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Phosphate based immobilization of uranium in an oxidizing bedrock aquifer

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Abstract

The unmined Coles Hill U deposit of south central Virginia represents a natural setting where U is stabilized by phosphate mineral precipitation in an oxidizing bedrock aquifer. Drill cores from the shallow portion of the deposit preserve a sharp Fe redox front defined by Fe(III) oxide staining. This front is located near a discontinuity in U mineralogy with U(IV) assemblages (e.g. coffinite, uraninite) on the reducing side, and U(VI) assemblages on the oxidizing side. The discontinuity in U mineralogy does not, however, represent a major discontinuity in whole rock U concentrations, with sample groups from both oxidized and reduced sides of the front generally ranging from 500 to 1000 ppm. This observation suggests that the volume of shallow bedrock associated with the deposit has not lost significant amounts of U during the oxidation and incipient chemical weathering. The precipitation of Ba uranyl phosphate (Ba meta-autunite) is responsible for U retention within this zone. Ground waters sampled from the weathered bedrock aquifer associated with the deposit contain less than $15 \mu\text{g l}^{-1}$ dissolved U. This suggests that the low solubility of the Ba meta-autunite limits U concentrations to values lower than the US-EPA maximum contaminant level of $30 \mu\text{g l}^{-1}$. Ground water speciation and mineral saturation calculations show that, in addition to Eh and pH, the most important factor controlling this U fixation process is the activity ratio of dissolved phosphate to dissolved carbonate. Experimental results suggest that, at the Coles Hill site, the oxidation of U(IV) to U(VI) and subsequent precipitation of uranyl phosphate occurs rapidly (time scale of weeks) relative to ground water transport (e.g. 20 m/a). Furthermore, based on the rate of downward migration of the redox front, it is estimated that the oldest U(VI) phosphate assemblages associated with the Coles Hill U deposit have been stable for up to 150 ka. These observations have important implications for the design and long term performance assessment of phosphate-based stabilization and reactive barrier techniques.

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1. Introduction

The transport of U in fractured bedrock by oxidizing ground waters is an important process in the cycling of this element from the geosphere to the biosphere. Of particular concern are areas where natural or anthro-

pogenic U sources have caused high dissolved U concentrations that threaten local drinking water. In U rich systems, such as natural U deposits and U tailings, the dissolution process typically involves oxidation and destabilization of U(IV) minerals such as uraninite ($\text{UO}_2 + x$) and coffinite ($\text{USiO}_4 \cdot n\text{H}_2\text{O}$) resulting in high concentrations of U(VI) aqueous species. In these types of environments U concentrations may reach values higher than $10,000 \mu\text{g l}^{-1}$ (e.g. Miekeley et al., 1992, Langmuir, 1997), which is over 300 times greater than the US-EPA maximum contaminant level (Environmental Protection Agency, 2000).

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Remediating U contaminated ground waters and soils by pump-and-treat and excavation methods can be costly and disruptive to local Environments. Therefore, in situ remediation techniques that stabilize the U by sorption or by incorporating it into low solubility solid phases are attractive because they are generally more cost effective (Conca et al., 1999) and less invasive than other options (e.g. Murray et al., 1983; Bostic et al., 2000). The addition of phosphate (e.g. hydroxyapatite) has been shown to reduce the solubility and bioavailability of U in contaminated soils from the US-DOE Savannah River Site (Arey et al., 1999), and the potential effectiveness of phosphate-bearing, reactive barrier systems for U removal from ground waters is demonstrated by the work of Naftz et al. (1999) and Fuller et al. (2002).

The role of U(VI) phosphate minerals in fixing U in weathering Environments was studied at the Koongara U deposit in northern Australia (e.g. Airey, 1986; Isobe et al., 1992; Murakami et al., 1994, 1997, 2001; Sato et al., 1997). Results of the Koongara studies show that, given high enough phosphate and Mg concentrations, U may precipitate as a Mg phosphate of the autunite mineral group (salleite). However, Murakami et al. (1997) indicate that the salleite grains within the Koongara weathered zone are currently undersaturated with respect to local ground waters and show dissolution textures. Other U(VI) phosphate phases studied at Koongara include micro-crystals (10–50 nm) of meta-torbernite and salleite, which formed by local saturation at the surface of Fe oxide and oxy-hydroxide grains (Murakami et al., 1997, 2001).

The work at Koongara represents a benchmark in our understanding of U phosphate mineral paragenesis as well as U sorption processes (e.g. Waite et al., 1994; Fenton and Waite, 1996; Payne et al., 2001; Davis, 2001). However, to better constrain the long-term effectiveness of phosphate based U remediation techniques there remains a need for data from natural rock–soil–ground water systems where U(VI) phosphate minerals are currently forming and have been stable over long time intervals (e.g. thousands of years).

This issue is addressed by examining the oxidation and alteration of an unmined U ore body (Coles Hill U deposit) that contains large amounts of apatite within the primary ore assemblage. Within this well-defined system, millions of kilograms of U are potentially made available for transport in oxidizing ground waters; however, natural geochemical processes are minimizing U transport. The U rich zone (~1000 ppm whole rock U) associated with the deposit extends up into an oxidizing bedrock zone and overlying saprolites. This paper focuses on processes inhibiting U transport within the oxidized bedrock zone. The stabilization of U in the overlying saprolite horizon is the subject of on-going research.

2. Description of the Coles Hill uranium deposit

In the late 1970s the Danville-Dan River Triassic basin in south central Virginia and north central North Carolina was assessed for U resources (Dribus, 1978). Detailed exploration of this region by the Marline Uranium Corporation led to the discovery of several significant radiometric anomalies, one of which was shown to be of economic significance (Marline Uranium Corporation, 1983). Further characterization of this anomaly revealed an extensive U deposit underlying a local topographic high known as Coles Hill (Fig. 1).

The Coles Hill U deposit is located along the north-western margin of the Chatham fault zone, which separates the Danville Triassic basin from polydeformed, polymetamorphosed crystalline rocks of the Piedmont Geologic Province (Henika and Thayer, 1983; Marline Uranium Corporation, 1983). The host rocks of the ore are proto-mylonitic quartzo-feldspathic gneisses and interlayered amphibolites that form the foot wall of the Danville Triassic basin border fault (Figs. 1 and 2; Marline Uranium Corporation, 1983; Jerden, 2001). No U mineralization is recognized in the clastic sequence of the Danville basin within the study area (Marline Uranium Corporation, 1983; Jerden, 2001).

The deposit consists of two coffinite-uraninite-apatite ore zones (Coles Hill north and south ore bodies; Fig. 1) that are cylindrical in shape and connect at depth (Marline U Corporation, 1983). The southern body contains 22×10^6 kg U_3O_8 with an average grade of 0.113% (958 ppm whole rock U; Halladay, 1989). The north ore body has similar total reserves but at a slightly lower grade (Halladay, 1989). The long axes of both orebodies plunge approximately 60° towards the SE, within the plane of the NE striking, SE dipping proto-mylonitic foliation of the Chatham fault zone (Marline U Corporation, 1983).

The primary ore assemblages are hosted in fractures associated with cataclastic zones that formed during Triassic normal faulting along the margin of the Danville basin (Jerden, 2001). Petrographic and structural studies suggest that the latest stage of ore-genesis associated with the Coles Hill deposit involved syn-tectonic, hydrothermal activity during the opening of the Danville Triassic basin (Marline Uranium Corporation, 1983; Jerden, 2001). Exploration drill cores indicate that the deposit extends to depths greater than 300 m (Marline Uranium Corporation, 1983). In the near surface the U rich zone (~1000 ppm whole rock U) associated with the deposit extends up into the weathered zone where the primary ore is altered to secondary assemblages during oxidation and chemical weathering. Despite extensive exploration, the deposit was never mined, and thus represents a relatively undisturbed U occurrence in which processes influencing the paleo- and present-day transport and retardation of U can be studied.

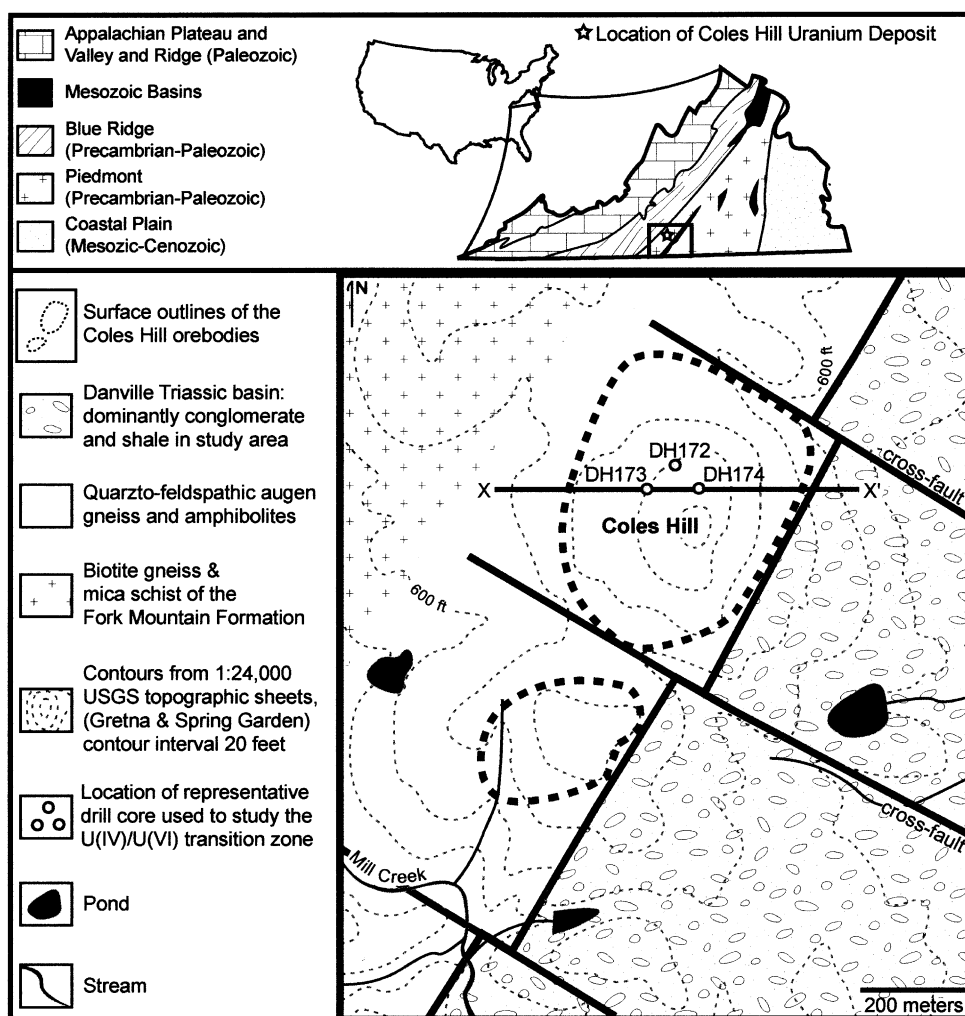


Fig 1. Location and geologic setting of the Coles Hill U deposit. Representative drill cores studied for this project are shown within the northern orebody of the deposit.

