Characteristics of Cu and U-V Deposits in the Paradox Basin (Colorado Plateau) and Associated Alteration

Isabel F. Barton,^{1,2,†} Mark D. Barton,^{2,3} Jon P. Thorson⁴

¹ Present affiliation: Department of Mining and Geological Engineering, University of Arizona, 1235 E. James E. Rogers Way in Tucson, Arizona 85721

> ² Lowell Institute for Mineral Resources, 1235 E. James E. Rogers Way Room 209, Tucson, Arizona 85721

³ Department of Geosciences, University of Arizona, Tucson, Arizona 85721 ⁴Consulting Geologist, 3611 South Xenia Street, Denver, Colorado 80237

Introduction

The complex, 300-m.y. evolution of the Paradox Basin featured numerous paleofluids of diverse types. Their flow through rocks, and interactions with each other and with the rocks, created zones of alteration and mineralization that are still visible today. Studying these provides valuable insights into the processes of paleofluid flow and rock alteration, not only in the Paradox Basin, but in basinal systems worldwide.

This article presents some preliminary geological and mineralogical descriptions of altered $(\pm \text{ mineralized})$ areas that we will visit on the field trip and discusses their implications for the nature, timing, and effects of paleofluid flow in the Paradox Basin. This work is part of an ongoing study of paleofluids in the Paradox Basin, so all results presented here are preliminary and are necessarily incomplete. For geologic and geochemical background, the reader is referred to the introductions by Jon Thorson (2018) and Mark Barton et al. (2018). Figure 1 provides a schematic overview of the stratigraphy and the stratigraphic distribution of some of the alteration and mineralization features we will see on the field trip.

Methods

Rock descriptions are based principally on polished thin sections made from hand samples taken during fieldwork in the summers of 2016 to 2018. Thin sections were examined using transmitted- and reflected-light petrography, a JEOL 6010LA benchtop scanning electron microscope, and a Gatan MonoCL4 panchromatic cathodoluminescence spectrometer. Hand samples were examined using an ASD FieldSpec Pro short-wave infrared spectrometer and TSG's Spectral Assistant software. The electron microprobe used to analyze U-V minerals was a Cameca SX100. Field-based remote infrared scans were performed by Headwall Photonics using a Micro-Hyperspec (400–2500 nm) system mounted on a DJI Matrice 6000 Pro drone. Data from the field scans were reduced with Headwall Photonics SpectralView software on a demo license at the University of Arizona.

[†]Corresponding author: e-mail, fay1@email.arizona.edu



Fig. 1. Schematic stratigraphic column of the Pennsylvanian through Cretaceous strata of the Paradox Basin, showing the (equally schematic) distribution of bleaching and mineralization at the sites of interest on this field trip.

Formulas of Ore and Related Alteration Minerals

ankerite, $CaFe(CO_3)_2$ aurichalcite, (Zn,Cu)5(CO3)2(OH)6 azurite, Cu₃(CO₃)₂(OH)₂ barite, BaSO₄ bornite, Cu₅FeS₄ carnotite, $K(UO_2)_2(VO_4)_{2^+} \cdot 3H_2O$ chalcocite, Cu₂S chalcophyllite, Cu₁₈Al₂(AsO₄)₄(SO₄)₃(OH)₂₄·36H₂O chalcopyrite, CuFeS₂ chalcotrichite, Cu₂O clinoclase, Cu₃(AsO₄)(OH)₃ coffinite, USiO₄ · nH₂O conichalcite, CaCu(AsO₄)OH cornwallite, Cu₅(AsO₄)₂(OH)₄ covellite, CuS cryptomelane, KMn₈O₁₆ cuprite, Cu₂O digenite, Cu₉S₅ djurleite, Cu₃₁S₁₆ dolomite, $CaMg(CO_3)_2$ enargite, Cu₃AsS₄ fluorapatite, Ca₅(PO₄)₃F galena, PbS greenockite, CdS greigite, Fe₃S₄ hematite, Fe₂O₃ illite, K_{0.65}Al₂[Al_{0.65}Si_{3.35}]O₁₀(OH)₂ ilmenite, FeTiO₃

