

Long-Term Stabilization of Uranium By U(VI) Phosphate Mineralization in Weathered Bedrock and Soils Developed Over a Granite-Hosted Uranium Deposit

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ABSTRACT

The unmined Coles Hill U deposit in the Virginia Piedmont represents a unique natural laboratory for studying the long-term containment of U by phosphate minerals. The primary ore assemblage consists of coffinite and apatite and is hosted in foliated granite. Geochemical and mineralogical studies of the weathered bedrock and soils developed over the primary ore body indicate that U transport is inhibited by the precipitation of meta-autunite group minerals. The lower part of the profile, which consists of ground water saturated saprolite, contains 1400 mg/kg U (in the solid). This concentration is 1.5 times greater than the mean ore grade of the deposit, indicating that the saprolites are enriched in U relative to the underlying primary ore. Uranium within the saprolite is dominantly associated with 10 to 500 μm long, tabular crystals of (Ba, Ca, Sr) meta-autunite. Ground waters from this zone contain less than 14 $\mu\text{g/L}$ dissolved U suggesting that the U(VI) phosphate minerals present are capable of controlling dissolved U concentrations at values lower than the US-EPA maximum contaminant level (30 $\mu\text{g/L}$). Mineralogical characterization of the unsaturated soil horizons indicate that geochemical conditions in these zones are not conducive to U stabilization by meta-autunite mineralization. In the vadose zone U is primarily associated with Al phosphate (crandallite) and with P adsorbed or coprecipitated with iron oxide mineral coatings. Geochemical gradients suggest that significant amounts of U have been leached from the vadose zone by infiltrating fluids and reprecipitated below the water table, where the activity ratio of dissolved phosphate to carbonate increases. Based on regional weathering rates, the processes responsible for stabilization of U within the Coles Hill system are estimated to have been active for hundreds of thousands of years.

INTRODUCTION

The development and implementation of scientifically sound strategies for the long-term containment of U requires knowledge of its geochemical behavior in natural systems. A promising method for U containment is in-situ stabilization involving amendments or reactive barriers that redirect the solid phase speciation to less soluble forms [1] [2]. Phosphates, such as apatite, may stabilize U by sorption and/or by facilitating the precipitation of U bearing secondary phosphate minerals [1] [2]. This paper presents results from a mineralogical and geochemical study of a site (Coles Hill U deposit) where millions of kg of U have been naturally stabilized by U(VI) phosphate mineralization. The goal of this work is to provide insights into the long-term effectiveness of phosphate stabilization of U in natural geologic systems.

METHODS

Solid samples were taken from bedrock core and auger holes drilled within and adjacent to the Coles Hill U deposit. Soil samples were dried immediately after collection in a clean air (+100) environment. Solid samples (~0.5kg) were pulverized using a tungsten carbide shatter box, dissolved and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Representative samples retaining textural integrity were impregnated with epoxy, polished and

carbon coated for analyses by scanning electron microscopy (SEM), energy dispersive x-ray spectrometry (EDS) and electron microprobe (EMP). Operating conditions for EMP analyses were: 15 kV acceleration voltage, 20 nA beam current with a spot diameter of approximately 0.5 μm . Heavy mineral separates from weathered rock and soil zones were analyzed by powder X-ray diffraction (XRD) by Dr. Robert Finch of Argonne National Laboratory. Ground water monitoring wells were installed in drill holes from which solid samples were obtained. Clean PVC well casing and granular bentonite were used to seal the holes down to the sampling target depths. Wells were purged and allowed to fully recharge before sampling and samples were taken using sterilized polyethylene bailers. Dissolved oxygen (DO) and pH were measured in situ after wells recharged. All samples were filtered (0.45 μm) and those to be analyzed for U and other metals were preserved (acidified to $\text{pH} < 2.0$) using ultra pure nitric acid immediately after filtering. Water samples were analyzed by ICP-MS and ion chromatography.