3. Sample collection and analysis

3.1. Mineral identification and characterization

The mineralogy and geochemistry of 3 typical core sections from the Coles Hill north orebody were characterized for this study (Fig. 2). Fresh and weathered bedrock samples were split from cores drilled during exploration of the deposit (samples on loan from the Virginia Museum of Natural History). Representative slabs were cut from each sample and mounted in epoxy, polished and coated with an approximately 250 Å thick film of C for analyses by scanning electron microscope (SEM), energy dispersive x-ray spectrometry (EDS) and

electron microprobe (EMP). 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. Operating conditions for EMP analyses were: 15 kV acceleration voltage, 20 nanoamp beam current with a spot diameter of approximately 0.5 μm. For EMP imaging the beam current was increased to 50 nanoamps. A representative heavy mineral separate of secondary minerals formed from oxidation of the primary U ore was analyzed by powder X-ray diffraction (XRD) by Dr. Robert Finch of Argonne National Laboratory. For this analyses samples were ground under ethanol and transferred to a

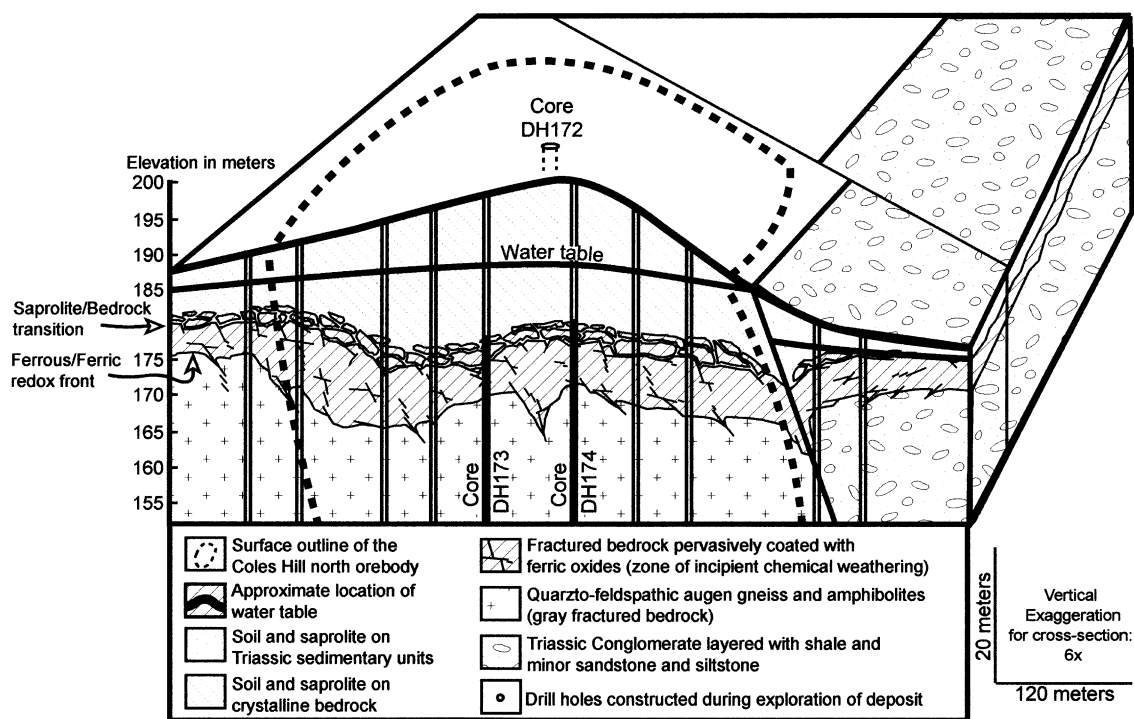


Fig. 2. Geologic cross-section through weathered zone overlying the Coles Hill U deposit. This section, which was plotted using exploration drill hole logs, indicates that the zone of Fe(III) oxide stained bedrock (zone of incipient chemical weathering) is continuous but varies in thickness and depth within the study area. The 3 core sections identified in the cross-section were used to characterize the mineralogy and geochemistry of U at redox fronts where primary U(IV) ore is exposed to oxidizing ground waters.

zero-background samples holder (single crystal oriented Si). Diffraction patterns were obtained using Cu K-alpha radiation (30kV, 15 mA).

3.2. Geochemistry of solid and fluid samples

Hand specimens of each sample were pulverized using a tungsten carbide shatter box and the powders were sent to an internationally accredited commercial laboratory for major, minor and trace element analyses. Whole rock samples were analyzed by a technique involving both lithium metaborate/tetraborate fusion and inductively coupled plasma mass spectrometry (ICP-MS; estimates of accuracy and precision given with data). It was necessary to process relatively small sample volumes (approximately 300 g per sample) in order to assess each core section at the centimeter scale. Variations in bulk concentration data result from a combination of analytical error and lithologic heterogeneity of the of the rock profile.

Ground water from the oxidized bedrock zone was sampled at a residential pump from a well that is cased off through the saprolite aquifer. Other shallow ground water samples from within and around the U deposit were obtained using polyethylene bailers after purging the wells. Dissolved O_2 and pH were measured in situ

after allowing the wells to recharge after purging. All samples were filtered (0.45 μ m) and samples to be analyzed for U and other metals were preserved (acidified to pH < 2.0) using ultra pure HNO_3 immediately after filtering. Water samples were sent to an internationally accredited commercial laboratory for analyses by ICP-MS for cations and ion chromatography for anions (estimates of accuracy and precision given with data).

3.3. Batch corrosion experiments

Batch-type alteration experiments were performed on primary ore samples to simulate the natural oxidation of the U(IV) ore. The materials for these experiments were obtained by crushing and sieving unweathered hand samples containing abundant U ore bearing fractures. Test specimens were taken from the 250–300 μ m size fraction and washed with deionized water to remove fine particles. Samples were from approximately 10 m below the redox front and showed no evidence of oxidation prior to initiation of the experiments. Approximately 200 mg of crushed sample was submerged in 5 ml of ground water extracted from the weathered zone overlying the deposit. The source of the ground water was a well adjacent to hole DH173 shown on Fig. 2. Test vessels (30 mL Teflon beakers) were covered to minimize

evaporation but were opened once a week to allow exchange with atmospheric gases. No effort was made to control the fugacities of CO₂ or O₂ during the experiments. The tests were stirred intermittently (generally twice a day) and every 2 weeks some of the reacted ore grains were mounted on C tape and examined by SEM-EDS. The type and amount of observed alteration was used to constrain the mineral paragenesis and general time frame of incipient oxidation.

4. Rock-system characterization of core samples

The host rocks of the Coles Hill U deposit consist of albite-quartz-chlorite/biotite-oligoclase-microcline augen gneiss interlayered with albite-chlorite/biotite-reibeckite/hornblende amphibolites. The augen gneisses are the most voluminous rock type in the study area and host the majority of the U ore. Unweathered samples of this lithology are light to dark-gray and contain a penetrative foliation defined mostly by oriented chlorite and relict biotite. The foliation is cross-cut by both barren and U ore-bearing fracture zones. In shallow core sections (less than approximately 30 m depth below surface) the unweathered (gray), ore-bearing host rocks transition abruptly to partially weathered rock that is pervasively “stained” by secondary Fe(III) mineral coatings (Fig. 3). Although this redox front marks a transition in mineralogy, it does not represent a discontinuity in radioactivity.

In hand sample, the oxidized core is mottled dark red and yellow brown with localized cm-thick zones of black botryoidal coatings that are identified by SEM-EDS and EMP as μm -scale mixtures of Fe and Mn oxides. Petrographic observations indicate that the secondary Fe(III) coatings are pervasive at the μm scale, occurring as 1–10 μm thick films along grain boundaries and along fracture surfaces. Although the Fe(III) stained core sections are partially weathered, they consist of intact, solid rock that retains primary structures such as the gneissic foliation.

Macroscopic examination of the Fe(II)/Fe(III) front in ultraviolet light reveals significant amounts of a strongly fluorescent green to yellow mineral (Fig. 3) that occurs as multi-granular coatings along fracture surfaces and pore spaces. Mineral chemical and XRD data (discussed below) confirm that this fluorescent mineral is a U(VI) phosphate of the meta-autunite mineral group. This phase occurs predominantly in oxidized (Fe(III) hydroxide stained) samples; however, it is also locally detectable (macroscopically) in fractures approximately 1 cm below, on the reducing side of the Fe staining front. The zone of U(VI) phosphate bearing bedrock ranges in thickness from 1 to 5 m and directly overlies the primary ore zone. The oxidized bedrock zone is overlain by a 10–20 m thickness of saprolite and soil.

These more highly weathered horizons also contain secondary U(VI) phosphate minerals and are the focus of on-going research.

5. Petrography and mineral chemistry

5.1. Unoxidized, primary uranium Ore

The Coles Hill primary ore contains 3 distinct U(IV)-mineral assemblages. The oldest and most abundant consists of fine-grained (10–20 μm long) F-rich apatite laths surrounded by thin (0.5–5 μm) rims of cryptocrystalline coffinite. The coffinite was originally identified by XRD analyses performed during exploration of the deposit (Marline Uranium Corporation, 1983). Fracture zones that host this assemblage also contain minor amounts of uraninite, subhedral coffinite, chlorite, Ti oxides and accessory sulfides. The second U(IV) assemblage in the primary ore cross-cuts the apatite-coffinite assemblage and consists of coarse-grained calcite, colloform uraninite, minor coffinite and accessory sulfides. This assemblage is cross-cut by the third U(IV) assemblage which consists of massive Ba zeolite (harmotome), colloform uraninite, coffinite, pyrite, quartz and Ti oxides. All three primary U mineral assemblages are locally cross-cut by barren fracture zones and veins containing barite, quartz or calcite $\pm$ sulfides.

Coffinite is the most abundant U(IV) mineral in the Coles Hill deposit. Compositions of typical coffinites from cores DH174 (28.9 m depth) and DH173 (28.6 m depth) were analyzed by electron microprobe (Table 1). The most variable chemical component within the Coles Hill coffinites is PbO, which ranges from below detection limits (less than approximately 0.1 wt.%) to as high as 3 wt.% in intergrown coffinite/uraninite aggregates. This is an important observation because Finch and Ewing (1992) indicate that the amount of Pb within U(IV) minerals may strongly influence the paragenesis of secondary U(VI) alteration assemblages. For example, they show that secondary U(VI)-Pb hydroxides may facilitate the growth of U(VI) phosphates by offering preferential nucleation sites (e.g. curite to autunite; Finch and Ewing, 1992). However, no uranyl Pb minerals have been identified at the Coles Hill site.

The concentration of P₂O₅ in the Coles Hill coffinites, varies from 0.3 to 4 wt.%, and is positively correlated with CaO suggesting that P₂O₅ is associated with inclusions of primary, ore-stage apatite. This is supported by SEM and SEM-EDS analyses of the primary ore zones (Jerden, 2001). The Coles Hill coffinites also show consistent BaO concentrations of approximately 0.3–0.7 wt.% (analyses by EMP; detection limit approximately 0.1 wt.%). Barium from coffinite and perhaps other sources (e.g. breakdown of Ba-zeolite) appears to have played an important role in the paragenesis of Ba-bearing

ing secondary U(VI) phases that form by oxidation of the primary ore.

5.2. Secondary uranium mineral assemblages

The U(VI) phosphate phase that occurs in oxidized ore-bearing core sections has been identified by XRD, SEM-EDS and EMP as the Ba end member of the meta-autunite mineral group (meta-uranocircite; ideal formula from Gains et al. (1997) is $\text{Ba}[(\text{UO}_2)(\text{PO}_4)]_2(6-8\text{H}_2\text{O})$). A representative heavy mineral separate

(SG > 2.9) sampled 4 cm above the Fe(II)/Fe(III) front (on oxidizing side) in core DH174 was examined by XRD and found to consist mostly of apatite (primary) and Ba meta-autunite (secondary; Fig. 4).