jarosite, KFe₃(SO₄)₂(OH)₆ kaolinite, Al₂Si₂O₅(OH)₄ luzonite, Cu₃AsS₄ lyonsite, $Cu_3Fe_4(VO_4)_6$ mackinawite, Fe₉S₈ malachite, Cu₂CO₃(OH)₂ montmorillonite, (Na,Ca)_{0.33}(Al,Mg)₂ Si₄O₁₀(OH)₂ · nH₂O montroseite, (V,Fe)OOH mottramite, PbCuVO₄OH olivenite, Cu₂AsO₄OH pyrite, FeS₂ pyrolusite, MnO₂ roscoelite, K(V,Al)₂[AlSi₃O₁₀](OH)₂ rutherfordine, UO₂CO₃ siderite, FeCO₃ tangeite, CaCu(VO₄)OH tennantite, (Cu,Zn,Fe)₁₂As₄S₁₃ tenorite, CuO tivanite, VTiO₃(OH) tyrolite, Ca₂Cu₉(AsO₄)₄CO₃(OH)₈ · 11H₂O tyuyamunite, $Ca(UO_2)_2(VO_4)_2 \cdot 6H_2O$ uraninite, UO₂ uranophane, Ca(UO₂)₂(Si₃OH)₂·5H₂O uvanite, $U_2V_6O_{21}$ · 15H₂O vesignieite, BaCu₃(VO₄)₂(OH)₂ volborthite, Cu₃(V₂O₇)(OH)₂·2H₂O wulfenite, PbMoO₄

Bleaching Alteration

The conversion of normally red rocks to white or grayish-green colors is a widespread feature of the Colorado Plateau. Recognized relatively early on (e.g., Keller, 1929), it is most noticeable in sandstones such as the White Rim (uppermost Cutler), Wingate, Navajo, Entrada, Salt Wash, and sandstones in the Burro Canyon (Fig. 1). In more clay-rich units, bleaching most often turns the rock from red or purplish to gray-green rather than white. Examples of this are widespread in the Chinle, most commonly in and around riparian facies, and local bleaching is also observed in the Hermosa Group and in the Kayenta formation. Bleaching alteration is ubiquitous in rocks that host Cu and U-V deposits and was identified in the 1950s as a prospecting criterion for U mineralization (e.g., Wright, 1955; Thorson, writ. commun., 2016).

Not all light-colored rocks on the Colorado Plateau have been bleached. The sandstone in the Cretaceous Dakota Formation, for instance, is white, and has been since it was deposited. The prevailing explanation for this is that shortly after they were deposited, the Dakota sands were buried by a thick layer of the Mancos shale, and never underwent the repeated wet-dry cycles that gradually break down detrital ilmenite, magnetite, and mafic silicates to hematite (Walker, 1976, 1989). Absent this diagenetic reddening, the Dakota sandstones remained white.

There are two main types of bleaching alteration (Fig. 2). In the first type, Fe^{3+} existing as hematite is converted to Fe^{2+} as Fe sulfide or carbonate, disseminated through the rock or as nodules. In the second type, Fe^{3+} existing as hematite is dissolved, reduced to Fe^{2+} , and carried out of the rock. Iron may be





completely conserved, in the first type, or almost quantitatively removed, or partly lost if the bleaching process is a combination of the two types. Iron in silicates may or may not be affected. A few cases are known of Fe^{3+} in biotite being reduced during the reductive type of bleaching, turning the biotite grain a green color and probably starting its transformation into smectite or chlorite. Less intense reductive bleaching does not reduce Fe in silicates, and bleaching by Fe removal generally leaves Fe in silicates intact. For this reason, quantitative removal of Fe during bleaching is rare in siltstones and shales. Bleaching clay-rich hematitic rocks results in a green color because it removes the hematite intermixed with the clay, which provides most of the red color, and Fe^{2+} is a green chromophore in silicates. Thus, a fluid may remove Fe from a sandstone but leave most of the Fe intact in the underlying shale. Both types of bleaching can be associated with the dissolution of carbonates. Kaolinite is the dominant clay mineral in both red and bleached rocks, and no consistent changes in clay mineralogy have been observed accompanying bleaching.