RESULTS

Geology of Primary Ore and Weathered Zone

The Coles Hill deposit is located in the Piedmont Physiographic Province of Virginia. The host rocks are hydrothermally altered foliated granite. Exploration studies indicate that the deposit contains >20 million kilograms U with an average ore grade of 958 mg/kg [3]. The primary ore consists of coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$) and minor uraninite (UO_{2+x}) associated with abundant fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). Ore-bearing fractures contain 10 to 40 vol.% fluorapatite, ~1 vol.% coffinite, and trace uraninite. The main non-ore minerals in these zones are: chlorite, albite, quartz and pyrite. The mineralogy and geochemistry of the unweathered and weathered bedrock ore zones are presented in [4]. A representative column through the Coles Hill deposit and overlying weathered zone consists of four physically and chemically distinct domains (from base to surface): (1) unweathered, primary ore-hosting bedrock, (2) incipiently weathered bedrock zone that is pervasively “stained” by ferric oxides, (3) kaolinite dominated saprolite (C-horizon) and (4) kaolinite-vermiculite-gibbsite bearing pedogenic soils (O, A, B soil horizons). In this profile the water table is within saprolites of the C-horizon. The U rich zone (> 900 mg/kg) extends from the base of the profile into the saprolite horizon overlying the deposit.

Geochemistry

Concentrations of key elements within a representative drill hole overlying the Coles Hill deposit are shown in Figure 1. In auger holes drilled directly over the Coles Hill deposit (such as the example shown in Fig 1), the abundance of U within the solid shows a pronounced high associated with the water table. The U concentrations near the water table are around 1400 mg/kg which is 1.5 times higher than those measured in the primary ore. Above the water table U concentrations decrease to around 250 mg/kg. Concentrations of P and Ca are highest below the water table but decrease above it. Within the pedogenic soil zone P increases while Ca remains at relatively low, suggesting that Ca is leached from the shallow portion of the profile.

The P and Ca trends reflect the abundance of relict apatite in the saturated zone and the loss (rapid weathering) of apatite in the vadose zone. Barium concentrations are, on average, higher below the water table than above it, but increase abruptly in the pedogenic soil zone. This increase in Ba corresponds to the increase in P within the upper part of the profile. This trend reflects the localized abundance of a Ba-Al phosphate mineral described in more detail below. Concentration profiles from auger holes down hydrologic gradient from the deposit contain 6 –

10 mg/kg U. Thus, despite the relatively high U concentrations in the weathered zone over the deposit, there is no evidence for lateral transport of U from the mineralized zone.

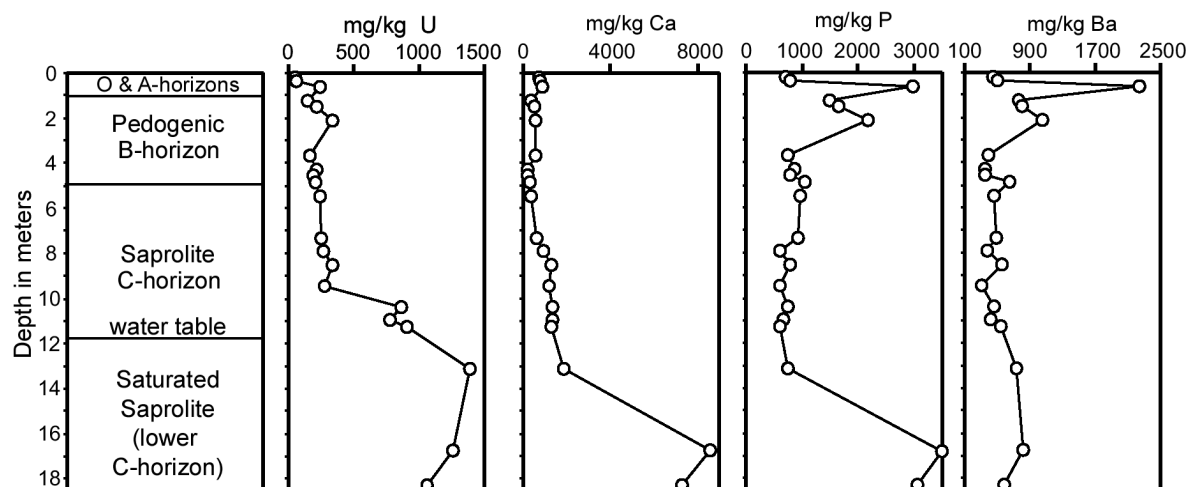


Figure 1. Bulk chemistry of saprolite and soil samples overlying the Coles Hill deposit (precision of data are $\pm 5\%$ relative standard deviation).