Electron microprobe analyses of representative meta-autunite grains are shown in Table 2. These minerals are compositionally uniform with average concentrations of 57.7 wt.% UO_3 , 15.2 wt.% BaO , and 15 wt.% P_2O_5 . Other cations that define autunite/meta-autunite end members (e.g. Ca, Mg, Sr, K, Pb) were analyzed for, but were below detection limits (less than approximately 0.1

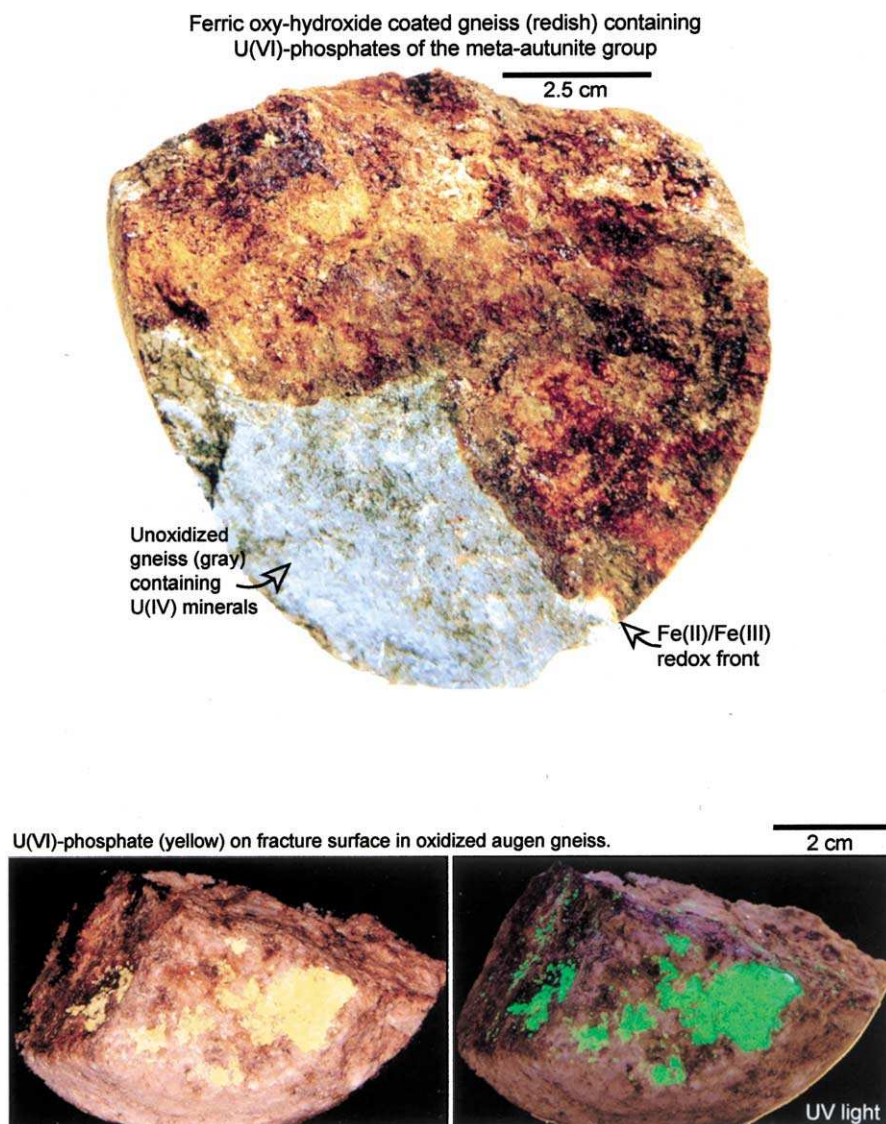


Fig. 3. Hand samples from near the Fe(II)/Fe(III) and U(IV)/U(VI) fronts in host rocks of the Coles Hill U deposit. The top image shows the Fe redox front (sample from DH173, 28.1 m depth) which corresponds to the chemical weathering front where primary chlorite alters Fe(III) oxides + clays and albite alters to kaolinite. The irregular shape of the Fe(II)/Fe(III) interface is caused by variations in grain-boundary permeability. Bottom images are of a typical Ba meta-autunite coating (yellow) on a fracture surface in oxidized U ore. The bottom right image shows the fluorescence color of the meta-autunite in ultraviolet light (core DH174, 27.1 m

Table 1

Electron microprobe analyses of coffinites from the Coles Hill primary ore zone

Wt.% (1)	(2)	(3)	(4)	(5)	Average (6)	(7)		
SiO ₂	17.7	17.6	17.4	17.4	17.2	17.5	10.6	16.1
UO ₂	66.7	69.7	68.1	64.7	67.5	67.4	77.7	64.7
PbO	0.2	<0.1	0.8	0.1	0.2	0.3	0.4	<0.1
CaO	3.3	2.5	2.2	1.5	1.7	2.2	2.7	5.1
P ₂ O ₅	1.1	0.7	0.9	0.4	0.5	0.7	0.3	4.1
BaO	0.6	0.6	0.4	0.7	0.8	0.6	0.4	0.5
Total ^a	89.7	91.2	89.9	84.7	87.9	88.7	92.1	90.5

Ions based on 4 oxygen equivalents

Si	0.99	1.00	1.00	1.05	1.02	1.01	0.71	0.85
U	0.83	0.88	0.87	0.87	0.89	0.87	1.16	0.76
Pb	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01
Ca	0.20	0.15	0.14	0.09	0.11	0.14	0.19	0.29
P	0.05	0.03	0.04	0.02	0.02	0.04	0.02	0.19
Ba	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01

^a Low totals due to water in coffinite structure (USiO₄·nH₂O). ThO₂ is below detection limit of approximately 0.1 wt.%. Samples (1)–(3) from core DH174, 102 m depth, samples (4)–(7) from core DH173, 90 m depth. Relative standard deviations of raw data (calculated from counting statistics) are: 1% for SiO₂ and UO₃; 3–5% for P₂O₅ and CaO; 5–10% for PbO and BaO.

wt.%). When normalized to ideal water content (12 wt.% as H₂O) the composition of Ba meta-autunite from the oxidized bedrock of the Coles Hill U deposit is very similar to synthetic meta-uranocircite II reported by Vochten et al. (1992).

The Coles Hill Ba meta-autunites occur in 3 distinct textural forms that show no compositional differences (Table 2). The observation that the meta-autunite assemblages do not cross-cut or overgrow one another as well as their compositional uniformity suggests that they precipitated during the same event (e.g. oxidation of primary U(IV) ore by oxygenated ground waters). The textural differences may reflect differences in microphysical and micro-chemical Environments in which they formed. For clarity throughout the textural descriptions the distinct Ba meta-autunite forms are designated type I, II, and III. These designations do not imply relative age relationships.

5.2.1. Type I: barium meta-autunite associated with manganese oxide

The most conspicuous Ba meta-autunite form (type I) occurs as 0.5–2 mm long, tabular, euhedral crystals found on open fracture surfaces. They are intimately associated with Ca and Ba bearing Mn oxides (Fig. 5a and 5b). The manganese minerals form 10–30 µm wide, botryoidal aggregates that commonly occur in dendritic growth patterns within the plane of the [001] surface of the meta-autunite. The intimate intergrowth of the Ba meta-autunites and Mn oxides suggests that they formed together as part of the same assemblage.

The composition of the Mn minerals associated with the type I Ba meta-autunites is variable. All EDS analyses of these grains show both Ca and Ba (in varying proportions) in addition to the dominant Mn peak. Some of these spectra also contain distinct peaks of Pb and U, which may be sorbed or co-precipitated with the Mn oxides.

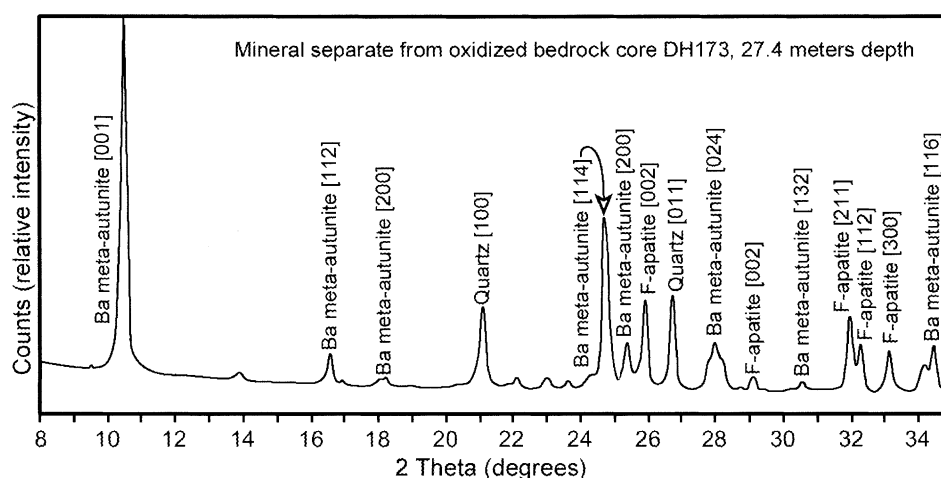


Fig. 4. X-ray diffraction pattern of a representative heavy mineral separate (SG > 2.9) sampled 4 centimeters above the redox front (on oxidizing side) in core DH173, 27.4 meters depth. Mineral and hkl identifications are from International Center for Diffraction Data—JCPDS cards 72–1496 (Ba meta-autunite), 28–0247 (Ca meta-autunite), 83–0557 (Fluor-apatite), 88–2302 (quartz), and 84–0752 (albite). Data collected by Dr. Robert Finch at Argonne National Laboratory.

Table 2

Electron microprobe analyses and mineral formula calculation of Ba meta-autunites from oxidized bedrock associated with the Coles Hill U deposit

Wt. %	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
UO ₃	57.0	57.2	57.9	58.1	57.6	57.9	58.9	58.9
P ₂ O ₅	14.9	15.1	14.9	14.8	14.9	14.4	14.4	14.4
BaO	16.1	15.7	15.2	15.1	15.4	15.5	14.6	14.6
Total ^a	88.0	87.9	88.0	88.0	87.9	87.8	87.9	87.9
<i>Ions based on 12 oxygen equivalents, ignoring interlayer H₂O</i>								
U	1.95	1.95	1.97	1.98	1.96	2.00	2.02	2.02
P	2.06	2.06	2.04	2.04	2.05	2.00	1.99	1.99
Ba	1.03	1.00	0.97	0.96	0.98	0.99	0.94	0.94

^a Total normalized to ideal H₂O. Totals of raw data are not representative due to dehydration of crystals in microprobe vacuum. Oxides CaO, SrO, MgO, Na₂O, K₂O and PbO are below detection limit of approximately 0.1 wt.%. Relative standard deviations of raw data (calculated from counting statistics) are 1% for UO₃; and P₂O₅, and 2–3% for BaO. Samples (1), (4) and (5) are Type I Ba meta-autunite, (2) and (3) are Type II Ba meta-autunite, and (6), (7) and (8) are Type II Ba meta-autunite (see text for description of textural “Types”).

5.2.2. Type II: barium meta-autunite associated with lanthanide phosphate

The type II Ba meta-autunites occur as scaly aggregates of 10–50 µm long, euhedral to subhedral crystals coating fracture surfaces (Fig. 5c and 5d). As shown in Table 2 the type II and type I meta-autunites are compositionally indistinguishable. The difference between these two forms is that the type II crystals are not associated with Mn minerals but are intergrown with a Ca-U-Pb bearing lanthanide phosphate. The lanthanide phosphate occurs in randomly oriented masses of subhedral to euhedral prismatic crystals that are less than a µm wide and approximately 5 µm long.

Locally the lanthanide phosphate occurs as coatings that precipitated on a substrate of Ba meta-autunite, while in other places the type II Ba meta-autunites cross-cuts the lanthanide phosphate. These textural observations suggest that these two phases formed contemporaneously within the same assemblage. The coatings and pore fillings of lanthanide phosphate are closely associated with micro-chemical Environments dominated by primary apatite, suggesting a genetic relationship between these minerals.

Typical EMP and EDS analyses of this lanthanide mineral are shown in Table 3 and Fig. 5 respectively. The negative Ce anomaly (Table 3) may reflect the fact that this mineral precipitated from oxic ground waters from which Ce had been previously fractionated by Ce(IV) oxide precipitation. This lanthanide phosphate averages 2.7 wt.% UO₃ (Table 6) and thus represents another locally important sink for U within the Coles Hill system.

