, M.J., Brown, L., Valette-Silver, N., Klein, J., Middleton, R., 1985. ¹⁰Be analysis of a quaternary weathering profile in the Virginia Piedmont. *Geology* 13, 39–41.
- Payne, T.E., Waite, T.D., 2001. Uranium(VI) adsorption of ferrihydrite in simple NaNO₃/HCO₃ systems, and in systems containing additional complexing ligands. In: Davis, J.A. (Ed.), *Surface Complexation Modeling of Uranium(VI) Adsorption on Natural Mineral Assemblages*, NUREG/CR-6708.
- Payne, T.E., Davis, J.A., Waite, T.D., 1996. Uranium adsorption on ferrihydrite—effects of phosphate and humic acid. *Radiochimica Acta* 74, 239–243.
- Robie, R.A., Hemingway, B.S., Fisher, J.R., 1979. Thermodynamic properties of minerals and related substances at 298.15K and 1 bar pressure and at higher temperatures. *U.S.G.S. Bulletin*, vol. 1452 (with corrections). 1456 pp.
- Sandino, A., Bruno, J., 1992. The solubility of (UO₂)₃(PO₄)₂·4H₂O(s) and the formation of U(VI) phosphate complexes: their influence in uranium speciation in natural waters. *Geochimica et Cosmochimica Acta* 56, 4135–4145.
- Sato, T., Murakami, T., Yanase, N., Isobe, H., Payne, T.E., Airey, P.L., 1997. Iron nodules scavenging uranium from groundwater. *Environmental Science and Technology* 31 (10), 2854–2858.
- Schwab, R.G., Herold, H., DA Costa, M.L., DE Oliveira, N.P., 1989. The Formation of Aluminous Phosphates Through Lateritic Weathering of Rocks, Weathering vol. II. Products, Deposits, Theophrastus, pp. 369–386.
- Schwab, R.G., Gotz, C., Herold, H., De Oliveira, N.P., 1993. Compounds of the crandallite type: thermodynamic properties of Ca-, Sr-, Ba-, Pb-, La-, Ce-to Gd-phosphates and -arsenates. *Neues Jahrbuch für Mineralogie-Monatshefte*, H., vol. 12, pp. 551–568.

- Soil Survey Staff, 1975. Soil taxonomy. U.S. Department of Agriculture Handbook, vol. 436. U.S. Government Printing Office, Washington, DC.
- Vieillard, P., Tardy, Y., Nahon, D., 1979. Stability fields of clay and aluminum phosphates: paragenesis in lateritic weathering of argillaceous phosphatic sediments. *American Mineralogist* 64, 626–634.
- Vochten, R.F., Van Haverbeke, L., Van Springel, K., 1992. Transformation of chernikovite into meta-uranocircite II, Ba $(\text{UO}_2)(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ and study of its solubility. *Mineralogical Magazine* 56, 367–372.
- Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., Nuttall, R.L., 1982. The NBS tables of chemical thermodynamic properties, selected values for inorganic and c1 and c2 organic substances in SI units. *Journal of Physical and Chemical Reference Data* 11 (2), 392.
- Yanase, N., Payne, T.E., Sekine, K., 1995. Groundwater geochemistry in Koongarra ore deposit, Australia (I): implications for uranium migration. *Geochemical Journal* 29, 1–29.