Mineralogy

Polarized light microscopy, XRD, SEM and EMP data indicate that U within the oxidized bedrock and saturated saprolite zone is associated with U(VI) phosphate minerals of the meta-autunite group. These minerals are particularly abundant near the water table. The mineralogy and chemistry of meta-autunite assemblages in the oxidized bedrock zone are presented in [4]. We will here focus on the U(VI) phosphates from the saprolite horizon. A representative example of a meta-autunite grain within an epoxy impregnated saprolite sample is shown in Fig 2a and an EMP image of part of that grain is shown in Fig. 2b. The image shows micrometer-scale compositional interlayering of Ba and Ca rich bands parallel to the prominent (001) mineral cleavage. This compositional layering may have resulted from an ion exchange process along the [001] crystallographic direction, which corresponds to the meta-autunite interlayer site. Analyses by EMP of the Coles Hill meta-autunites are shown in Table I.

Uranium in the vadose zone is also associated with P, however, the mineralogy controlling this association is significantly different from that observed in the saturated zones. The two main sinks for U in the unsaturated zone are: (1) Ba Al phosphates identified by XRD and EMP as crandallite group minerals, and (2) U associated with P and iron oxide mineral coatings. Table I lists EMP analyses of the crandallite and a U bearing iron oxide mineral coating. The reason for the high Al and Si concentrations in the iron oxide analyses is that the EMP analytical volume included the ferric mineral coating as well as the underlying kaolinite+quartz substrate.

Crandallite grains from the Coles Hill soils consistently show >1 wt.% UO_3 by EMP analyses. Concentrations of U and P in iron oxide mineral coatings are positively correlated, and yet no U phosphate phases are detected by SEM in these zones. This correlation may reflect an adsorption process (uranyl-phosphate surface complex) or the presence of nanometer-scale uranyl phosphate precipitates, perhaps similar in origin to iron oxide hosted Mg autunite crystals characterized by Murakami et al, [5].

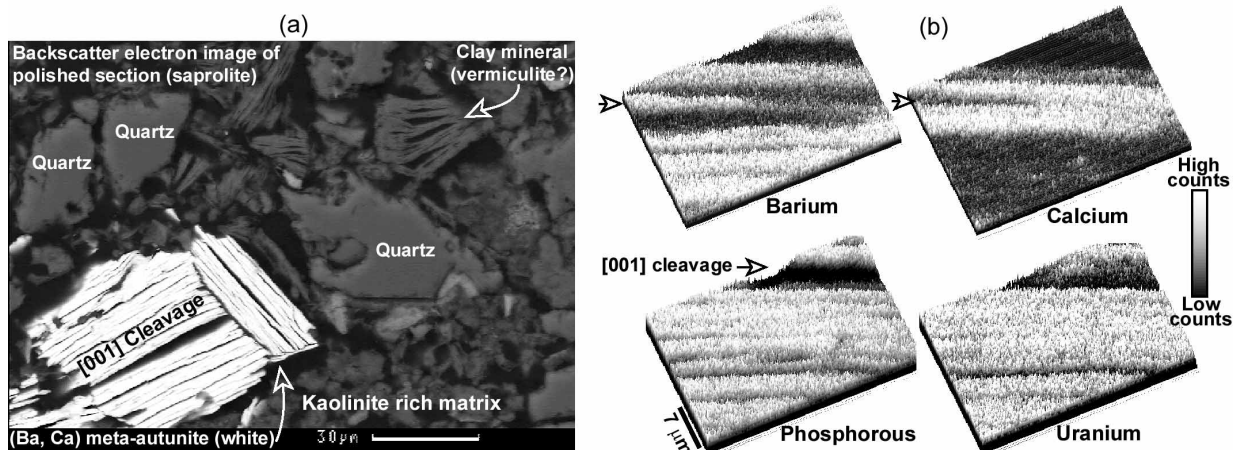


Figure 2. (a) Backscatter electron image of epoxy impregnated saprolite sample from the saturated C-horizon overlying the U deposit. (b) EMP images of a meta-autunite grain from the saturated C-horizon showing μm -scale interlayering of Ba and Ca rich zones parallel to the [001] cleavage direction.