5.2.3. Type III: monomineralic barium meta-autunite in grain-boundary fractures

The type III Ba meta-autunite occurs as anhedral fillings within 1–10 µm wide regions between partially

weathered primary minerals and within 10–50 µm wide pore spaces (Fig. 6). This uranyl phosphate form occurs on quartz, albite and chlorite substrates, is locally associated with secondary barite veins and is pervasive within oxidized apatite rich zones (e.g. Fig. 6b). In these apatite dominated micro-Environments the Ba meta-autunites occur as 5–10 µm thick rims surrounding fine grained fluor-apatite laths.

Electron microprobe imaging at the µm scale (Fig. 7) indicates that even directly adjacent to the apatite laths the Ba meta-autunite shows negligible counts of Ca. The thickness and textural style of these rims of U(VI) phosphate are nearly identical to the rims of coffinite that occur around apatite grains within the unoxidized primary ore. This observation suggests that the meta-autunite might have replaced the coffinite, and that the scale of U redistribution (e.g. transport distance) during oxidation was on the order of millimeters to centimeters within these zones.

6. Petrography of secondary phases from primary ore alteration experiments

Four weeks after the initiation of the ore alteration experiments the primary coffinite showed clear signs of pitting, cracking and alteration to secondary U(VI) phases (Fig. 8). The pitting is interpreted as a dissolution feature while the cracking is likely caused by a volume change brought about by oxidation of U on the near-surface of the coffinite crystals. The secondary minerals are 1–5 µm in diameter, have tabular, tetragonal or pseudo-tetragonal crystal forms and grow in book-like aggregates consisting of thin (< 1 µm) sheets stacked perpendicular to the C-axes. These grains show strong green fluorescence and EDS patterns consistent

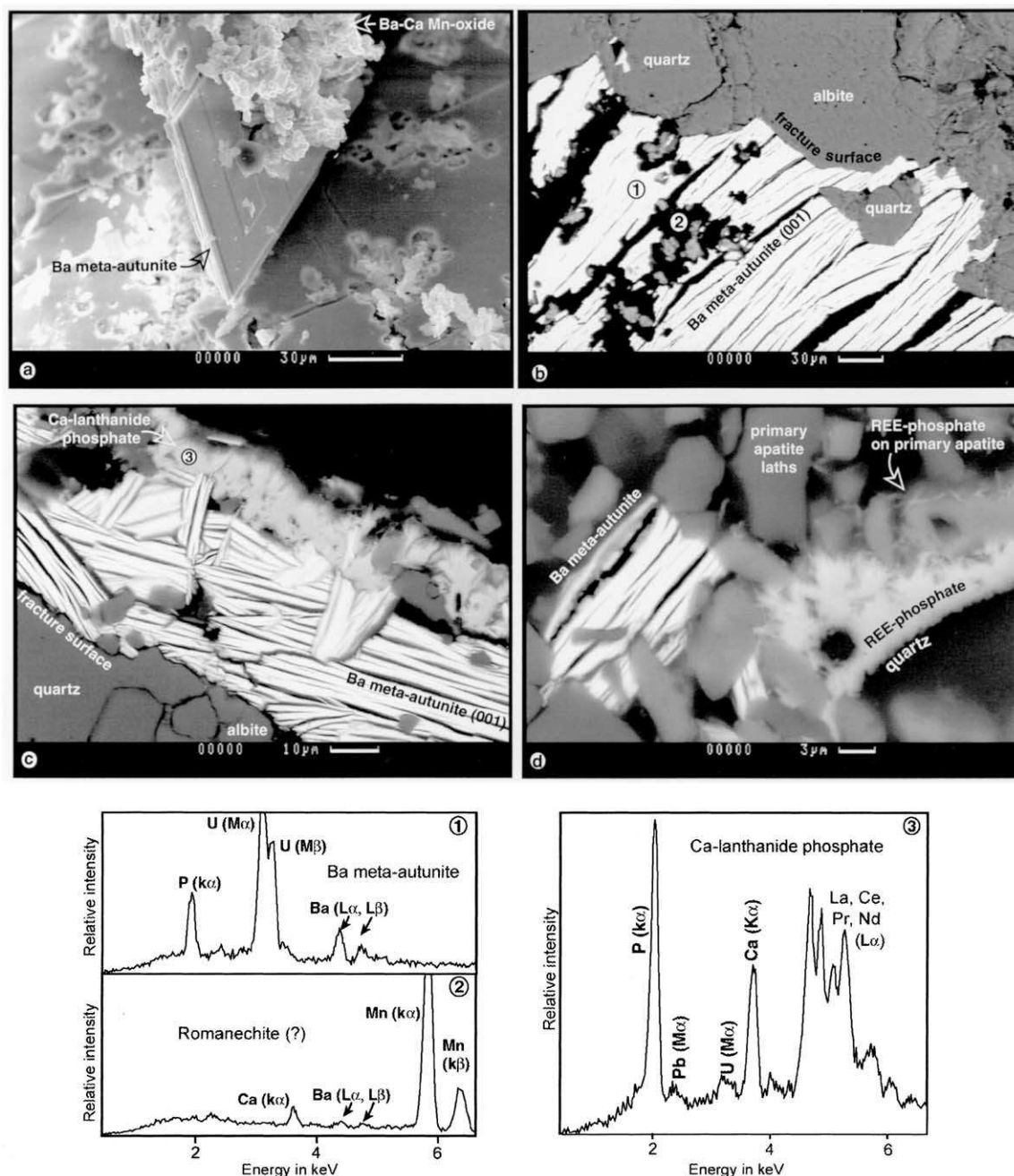


Fig. 5. Electron images and energy-dispersive X-ray spectra (EDS) of the Type I and Type II Ba meta-autunite assemblages. (a) Scanning electron image of euhedral Ba meta-autunite crystal associated with Mn-oxides (sample from core DH173, 26 m depth). (b) Back scatter electron (BSE) image of a polished section cut across a Ba meta-autunite coated fracture surface (sample from DH174, 27 m depth). U(VI) phosphate and Mn-oxide are identified by EDS numbers 1 and 2. (c) BSE profile of Ba meta-autunite coating a fracture surface within the host rock quartz-feldspar gneiss. The Ba meta-autunite is overgrown by a Ca-rich lanthanide phosphate (REE-phosphate) identified by EDS number 3 (sample from core DH174, 25.5 m depth). (d) BSE profile showing Ba meta-autunite and REE-phosphate associated with primary, ore-stage apatite. Note micro-crystals of REE phosphate on surface of apatite lath (sample from core DH174, 25.5 m depth).

Table 3

Electron microprobe analyses of lanthanide phosphate associated with Type II Ba meta-autunite, Coles Hill U deposit^a

Wt. %	(1)	(2)	(3)	(4)	(5)	(6)	(7)	Average
P ₂ O ₅	27.8	27.8	28.3	28.3	28.5	28.7	29.6	28.4
La ₂ O ₃	18.8	20.0	19.7	19.6	20.1	20.6	20.9	20.0
Ce ₂ O ₃	18.3	18.1	16.7	17.2	16.	15.8	16.6	17.1
Pr ₂ O ₃	4.6	4.8	4.6	4.6	4.4	4.8	4.6	4.7
Nd ₂ O ₃	6.9	7.7	7.7	7.6	7.4	7.6	7.9	7.5
Yb ₂ O ₃	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CaO	5.3	5.1	5.4	4.9	6.0	5.1	5.0	5.3
PbO	2.2	2.1	2.1	2.0	1.9	2.2	2.1	2.1
UO ₃	2.6	2.7	2.6	2.6	2.7	2.8	3.0	2.7
Total:	86.5	88.4	87.1	86.8	87.7	87.8	89.7	87.7
(Ce _N /Ce _N) ^b	0.45	0.42	0.40	0.41	0.40	0.36	0.38	0.40

^a (N) value normalized to average chondrite of Evensen et al. (1978).

^b Monitor of the size of the negative Ce anomaly, calculated by dividing Ce_N by an interpolated Ce value obtained by (La_N + Pr_N)/2. Relative standard deviations of raw data (calculated from counting statistics) are: 1–2% for P₂O₅; 2–3% for CaO, La₂O₃, Ce₂O₃ and Nd₂O₃, and 4–6% for other elements. Low totals are due to lack of data for other lanthanides and the possible presence of *n*H₂O. All analyses from core DH174, 25.5 m depth.

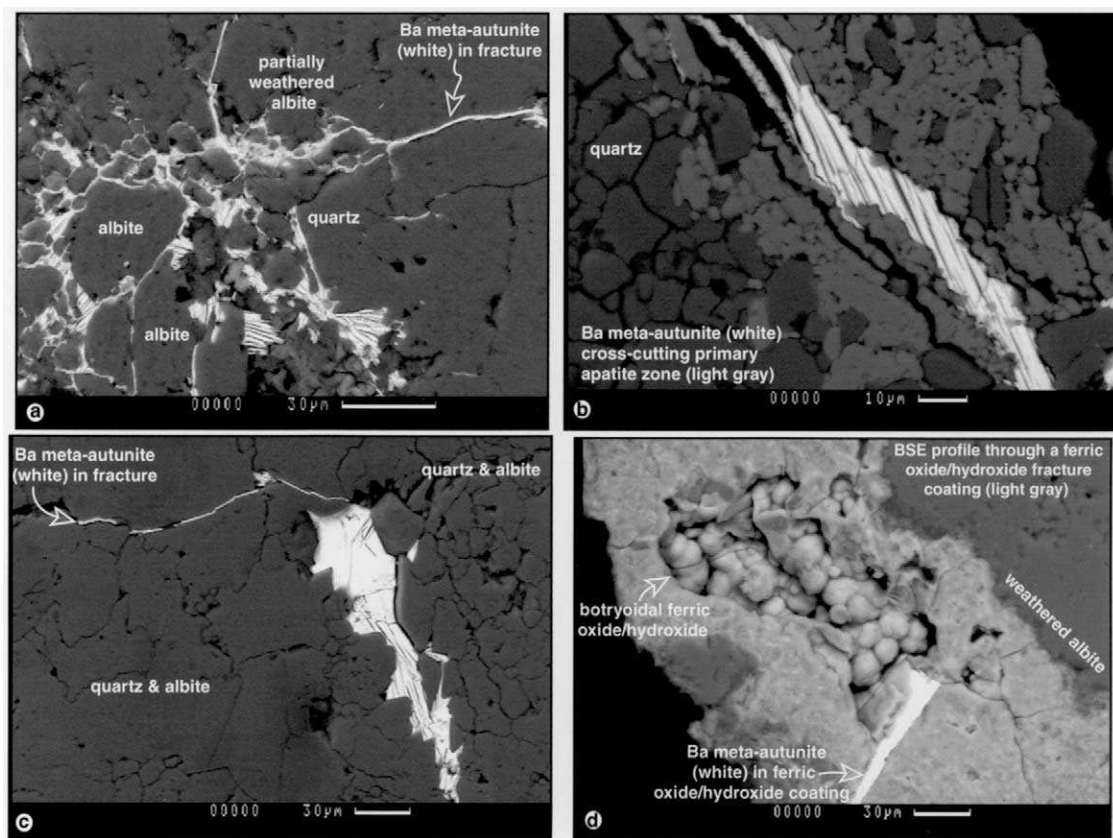


Fig. 6. Backscatter electron images of polished sections showing the Type III Ba meta-autunite assemblage. (a) Ba meta-autunite filling in grain boundaries between weathered primary minerals (mainly albite) (sample from core DH172, 26 m depth). (b) Fracture filled with Ba meta-autunite within primary, ore-stage apatite zone (sample from core DH173, 27.4 m depth). (c) Mono-minerallic occurrence of Ba meta-autunite within an open pore space and fracture in quartz-feldspar gneiss host rock (sample from core DH173, 27 m depth). (d) Ba meta-autunite grain within Fe (III) oxide/oxyhydroxide fracture coating (sample from core DH174, 27 m depth).

with autunite or meta-autunite group minerals. Although reaction rates for granular samples (250–300 μm grains) such as those used in these tests will be accelerated relative to field conditions these experiments suggest that, for highly fractured zones with high fluid/rock ratios the rate of coffinite alteration to secondary U(VI) phosphates may occur on a time scale of weeks. These results are thus applicable to the meta-autunite bearing samples from the Coles Hill oxidized bedrock, as most of them come from highly fractured zones that retain the cataclastic structure of the primary ore.