The different types of bleaching probably reflect different reducing agents. Any reducing fluid could dissolve hematite by converting Fe³⁺ to Fe²⁺. In the absence of CO_3^{2-} or S²⁻, Fe²⁺ is generally soluble and would remain in the fluid, being transported out of the system. If the reducing fluid contained H₂S (e.g., a sour gas) or H₂CO₃, the released Fe²⁺ would immediately saturate the fluid in pyrite, pyrrhotite, ankerite,

or siderite, which would then precipitate. Known reducing fluids include liquid and gaseous hydrocarbons, methane, H₂S, CO₂-rich groundwaters, and hydrothermal fluids equilibrated with reduced rocks. All of these are known or inferred to have been present in the Paradox Basin and produced disparate types of bleached rocks throughout (Beitler et al., 2003; Loope et al., 2010; Whidden et al., 2014).

Bleaching in Action: The Sinbad Seep (Stop 2-7)

The Sinbad anticline is home to the Sinbad seep, an active geochemical system that is analogous to the ones that bleached large volumes of sandstone throughout much of the Paradox Basin in the past. An H_2S -bearing brine, likely related to hydrocarbons in the Paradox formation, bubbles up along the salt wall to the surface amid an outcrop of lower Cutler red bed sands. Where the red beds contact the sulfide-bearing water, they turn gray to black, weathering yellow when exposed again under the air. The black shales of the Paradox Formation are also exposed near the seep and consists of a dark, fine-grained and decemented rubble stained white on the surface by recent gypsum formation.

The Cutler in this area is a red siltstone to coarse sandstone with an arkosic composition, dominated by quartz but rich in clays, mica, albitic plagioclase, and K-feldspar and containing accessory detrital zircon and fluorapatite. The micas include both biotite and muscovite and the biotite is noticeably titaniferous. Plagioclase and K-feldspar commonly show intergrowth and replacement textures. Barite, almost devoid of Sr, is also present but textural evidence suggests an authigenic origin. The detrital grains are poorly sorted and subrounded, some having mildly ragged edges. The cement is typically a mixture of clays and carbonate, mainly dolomitic although in one sample the carbonate cement consisted of calcite rims overgrowing euhedral dolomite cores. Neither calcite nor dolomite had detectable Mn, and both had about 0.1-0.2 atom% Fe. The carbonates are fine grained but well crystallized and form euhedral rhombs that overgrow detritral grains. In the unbleached parts of the Cutler rocks, fine-grained hematite is intermixed with the clay cement. Submillimeter-wide veinlets of quartz crosscut the rock fabric, many of them incorporating detrital mica grains. Crystals in the quartz veins typically display slightly undulose extinction.

The bleaching by H_2S in the Sinbad seep leaves the rock with several vol % pyrite (Fig. 3). Most of the pyrite forms euhedral to subhedral crystals disseminated through the rock, some of which grow on the edges of detrital grains and others of which replace detrital oxides. Pyrite also commonly forms thin rims, some with colloform textures, around the edges and cleavage planes of biotite and muscovite. Analyses by SEM-EDS indicated that the pyrite is within error of stoichiometric FeS₂. A bladed habit indicates that a few of the crystals may be marcasite or pseudomorphs of marcasite, but cubes were more frequently observed. Most of the pyrite had no trace metals detectable by SEM-EDS, but a few analyses showed slight enrichment in Cu (<0.3 at. %).

The bleaching is of the purely reductive type, conserving Fe. Whole-rock analysis of paired samples of red and bleached Cutler from the same bed determined the Fe₂O₃ contents at 3.49% for the red rock and 3.42% for the bleached equivalent (J. Thorson, unpub. data). A detailed SEM analysis makes it doubtful whether any of the Fe was even locally remobilized, since the occurrence patterns of pyrite in the bleached rocks mimic those of hematite in the red ones. Extremely fine-grained pyrite is mixed with the clay cement in the bleached rocks and with hematite in the red ones. No framboids were observed. Figure 3 shows a polycrystalline grain from a bleached Cutler siltstone, which consists of intergrown pyrite and rutile. Based on the textures, the grain was probably once detrital ilmenite that was replaced by hematite and rutile during diagenetic reddening, and recent bleaching has since converted the hematite to pyrite. Similar examples were observed in many of the bleached samples from the Sinbad seep.