Table I. Electron microprobe analyses of autunite, crandallite, and iron oxides from the weathered zone overlying the Coles Hill uranium deposit

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
Al_2O_3	na	na	na	na	na	na	na	na	31.2	31.1	30.5	2.9	4.8	4.5
P_2O_5	14.4	15.6	15.0	15.1	16.2	15.8	15.2	15.5	26.5	26.1	26.5	4.2	6.1	7.7
SiO_2	na	na	na	na	na	na	na	na	5.1	5.8	5.2	33.0	20.5	10.24
CaO	<0.1	1.6	1.3	3.2	5.3	3.7	3.6	3.9	2.3	2.3	2.4	<0.1	<0.1	<0.1
Fe_2O_3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.9	1.1	1.0	26.5	31.9	42.31
SrO	<0.1	<0.1	0.4	<0.1	<0.1	1.2	0.9	1.2	2.5	2.4	2.6	na	na	na
BaO	15.5	11.1	11.6	5.6	0.8	1.8	2.4	1.7	15.8	15.4	15.9	<0.3	0.4	0.4
UO_3	58.0	59.7	59.6	60.8	62.7	62.4	62.9	62.7	1.4	1.3	1.2	5.4	7.55	6.2
Total*	87.8	88.0	87.9	85.0	85.0	85.0	84.9	84.9	85.8	85.5	85.3	72.5	71.2	71.4

*Totals <100 due to H_2O in contents. na = not analyzed. (1) meta-autunite from the oxidized bedrock zone, (2)–(8) meta-autunites from the saturated saprolite zone. Na_2O , K_2O and MgO were also analyzed for in the meta-autunite but were all <0.1%. (9)–(11) crandallite from pedogenic soil zone, (12)–(14) Spot analyses of ferric mineral coatings on soil grains (Al and Si are from kaolinite/quartz substrate). Relative standard deviations for raw data (calculated from counting statistics) are: 2% for UO_3 , P_2O_5 , BaO , 8% for CaO , SrO [samples (1)–(8)]; 2% for Al_2O_3 , P_2O_5 , SiO_2 , BaO , 5% for SrO , UO_3 , 10% for other elements [samples (9)–(11)]; 2% for Al_2O_3 , P_2O_5 , Fe_2O_3 , SiO_2 ; 5% for UO_3 , 50% for BaO [samples (12)–(14)].

Ground water chemistry

A representative analysis of a ground water from the U rich part of the saprolite zone is shown in Table II. Samples from streams and wells down hydrologic gradient from the deposit contain less than $1 \mu\text{g/L}$ dissolved U, indicating that U is not transported laterally away from the deposit by shallow ground waters. The software Geochemist's Workbench, (version 3.0) was used to calculate ion activities and mineral saturation indices from the water analyses in Table II. Activity coefficients were calculated using the "B-dot" extended Debye-Huckel equation. Thermodynamic data are from [6] except for Ba meta-autunite from [7] and Na autunite from [8]. Saturation index ($\text{SI} = \log_{10}[\text{ion activity product/solubility product}]$) calculations show that the ground waters represented by the data in Table II are supersaturated with respect to the observed phase Ba meta-autunite ($\text{SI} = 1.7$) and are undersaturated with respect to other uranyl phases such as schoepite ($\text{SI} = -2.2$), Na autunite ($\text{SI} = -2.2$) and uranophane ($\text{SI} < -3.0$).

Figure 3 is an Eh-pH diagram calculated using activities shown in Table II, and assuming a $\text{CO}_2(\text{g})$ fugacity of $10^{-2.0}$, which is consistent with measured dissolved carbonate concentrations. It shows a generalized reaction path for the oxidation and weathering of the Coles Hill primary ore. The reaction path is based on mineralogical observations. For example, the observation that the path crosses the U(IV)-U(VI) and Fe(II)-Fe(III) transitions nearly simultaneously is supported by the examination of core from the site showing an abrupt transition from coffinite to Ba meta-autunite within centimeters of the ferrous/ferric front defined by iron oxide staining. The peak Eh value is estimated for the path is based on the presence of MnO_2 and related phases in the soils. The decrease in pH at the end of the path corresponds to increased H^+ activity in soil pore waters in the pedogenic soils.