7. Whole rock geochemistry

Whole rock samples from above and below the redox front have similar average major element compositions. Averages for major elements Na_2O , SiO_2 , K_2O , Fe_2O_3 , and LOI (estimate of total volatiles) for the unoxidized and oxidized sample groups are given in [Tables 4 and 5](#) respectively. Sample DH173, 28 m depth was excluded

from the average of the oxidized samples because it contains an unusually large amount of Ba meta-autunite. This sample is important, however, because it represents a geochemical signature dominated by the U(VI) minerals.

The whole rock chemical data suggest minimal mass or volume change across the redox front, because elements shown to behave in a conservative manner during chemical weathering (e.g. Ti, Zr; [Krauskopf, 1967](#), [Nesbitt and Wilson, 1992](#)) show no significant change in bulk concentration across the redox front ([Tables 4 and 5](#)).

7.1. U concentration profiles across the iron and uranium redox transition zone

In unoxidized samples U content varies from 138 to 1030 ppm with an average of 565 ppm, while the oxidized samples range from 305 to 3070 ppm with an average of 575 ppm (excluding the unusually U rich sample, DH173, 28 m depth from average). Uranium concentrations show significant variations within

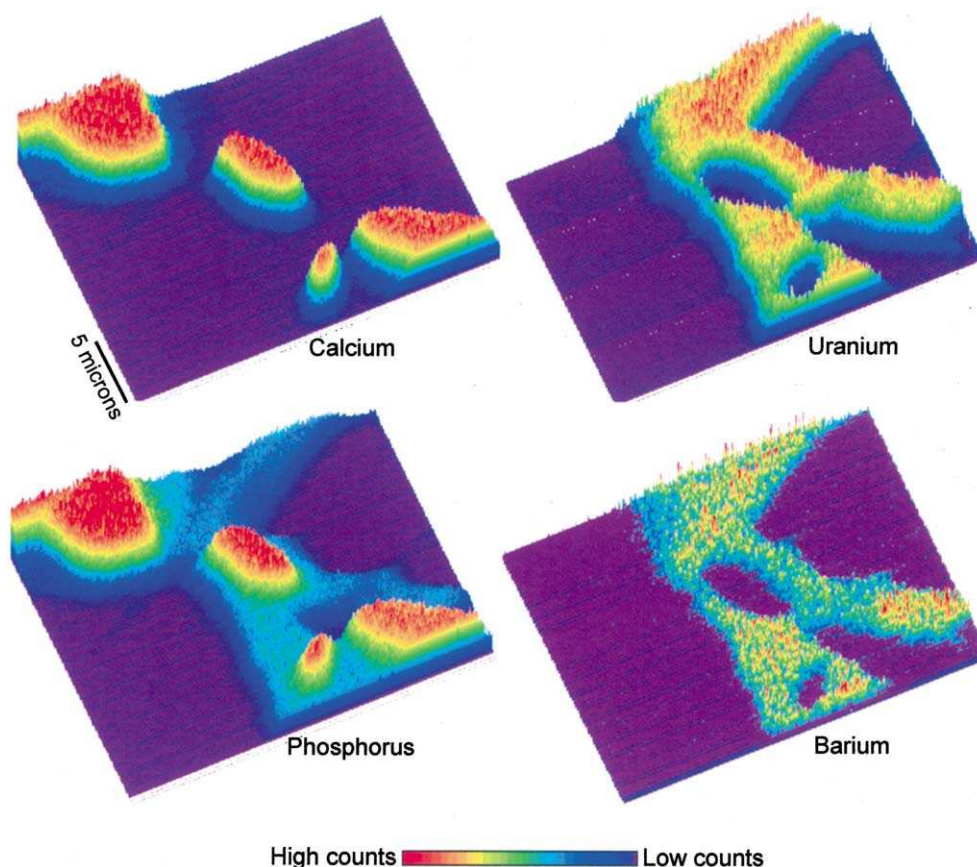


Fig. 7. Electron microprobe X-ray maps of Ba meta-autunite surrounding primary apatite grains. The apatite crystals show up as “islands” on the Ca image. Note that even directly adjacent to the apatite grains the U(VI) phosphate is of the Ba end-member (e.g. no Ca-autunite detected).

individual depth profiles (Fig. 9); however, these variations are not systematically related to the location of the redox front. This result coupled with petrographic observations indicates that the variations in U reflect spatial heterogeneity of both primary and secondary U bearing assemblages. For example, sample DH173, 28 m depth which was obtained from approximately 15 cm above the redox front (oxidized side) in core DH173, contains over 3000 ppm U and is characterized by a localized abundance of fractures coated with Ba meta-autunite. On average, U is not significantly depleted or enriched across the Coles Hill oxidation fronts. This suggests that a minimal amount of U is removed during oxidation of the primary ore.

7.2. Barium, calcium, phosphorus and Iron concentration profiles across the redox transition zone

The average Ba concentrations for the two sample groups are: 422 ppm for unoxidized samples and 974

ppm for oxidized samples (excluding sample DH173, 28 m depth). This enrichment in Ba above the redox front is most dramatic in core DH174 where the concentration varies from 200 ppm below the front to values ranging from 450 to 1500 ppm in oxidized samples (Fig. 9). This trend may be explained by the precipitation of the Ba meta-autunite and secondary barite which locally occurs as fracture coatings on the oxidized sections of core. The Ba enrichment trend is not as clearly defined in core DH173, possibly due to a higher percentage of the hydrothermal barite and Ba-zeolite below the redox front.

The concentration profiles of Ca and P show more significant variations than other key elements (Fig. 9). This indicates that spatial variations in the amount of the primary ore-stage apatite assemblage controls the concentrations of these elements in these cores. The minor decoupling of the CaO, and P₂O₅ profiles in core DH174 (particularly at 29 m depth) suggests that higher proportions of non-apatite bearing primary ore

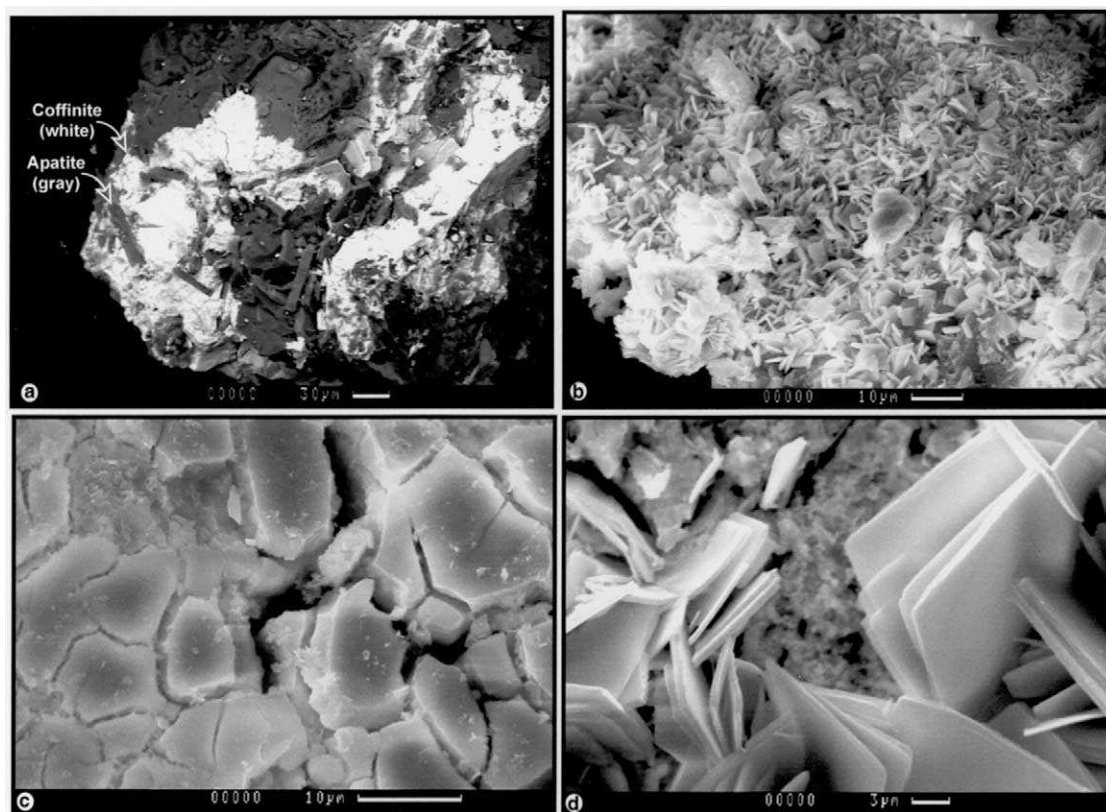


Fig. 8. Electron images of samples from the batch alteration experiments. (a) BSE image of a grain of unreacted Coles Hill primary ore. White material is coffinite, gray material is mostly apatite with minor albite and quartz. Note lath shaped apatite surrounded by coffinite on left side of grain. (b) Secondary electron image of an ore grain that has been reacted with Coles Hill ground water (sample (1) On Table 6) for 38 days. The surface of the primary grain is nearly completely coated with secondary U(VI) phosphate. (c) Secondary electron image of the surface of a coffinite grain reacted with Coles Hill ground water for 28 days. Cracking may be due to volume change of surface layers during U(IV)/U(VI) transition. (d) Secondary electron image showing enlarged view of secondary U(VI) phosphates (tabular grains) on pitted coffinite surface (background in center of image).

assemblages are present in this section such as calcite-uraninite veins.

The Fe concentration profiles show variations from 0.5 to 3.0 wt.% $\text{Fe}_2\text{O}_{3(\text{total})}$ (Fig. 9). These variations are not systematically related to the location of the redox

front, suggesting that Fe variability is primarily determined by spatial heterogeneity of primary Fe minerals in the reduced samples (e.g. chlorite, biotite) and fracture coating Fe(III) oxyhydroxides in the oxidized samples.

Table 4

Whole rock geochemistry of unoxidized samples of Coles Hill U ore^a

	DH 174	DH 174	DH 174	DH 173	DH 173	DH 173	DH 172	DH 172	Average
Depth (m)	30.8	29.0	28.4	29.0	28.7	28.4	28.0	27.7	
Na_2O	8.2	8.8	9.1	7.4	7.3	8.1	9.0	9.5	8.4
MgO	0.9	0.7	0.6	0.6	0.9	0.8	0.8	0.5	0.7
Al_2O_3	16.3	16.8	16.5	13.7	14.5	15.8	17.1	17.3	16.0
SiO_2	64.3	65.4	67.2	52.7	68.2	63.9	66.9	62.7	63.9
P_2O_5	1.4	1.5	1.1	8.5	1.1	1.1	0.3	1.8	2.1
K_2O	0.2	0.1	<0.1	0.2	0.1	0.1	0.2	0.2	0.1
CaO	3.0	2.6	2.0	11.8	2.8	4.0	1.0	2.9	3.8
TiO_2	0.5	0.4	0.2	0.4	0.5	0.4	0.5	0.3	0.4
MnO	0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
$\text{Fe}_2\text{O}_{3(\text{total})}$	3.1	2.4	1.8	2.2	2.7	2.8	2.9	1.9	2.5
LOI	2.3	1.4	1.6	1.9	2.1	3.0	1.6	1.5	1.9
Total	100.2	100.1	100.3	99.5	100.3	100.1	100.2	98.6	99.9
Ba	164.5	196.3	126.1	171.9	790.9	1150.0	232.2	543.0	421.9
U	138.2	521.0	211.2	706.4	1030.0	955.5	496.3	459.9	564.8

^a Oxides in wt.%, Ba and U in ppm. Sample names indicate drill core identifications (DH174, DH173 and DH172 on Figs. 1 and 2) followed by sample depth in meters. Based on 9 standard runs, the short-term precision (repeatability) of the whole rock data are as follows (given as percent relative standard deviation): 1% for Na_2O , MgO , Al_2O_3 , SiO_2 , K_2O , CaO , TiO_2 ; and $\text{Fe}_2\text{O}_{3(\text{total})}$, 2% for P_2O_5 and MnO , and 5% for Ba and U. The long-term accuracy (percent deviation) for these data is estimated to range from –5 to 5%.