Although pyrite was the only Fe sulfide observed in the bleached Cutler at the Sinbad Seep, it may not represent what is actually precipitating in the H_2S -rich water there. In most sedimentary and lowtemperature diagenetic environments, direct nucleation of pyrite is rare and the phase that initially precipitates is iron monosulfide (FeS) or mackinawite (Fe₉S₈), which ripen into pyrite through a series of redox and diffusive steps in the presence of aqueous sulfide. Wilkin and Barnes (1996) give an overview of the formation processes of pyrite in the low-temperature environment. None of the precursor minerals



Fig. 3. Petrographic characteristics of bleached and red Cutler in the Sinbad seep. A: unbleached, red Cutler in reflected light, showing the mixture of hematite and clay that acts as cement and the paucity of distinct hematite grains (UT18-228426). B: Bleached, pyritized Cutler in reflected light, showing pyrite rims around detrital quartz and pyrite replacing the hematite that (along with rutile) replaced a detrital ilmenite grain (UT18-228425). C: SEM photomicrograph showing fine-grained disseminated pyrite (bright grains) in bleached Cutler (UT180228427).

they mention was observed in this study, but it is possible that the ripening process was already complete in all of the samples examined.

The pyritization of the Cutler in the Sinbad seep is analogous to reductive bleaching processes that have affected many of the red beds in the Paradox Basin, and represents some of the ground preparation that enables a sandstone to trap Cu (see Thorson and MacIntyre, 2005; Barton, 2018; Thorson, 2018). For example, the Wingate is extensively bleached with pyritization in La Sal Creek Canyon and the Paradox salt anticline, and the sandstones of the Burro Canyon formation are pyritized around Lisbon Valley. The bleaching processes in both cases would have been chemically similar to the processes going on at the Sinbad Seep, although they may not have been exposed at the land surface and the sulfide that originally precipitated may not have been pyrite.

The analogy between the modern Sinbad seep and the preparation of the Wingate to trap Cu is evident within a kilometer or two of the seep. The Copper Rivet mine is visible on the western wall of the canyon across the road. Mineralization here is present in and near a NE-striking, subvertical fault zone with about 30 m normal displacement. Most ore is in the lower Wingate but a few other units in the section show minor mineralization in areas where they are bleached close to the fault. Reported primary ore minerals are chalcopyrite, bornite, and luzonite, now mainly replaced by chalcocite (Fischer, 1936). Mineralization probably took place when a Cu-bearing fluid entered an area pyritized like the system at the Sinbad Seep, and Cu sulfides precipitated at the sulfide trap. We will see several better examples of this two-stage bleaching and mineralization process on this trip, starting with the Cashin and Cliffdweller mines.

Wingate-Hosted Copper (Stop 2-10)

Sometimes collected into the "La Sal district," the Cashin and Cliffdweller mines are two small deposits of copper with accessory silver, hosted in the Jurassic Wingate formation. Intermittent mining between 1896 and 1946 produced a total of 1.8 M lbs. Cu and 425,000 oz. Ag from average ore grades of 4% Cu and 18.5 opt Ag (Mach, 2006). The Cashin deposit still contains copper reserves estimated at 62.4 M lbs Cu (Mach, 2006). There are no current estimates for the mineralization remaining in the Cliffdweller. The vast majority of ore minerals occur in the Wingate sandstone, which is about 80 m thick in the area. Minor, probably uneconomic mineralization is also found in the underlying Chinle and the overlying Kayenta, mainly in fractures. All strata are within a few degrees of horizontal in the La Sal district.

Two small faults, the Cashin and the Cliffdweller, dominate the distribution of bleaching and mineralization. These are normal faults with about 15 m of displacement and roughly meter-wide damage zones. The Cliffdweller trends about 020° (dip 70° E), the Cashin about 040° (dip 65° NW). The largest splay of the Cashin fault, called the Michigan fault, roughly parallels the Cliffdweller, and much of the mineralization at the Cashin deposit occurs where the Michigan fault intersects the Cashin fault. Deformation bands and veins of barite and dolomite are prominent features of the Wingate sandstone close to these faults and decrease in frequency with distance away from them.