Table II. Representative ground water analyses from the weathered zone overlying the Coles Hill uranium deposit.

	Ground water*	Log ₁₀ Activity
Date sampled	June 7 2001	---
Field pH	5.9	---
Field DO (mg/L)	8.1	-3.6
<i>Major Constituents (mg/L)</i>		
Na^+	19.8	-3.1
$\text{SiO}_2(\text{aq})$ (as Si)	11.2	-3.4
Ca^{2+}	2.1	-4.4
$\text{CO}_2^{3-} + \text{HCO}_3^-$	22.6	-4.0
SO_4^{2-}	12.5	-3.7
<i>Minor & Trace Constituents ($\mu\text{g/L}$)</i>		
Mg^{2+}	463.7	-4.8
K^+	561.1	-4.9
Mn^{4+}	24.6	-6.4
Fe^{3+}	48.0	-6.3
Ba^{2+}	688.0	-5.4
UO_2^{2+} species (as U)	13.6	-7.2
PO_4^{3-} (as P)	100	-7.3

*Sample passed through 0.45 micron membrane. Precision of data (% relative standard deviation): 10% and 20% for major and minor constituents respectively.

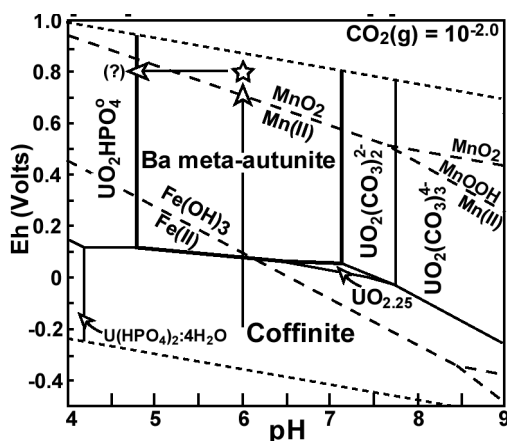


Figure 3. Eh-pH diagram (25°C) plotted for a representative ground water sample from the weathered zone overlying the Coles Hill uranium deposit (see Table II).

DISSCUSSION

Measured gradients in bulk geochemistry indicate that the saturated saprolites overlying the Coles Hill deposit are enriched in U relative to the underlying primary ore. Uranium within this zone is dominantly associated with U(VI) phosphates of the meta-autunite mineral group.

Ground waters from this zone contain less than 14 µg/L U and are supersaturated with respect to the observed U(VI) phosphate (Ba meta-autunite). Above the water table, U(VI) phosphates of the type found in the saturated saprolite zone are not present and the U concentration in the soil drops to an average value of 250 mg/kg. Mineralogical characterization of the unsaturated horizons suggests that geochemical conditions are not conducive to U stabilization by meta-autunite group minerals in this zone. Rather, U in the shallow soils is associated with aluminum phosphates (crandallite), and with P adsorbed or co-precipitated with ferric oxide mineral coatings.

Results of this study suggest that U is leached from the unsaturated part of the profile (meta-autunite unstable) and reprecipitated below the water table where the activity ratio of dissolved phosphate to carbonate increases. Based on estimates of weathering rates for this region (see [4] and [10]) the processes responsible for U immobilization in the Coles Hill system are estimated to have been active for hundreds of thousands of years.

CONCLUSIONS

Our study of the weathering zone overlying the Coles Hill U deposit indicates that U may be stabilized within oxidizing, fluid-rich environments by the precipitation of low solubility U(VI) phosphates. Ground waters from U-rich saprolites overlying the deposit contain less than 14 µg/L dissolved U, suggesting that the U(VI) phosphate minerals present are capable of controlling dissolved U concentrations at values lower than the US-EPA maximum contaminant level (30 µg/L [9]). Based on regional weathering rates and the lack of lateral dispersion of U around the deposit, it is estimated that this natural stabilization process has effectively immobilized U at this site for hundreds of thousands of years.

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