Table 5

Whole rock geochemistry of oxidized samples of Coles Hill U ore^a

	DH 174	DH 174	DH 173	DH 173	DH 173	DH 173	DH 172	DH 172	Average
Depth (m)	27.1	24.7	28.0	27.7	27.4	27.1	27.4	27.1	
Na_2O	8.2	8.4	5.6	8.8	8.5	8.2	8.2	8.5	8.0
MgO	0.4	0.3	0.5	0.4	0.3	0.7	0.6	0.5	0.5
Al_2O_3	16.1	16.5	12.1	16.7	16.0	16.3	15.8	16.6	15.8
SiO_2	68.2	64.9	75.6	65.3	61.7	63.1	68.3	64.4	66.5
P_2O_5	0.7	1.9	0.9	1.8	4.1	2.1	1.2	2.1	1.9
K_2O	0.2	0.1	0.6	0.2	0.1	0.2	0.1	0.1	0.2
CaO	1.0	2.9	1.2	2.5	5.7	3.0	1.9	2.8	2.6
TiO_2	0.5	0.4	0.4	0.4	0.2	0.4	0.5	0.5	0.4
MnO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
$\text{Fe}_2\text{O}_{3(\text{total})}$	2.8	2.2	1.5	2.4	1.6	3.5	2.3	2.6	2.3
LOI	2.0	2.0	2.0	1.9	1.8	2.6	1.6	2.1	2.0
Total	100.1	99.7	100.3	100.5	100.0	100.1	100.5	100.1	100.2
Ba	447.0	1530.0	1340.0	1120.0	666.5	909.5	862.4	916.6	974.0
U	304.9	474.9	3070.0	452.1	1210.0	717.1	336.2	528.0	574.7

^a Oxides in wt.%, Ba and U in ppm. Sample names indicate drill core identifications (DH174, DH173 and DH172 on Figs. 1 and 2) followed by sample depth in meters. Based on 9 standard runs, the short-term precision (repeatability) of the whole rock data are as follows (given as percent relative standard deviation): 1% for Na_2O , MgO , Al_2O_3 , SiO_2 , K_2O , CaO , TiO_2 ; and $\text{Fe}_2\text{O}_{3(\text{total})}$, 2% for P_2O_5 and MnO , and 5% for Ba and U. The long-term accuracy (percent deviation) for these data is estimated to range from –5 to 5%.

8. Uranium mineral stability and aqueous speciation

8.1. Uranium content of ground waters and solubility data used for geochemical assessment

The chemistry of filtered (0.45 μm) ground waters from the shallow bedrock and overlying saprolite associated with the Coles Hill north orebody are shown in Table 6. All filtered samples from the Coles Hill north orebody contain less than $15 \mu\text{g l}^{-1}$ dissolved U, which is lower than the US-EPA (2000) maximum contaminant level of $30 \mu\text{g l}^{-1}$. This suggests that Ba meta-autunite is effective at immobilizing U within the present-day hydrologic system. To further investigate this U fixation process ground water data were used to assess both the solid and aqueous speciation of U.

The 3 ground water analyses shown in Table 6 are considered representative of the range of compositions found in the zone of interest. Ground water data reported in this paper are supported by 85 analyses performed by the Marline Uranium Corporation (1983) as

part of an environmental baseline study of the area. This baseline study reported no U concentrations greater than $15 \mu\text{g l}^{-1}$ (Marline Uranium Corporation, 1983) and concentrations of major cations and anions were similar to those measured for the current study (see Table 6 for comparison). This suggests that the ground water chemistry for the Coles Hill bedrock is not widely variable from year to year (samples taken in 1983, 1999, 2000 and 2001) and thus supports the claim that the ground water chemistry reported in Table 6 is representative of the zone of interest. Furthermore, no major seasonal variations were noted in the ground water chemistry. A water sample from the saprolite aquifer overlying the north orebody (sample (1), Table 6) is included in this analyses because, as shown by Marline Uranium Corporation (1983), waters from this zone recharge the bedrock aquifer. The DH2 sample is representative of oxygenated recharge water (up to 8 mg l^{-1} dissolved O_2) that interacts with the primary ore near the Fe(II)/Fe(III) front.

For mineral stability assessments the activities of ions in solution were calculated using the “Geochemists

Table 6

Selected ground water analyses from the weathered zone overlying the Coles Hill north ore body^a

	(1)	(2)	(3)
Date sampled	June 7 2001	August 8 1999	July 25 1983
Field T ($^{\circ}\text{C}$)	14.3	15.6	17.0
Field pH	5.9	6.0	6.0
Field DO (ppm)	8.0	4.1	–
<i>Major constituents (mg l⁻¹)</i>			
Na ⁺	10.2	12.2	14
Mg ²⁺	0.7	4.2	2.3
SiO ₂ (aq) (as Si)	16.3	16.1	–
K ⁺	0.3	0.1	0.4
Ca ²⁺	3.0	17.1	8.7
CO ₃ ²⁻ + HCO ₃ ⁻	24.1	25.1	23
SO ₄ ²⁻	4.9	8.0	5
Cl ⁻	3.1	10.0	3.4
<i>Selected minor & trace constituents ($\mu\text{g l}^{-1}$)</i>			
Al ³⁺	26.6	2.0	< 500
Mn ⁴⁺	12.0	4.2	29
Fe ³⁺	30.3	78.4	64
Ba ²⁺	331.7	682.7	260
UO ₂ ²⁺ species (as U)	5.0	13.9	13
NO ₃ ⁻ (as N)	210	300	230
F ⁻	170	370	–
PO ₄ ³⁻ (as P)	120	105	320

^a (1) is ground water from saprolite aquifer (from well adjacent to 41–173, see Fig. 2), (2) is ground water from residential well tapping oxidized bedrock zone. This analysis is used for speciation and mineral stability calculations, (3) is ground water from oxidized bedrock zone sampled and analyzed by the Marline Uranium Corporation (1983). Based on 270 standard runs, the precision (percent relative standard deviation) and percent accuracy (listed respectively) of the ground water data are as follows: Na⁺ = 9.5, –6.8; Mg²⁺ = 8.1, –2.1; SiO₂(aq) = 9.0, –5.0; K⁺ = 8.3, 1.1; Ca²⁺ = 10.1, –4.0; Al³⁺ = 9.2, –4.2; Mn⁴⁺ = 9.5, –5.0; Fe³⁺ = 13.6, 3.3; Ba²⁺ = 8.3, 1.0; and UO₂²⁺ = 15, 1.1. The precision for all anions is 2% and accuracy is within 85–115% recovery of spiked samples.

Workbench” software package which employs an extended form of the Debye-Huckle equation (Helgeson, 1969). The thermodynamic database used for U speciation calculations is based on the Nuclear Energy Agency, critical review by Grenthe et al. (1992) with specific additions for phases and species of interest. Where possible additions to the database were made based on measured solubility or stability constants (log K values) as this method minimizes errors introduced from combining solubility data from different sources

(Nordstrom et al., 1990). Species and minerals added in this manner include aqueous complex $\text{UO}_2(\text{OH})_2(\text{aq})$ from Silva (1992), Ba meta-autunite from Vochten et al. (1992), and Mg autunite and Na autunite, both from Magalhaes et al. (1985). The solubilities of other phases added to the data base were calculated using reported free energy of formation values for the minerals and the auxiliary species used by Grenthe et al. (1992). The minerals added in this way are autunite (Ca end member) from Viellard and Tardy (1984), and uranophane

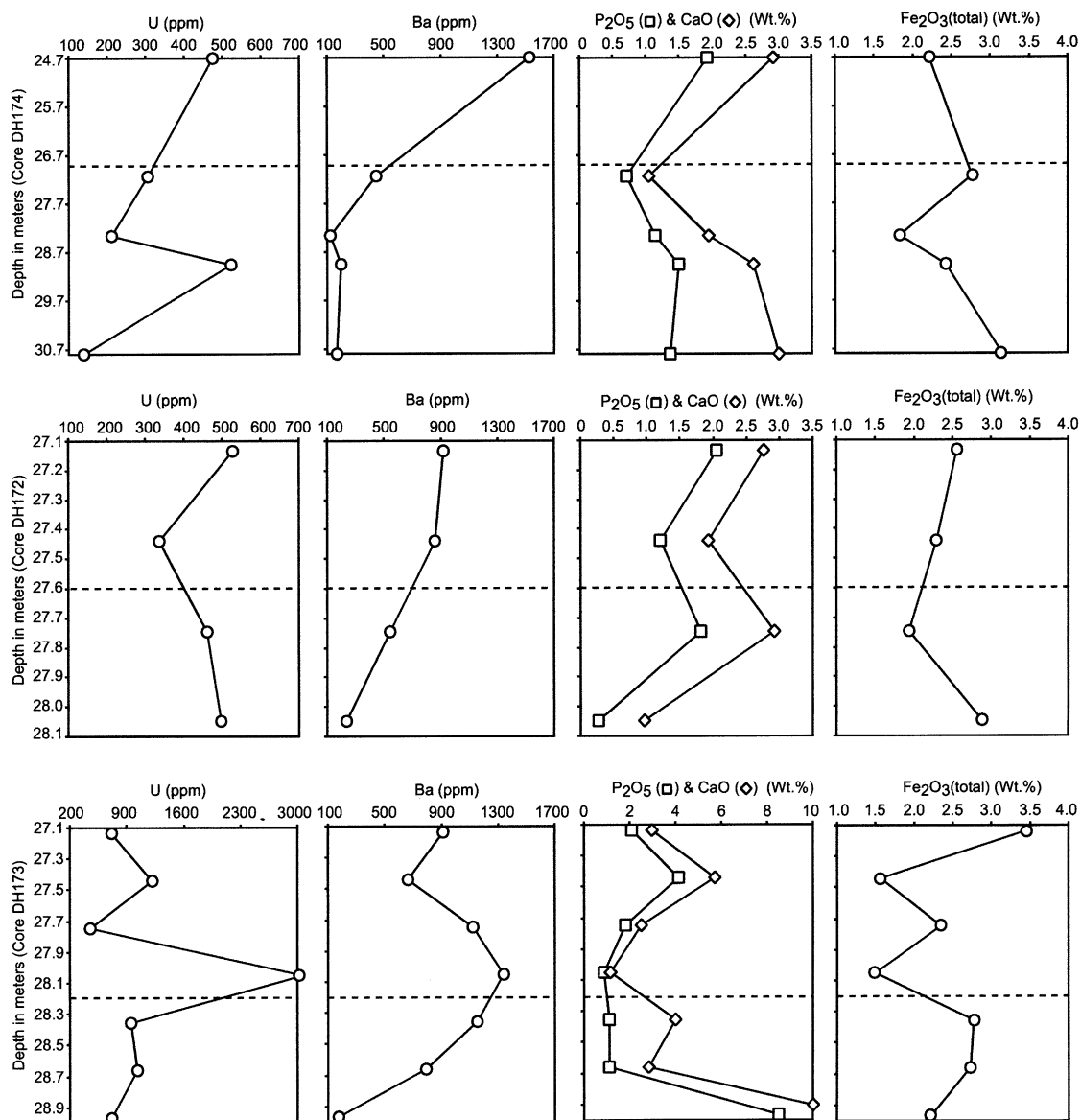


Fig. 9. Whole rock U depth profiles within the core sections under investigation. The dotted lines indicate the locations of the Fe(II)/Fe(III) redox fronts. The fluctuations noted in these profiles are due to differences in primary U concentrations (e.g. localization of primary ore zones) and/or by centimeter scale redistribution of U associated with the growth of Ba meta-autunite on fractures and grain boundaries.

from Chen et al. (1999). Solubility and stability constants for all other minerals and aqueous species are from Grenthe et al. (1992).

8.2. Eh–pH assessment and activity ratio of dissolved phosphate to carbonate

The Eh–pH stability field of Ba meta-autunite and the estimated reaction path required to produce the observed assemblage is shown in Fig. 10 a. The diagram is plotted for a $\text{CO}_2(\text{g})$ fugacity of $10^{-2.0}$, which gives total dissolved carbonate concentrations ($\text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}$) closely matching those measured for Coles Hill ground waters (e.g. 25 mg l^{-1} dissolved carbonate at pH 6.0). The diagram illustrates that for Coles Hill ground water, the stability field of Ba meta-autunite spans from a pH of 4.8–7.3. At lower pH values uranyl phosphate complexes are prevalent while at higher pH values uranyl carbonate species are dominant. For lower total carbonate values such as $\text{CO}_2(\text{g})$ fugacity of $10^{-3.5}$ the Ba meta-autunite field expands to pH 8.1 and part of the uranyl carbonate field is replaced by the U(VI) silicate uranophane. Although ground waters in the Triassic basin have pH values as high as 7.8 (Marline Uranium Corporation, 1983), no uranyl silicate minerals have been found within the study area.

The estimated reaction path on Fig 10a illustrates that, for Coles Hill ground water, the transition from coffinite to Ba meta-autunite occurs at an Eh of approximately 100 mV which closely corresponds to the transition from Fe(II) to Fe(III). These Eh–pH estimates are in accord with the field observation that the Fe(II)/Fe(III) front occurs within a few centimeters of the uranous/uranyl transition (coffinite/meta-autunite). The association of type I Ba meta-autunite with Mn oxides implies that the Eh for this assemblage may have been as high as 700 mV suggesting that the redox gradient preserved in these rocks involved highly oxidizing conditions.

In addition to the master variables Eh and pH, U speciation in this type of system is fundamentally influenced by the relative amounts of dissolved phosphate and carbonate. This is illustrated by plotting U speciation on a diagram of log activity $[(\text{HPO}_4)^{2-}/(\text{HCO}_3)^-]$ vs. pH (Fig. 10b). For water with a U activity of $10^{-7.3}$ (typical of Coles Hill shallow ground water) the lower stability limit of Ba meta-autunite will range from a phosphate/carbonate activity ratio of approximately $10^{-4.0}$ at pH 5 to approximately $10^{-2.7}$ at pH 7.5. At ratios below these limits U is predicted to be in solution as a uranyl carbonate complex. These observations are in general agreement with Byrne et al. (1990) who show that phosphate complexes are dominant when $(\text{HPO}_4)^{2-}/(\text{HCO}_3)^-$ is greater than 10^{-3} .

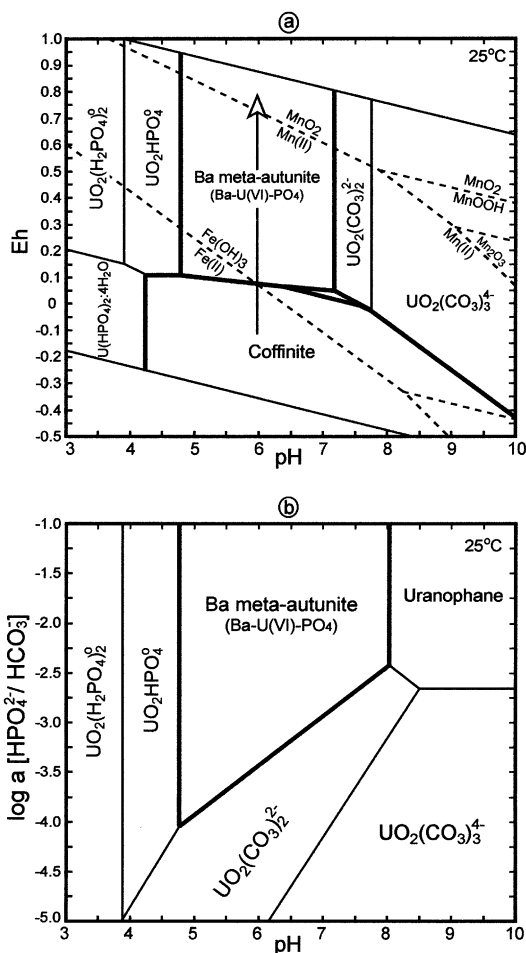


Fig. 10. Activity diagrams showing the stability field of Ba meta-autunite. Activities used for these plots, as well as the speciation models (Fig. 11), were calculated from measured ground water chemistry (sample (2), Table 6): $\text{SiO}_2(\text{aq}) = 10^{-3.2}$, $\text{Na}^+ = 10^{-3.2}$, $\text{Ca}^{2+} = 10^{-3.4}$, $\text{Mg}^{2+} = 10^{-3.8}$, $\text{K}^+ = 10^{-5.5}$, $\text{Ba}^{2+} = 10^{-5.4}$, $\text{U} = 10^{-7.3}$, $\text{Cl}^- = 10^{-4}$, $\text{SO}_4^{2-} = 10^{-4.2}$, $\text{F}^- = 10^{-4.7}$, $\text{NO}_3^- = 10^{-4.2}$, $\text{HPO}_4^{2-} = 10^{-5.5}$, $\text{fCO}_2(\text{g}) = 10^{-2.0}$ (for Fig. 10a) and $\text{O}_2(\text{aq}) = 10^{-3.7}$ (for Fig. 10b). The sources of solubility data used are discussed in text. (a) Eh–pH diagram for the Coles Hill ground water system showing estimated reaction path (based on mineralogical observations) during oxidation of the primary ore (Eh in Volts). (b) Diagram showing U(VI) mineral stability as a function of the activity ratio of dissolved phosphate to carbonate vs. pH.

8.3. Uranium mineral saturation and aqueous speciation

Uranium mineral saturation indices ($\text{SI} = \log_{10}[\text{ion activity product/solubility product of mineral}]$) and speciation of dissolved U were calculated from a representative ground water sample (Sample (2), Table 6) and plotted as a function of pH (Fig. 11). This speciation model is calculated assuming a constant $\text{CO}_2(\text{g})$ fugacity

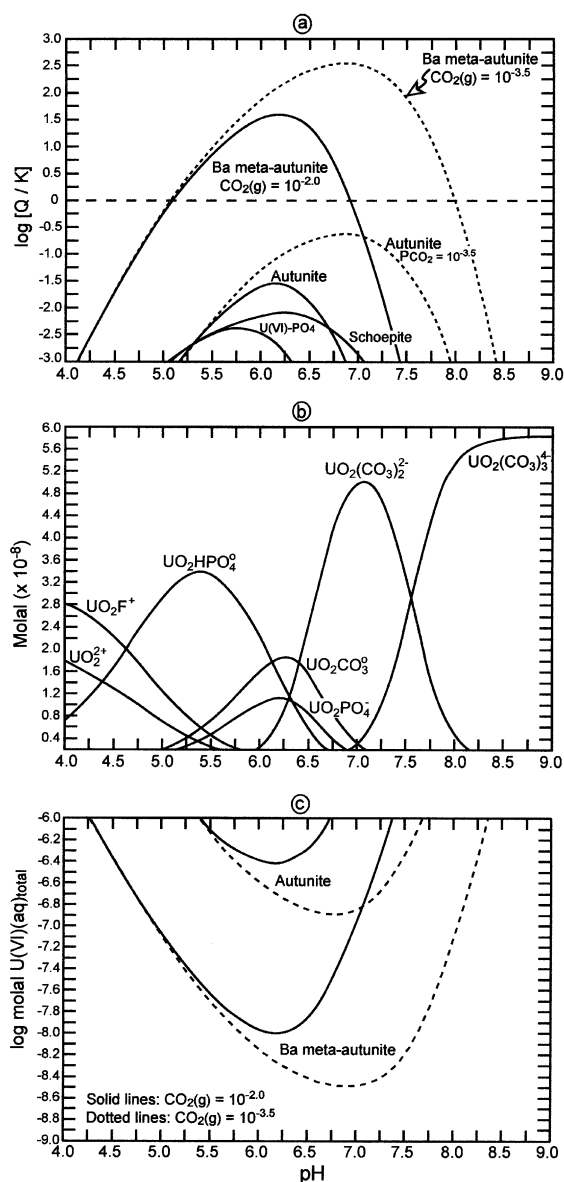


Fig. 11. Speciation diagrams for ground water from the shallow bedrock zone associated with the Coles Hill north orebody. The water composition used to produce these diagrams is sample (2) in Table 6. (a) Solid phase speciation diagram showing saturation indices for potentially important U minerals plotted as a function of pH. The ground water is supersaturated with respect to Ba meta-autunite. Solid lines are plotted for $\text{PCO}_2(\text{g}) = 10^{-2.0}$ and dotted lines for $\text{PCO}_2(\text{g}) = 10^{-3.5}$. (b) Aqueous speciation for the same ground water sample showing the importance of uranyl phosphate and uranyl carbonate complexes within the pH range of interest (6–7). (c) Modeled solubility of Ba meta-autunite and Ca-autunite in Coles Hill ground water. This plot compares the extent to which these minerals may limit the amount of U available for transport in this type of environment. Sodium and Mg autunites have solubilities similar to Ca-autunite in this system.

of $10^{-2.0}$ which is in accord with measured ground water values. At pH less than 4.7 the model predicts that UO_2F^+ and UO_2^{2+} are the most important U complexes with the uranyl phosphate $\text{UO}_2\text{HPO}_4(\text{aq})$ dominating from pH 4.7 to 6.2. Above a pH of 7.0 the dissolved carbonate concentration increases to greater than 100 mg l^{-1} resulting in the formation of stable uranyl carbonate species.

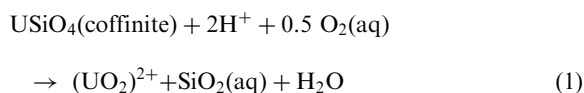
Ground water from the oxidized bedrock zone is supersaturated with respect to Ba meta-autunite with a maximum SI of 1.6 at a pH of 6.2 (Fig. 11b). The ground water is undersaturated with respect to other uranyl phases, with the U(VI) phosphates Na-autunite, Ca-autunite and Mg-autunite being the least undersaturated (SI of approximately -1.5 at pH 6.2). The speciation model thus agrees with mineralogical observations.

The solubility of Ba meta-autunite and other U(VI) phosphates were calculated over the pH range 4–9 (Fig. 11c) to constrain the extent to which these minerals may limit U transport in the Coles Hill ground waters. This calculation indicates that over the pH range 5–7 Ba meta-autunite limits dissolved U concentrations from $19 \text{ } \mu\text{g l}^{-1}$ (-7.1 log molal) at pH 5 to $24 \text{ } \mu\text{g l}^{-1}$ (-7.0 log molal) at pH 7.0 with a minimum solubility of $3 \text{ } \mu\text{g l}^{-1}$ (-7.9 log molal) at pH = 6.2. However, if Ba meta-autunite were kinetically inhibited from forming or if there was not enough Ba to reach saturation, this model predicts that U concentrations would increase to $93 \text{ } \mu\text{g l}^{-1}$ (-6.4 log molal) if controlled by Ca autunite (Fig. 11c). U concentrations of around $95 \text{ } \mu\text{g l}^{-1}$ were predicted for Na and Mg autunite in this system. It is possible however that, in the absence of barium meta-autunite, U concentrations would never reach levels high enough to become saturated with respect to other autunite minerals due to sorption onto iron and manganese oxides (e.g. Langmuir, 1978; Hsi and Langmuir, 1985).

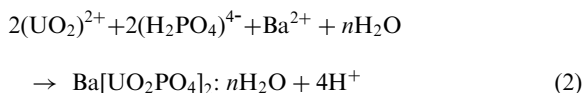
9. Discussion

The extent of U dispersal into the environment surrounding the Coles Hill deposit depends on the competing rates of advective transport by ground water and sequestration by precipitation of U(VI) phosphates. If the rate of U incorporation into the low solubility U(VI) phosphate minerals is relatively rapid then U may be effectively immobilized.

The process by which U is released into ground water through oxidation and dissolution of the primary Coles Hill ore can be represented by the following reaction:



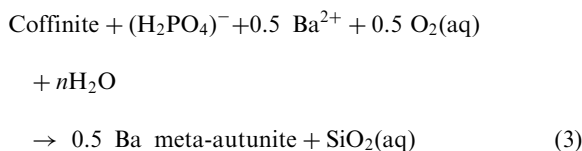
The process by which U is removed from ground water and incorporated into the oxidized rock reservoir involves both precipitation of secondary U(VI) minerals as well as U(VI) sorption onto secondary mineral coatings and clays. The precipitation process can be represented by the following reaction:



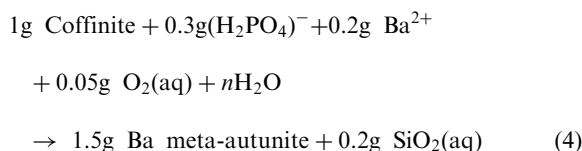
The kinetics of coffinite dissolution are not well understood, however, the batch alteration experiments suggest that the transition from coffinite to secondary U(VI) phases, specifically Ba meta-autunite, may occur within 4–5 weeks in highly fractured zones with high fluid/rock ratios.

Results of hydrologic studies by the [Marline Uranium Corporation \(1983\)](#), indicate that the average hydraulic conductivities for the weathered and unweathered bedrock aquifers are 40 m/a and 18 m/a respectively. These rates of ground water movement are sufficiently slow that U dissolved during coffinite alteration should be locally retained within the U(VI) phosphates that form.

The net alteration reaction of coffinite at the Coles Hill U deposit can thus be represented by the following reaction:



Recasting this reaction in terms of grams shows that for every gram of coffinite reacted 1.5 g of Ba meta-autunite are produced:



Possible sources of phosphate are primary ore-stage fluor-apatite and the coffinite grains themselves, which consistently contain over 0.5 wt.% P_2O_5 (present in lattice or as inclusions; [Table 1](#)). An important source of Ba may be the Ba-zeolite (harmotome) associated with the primary ore. Another possible source of Ba is the primary coffinite, which contains over 0.3 wt.% BaO ([Table 1](#)). Some Ba may have been transported to the Coles Hill site by ground water, as some local ground waters contain up to $800 \mu\text{g l}^{-1}$ dissolved Ba ([Marline Uranium Corporation, 1983](#)).

9.1. Redox front formation and rate of migration

A schematic diagram summarizing processes acting within the Coles Hill U and Fe redox transition zone is shown in [Fig. 12](#). The sharpness of the Fe redox front in the Coles Hill cores ([Fig. 3](#)) suggests that, like the U redox reactions, the Fe redox transition occurs rapidly relative to transport rates of the reacting species. The Fe redox front forms as primary chlorite alters to Fe(III) hydroxides and an Fe rich clay mineral (vermiculite?). This process is represented in the whole rock data by the depletion in Mg in samples from the oxidized zone.

The rate of Fe redox front propagation is thus dominantly influenced by the rate of chlorite weathering, whereas the propagation of the zone containing secondary U(VI) minerals, is determined by the kinetics of weathering of the coffinite-apatite ore. This may explain why the U(VI) phosphate assemblages locally occur in fractures approximately 1 cm below (on unoxidized side of) the Fe redox front. If the rate of Fe(III) release from chlorite weathering is slower than the rate of $(\text{UO}_2)^{2+}$ and $(\text{H}_2\text{PO}_4)^-$ release from near-by coffinite-apatite zones, then secondary U(VI) phosphates may nucleate and grow while chlorite alteration to Fe(III) oxides lags behind. This mechanism accounts for both macroscopic and microscopic characteristics of the Coles Hill redox front.

The rate of migration of the redox front is estimated based on weathering rates calculated by [Pavich et al. \(1985\)](#) and [Pavich \(1986\)](#). Using measurements of

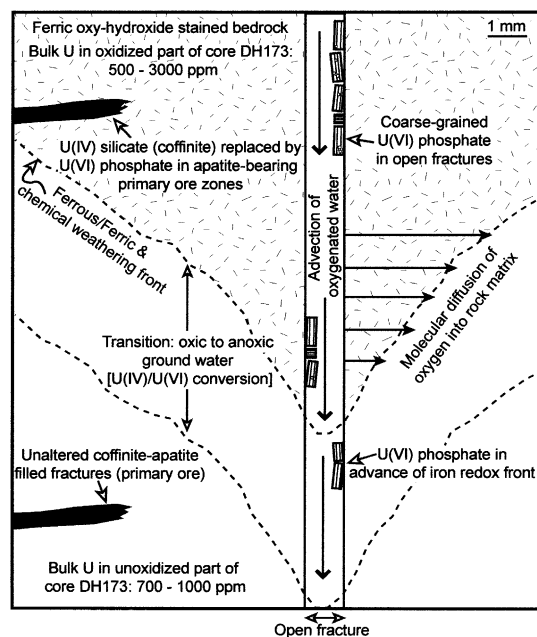


Fig. 12. Schematic diagram illustrating processes responsible for the redistribution and natural immobilization of U in the shallow bedrock overlying the Coles Hill U deposit.

dissolved solids in stream base-flow Pavich (1986) calculated a minimum rate of saprolite production of 4 m/Ma for a weathering profile developed over quartzofeldspathic crystalline rocks in the Virginia Piedmont. A maximum saprolite production rate of 20 m/Ma for the same area was calculated using measurements of cosmogenic ^{10}Be inventories of saprolite/soil cores (Pavich et al., 1985). For upland weathering profiles in the Piedmont, such as Coles Hill, the rate of saprolite production corresponds to the rate at which the chemical weathering front descends into unweathered bedrock (Pavich, 1986). At the Coles Hill site the chemical weathering front corresponds to the Fe redox interface where chlorite alters to $\text{Fe}(\text{OH})_3$ + clay and albite alters to kaolinite.

Thus, using the maximum rate of weathering front migration of 20 m/Ma and assuming that the age of the present redox interface is approximately zero, it is estimated that a sample collected from 1 m above the redox interface (e.g. sample DH 173, 27.1 m depth) has resided in an oxidizing environment for approximately 50 ka. This age estimate increases to approximately 250 ka assuming the slower weathering rate. Thus, Ba meta-autunite present in the oxidized bedrock zone may have been stable for time scales on the order of hundreds of thousands of years (Fig. 13).

9.2. Implications for phosphate based remediation of uranium

This study suggests that phosphate-based strategies for the in situ stabilization of U in oxidizing, fluid rich

Environments may be effective for long-term containment. The sorption of U by phosphate-based materials such as bone-char and apatite minerals is well established (e.g. Murray et al., 1983; Naftz et al., 1999; Conca et al., 1999; Bostic et al., 2000; Fuller et al., 2002), the present observations complement this work by focusing on the role of secondary phosphate mineral precipitation in a relatively undisturbed natural system. It is shown that phosphate amendments such as apatite may alter to form low solubility (10^{-8} molal) uranyl phosphate crystals that may be stable for hundreds of thousands of years. The use of phosphate amendments may initially immobilize U through sorption; however, over time U may eventually be incorporated into stable crystalline phases such as autunite or meta-autunite group minerals through alteration of the apatite additives. As shown at the Coles Hill site, this process may produce, in situ, a geologically robust waste form that is appropriate for the long-term stabilization of U.

10. Conclusion

Geochemical data from the Coles Hill U deposit indicates that there is minimal loss of U from the deposit during oxidation and incipient chemical weathering of the primary U(IV) ore. Petrographic and mineral chemical data (EMP, SEM-EDS, XRD) shows that the dominant process responsible for U retention is the precipitation of low solubility U(VI) phosphate (Ba meta-autunite). The physical characteristics (i.e. grain

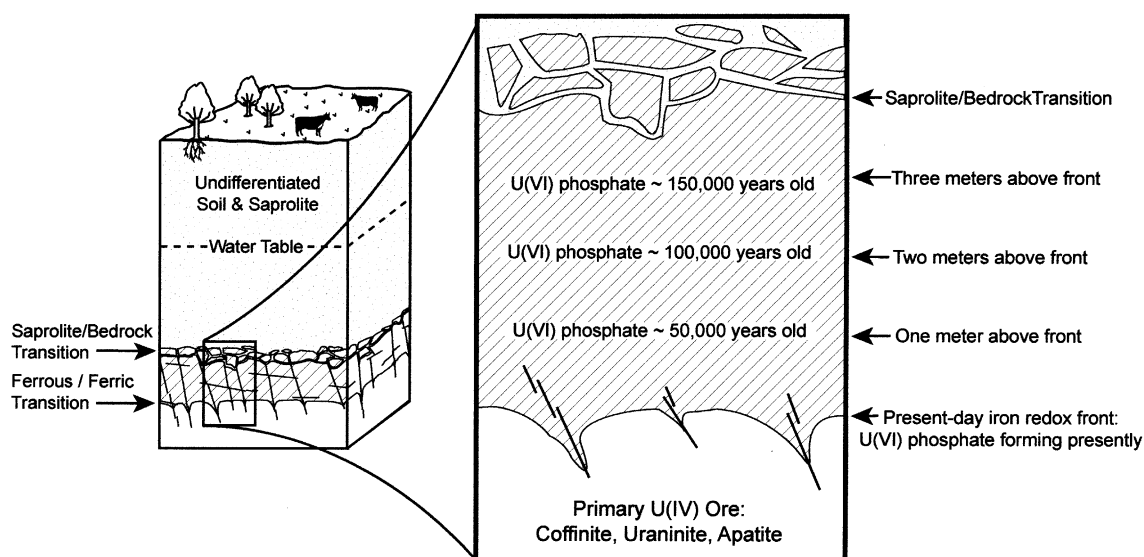


Fig. 13. Generalized column through the weathered zone overlying the Coles Hill U deposit. The diagram summarizes the estimated ages of the Ba meta-autunite (U(VI) phosphate) present in the oxidizing bedrock aquifer. Ages were estimated assuming a rate of downward migration for the redox front of 20 meters per million years (representative maximum rate for the Virginia Piedmont from Pavich, 1989).

size, and growth habit) and mineral associations of the Ba meta-autunites depend on the micro-environments in which they form.

The chemistry, mineral saturation state and aqueous speciation of waters from the oxidizing bedrock aquifer indicate that the low solubility of stable U(VI) phosphate minerals can limit U concentrations to less than $15 \mu\text{l}^{-1}$. The phosphate precipitation process is facilitated by high phosphate activities (e.g. $10^{-5.5}$) relative to dissolved carbonate, in oxic, slightly acidic ($\text{pH} \sim 6$) conditions.

Experimental results suggest that the rates of U(IV) oxidation to U(VI) and subsequent precipitation of uranyl phosphate phases occurs on a time scale of weeks and that these secondary U(VI) phases are stable for tens to hundreds of thousands of years. The Coles Hill U deposit therefore demonstrates the natural long-term attenuation of U within an oxidizing apatite-rich environment, and thus lends confidence to the use of apatite-based technologies for U remediation and containment.

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