Bleaching is pervasive and affects all stratigraphic units within the fault zones. With distance from the faults, bleaching decreases rapidly in the less permeable strata; a few hundred meters away from the faults, the Kayenta and Chinle are unbleached except for the few meters adjoining their contacts with the Wingate (Fig. 4). In the Wingate itself, bleaching persists over the entire thickness of the unit for several kilometers. This Wingate bleaching extends about 1 km southeast from the Cashin fault and about 4 km northwest of the Cliffdweller fault, an asymmetry that suggests that the bleaching fluid flowed roughly north (Thorson and MacIntyre, 2005; MacIntyre, 2008). The bleaching is mainly of the Fe-reducing type, having left the sandstone impregnated with fine disseminated pyrite and abundant nodules of pyrite up to 10 cm in size. These can be seen at several places in roadcuts on the highway leading into the Paradox anticline, and the nugget effect they cause is the principal reason no whole-rock analyses of bleached versus unbleached Wingate have been performed in this study. Average Fe content of the unbleached Wingate, however, is around 1%, and visual estimates of pyrite abundance suggest that bleaching cannot have removed much of this, indicating that bleaching is of the reducing type (MacIntyre, 2008). In addition to the pyrite, globules of bitumen and hydrocarbon-bearing fluid inclusions have both been



Fig. 4. Distribution of bleaching (sulfidization) and Cu mineralization in relation to the Cashin fault. Modified from MacIntyre (2008).

reported from the Wingate near the Cashin fault, implicating hydrocarbons as the bleaching fluids (Carter and Gualtieri, 1965; MacIntyre et al., 2004; Thorson and MacIntyre, 2005).

The host Wingate sandstone is mainly a quartzarenite, but in some beds has enough feldspar and clay to be classified as a subarkose. Large-scale crossbedding is generally visible at the outcrop to hand sample scale but is not evident in thin section. Grains are subrounded to well-rounded and are well-sorted. In unbleached, red Wingate, cement is not common and porosity is > 10%, but where cement is present it is typically dolomite or clay (MacIntyre, 2008) and surrounds the tiny grains of hematite that fringe detrital grains and give the rock its red color. In bleached Wingate, cements are typically similar but less abundant, and the fringing hematite grains are absent. Overgrowths of euhedral quartz on detrital quartz grains are common in both red and bleached Wingate in the area (MacIntyre, 2008; this study). These overgrowths, and the detrital grains, commonly feature ragged edges in both bleached and unbleached sandstone, probably reflecting corrosion, and quartz grains are found sutured together in some samples. Trace heavy-mineral constituents include magnetite and ilmenite, which are partly replaced by hematite and rutile in both bleached and unbleached areas. The main petrographic differences caused by bleaching of the Wingate are the absence of hematite and the presence of pyrite and of small bits or globules of an opaque, brownish-black substance tentatively identified as bitumen (MacIntyre, 2008; I. Barton, unpub. data). These globules occur in interstices between detrital grain and are similar in size and occurrence to the hypogene Cu minerals. Clays present in both bleached and unbleached rocks are dominantly kaolinite and illite, with minor smectite (MacIntyre, 2008).

The copper mineralization is confined to a sub-zone of the bleached zone, mainly in and near the Cashin and Cliffdweller faults (Fig. 4). The mineralization extends for about 150 m perpendicular to the faults (Mach, 2006) and for about 1 km along them (Thorson and MacIntyre, 2005). Ore minerals are disseminated through the sandstone or form nodules after the pyritic nodules common in the bleached Wingate outside the ore zone. Near the faults, ore minerals also occur as clasts in breccias and as vein

fills (Fischer, 1936). The primary ores are Cu and Cu-Fe sulfides, but have been extensively altered by oxidizing waters descending along the Cashin and Cliffdweller faults, with the result that at least at Cashin most of the known reserves are supergene (Mach, 2006). Most of the supergene ores occur along the fault and within a few hundred feet of the topographic surface; at depth the hypogene ores are intact (MacIntyre, 2008). Accessory sphalerite and galena are present in the distal portions of the hypogene zone and account for an observed halo of anomalous Pb and Zn around the edges of the economic mineralization (Fischer, 1936; Thorson and MacIntyre, 2005).

Chalcopyrite, bornite, covellite, chalcocite, and digenite form interstitial fillings or line the corroded edges of detrital grains, in places forming a cement to the rock and partially replacing the clasts (Fig. 5a). Fischer (1936) suggested that the Cu minerals replaced original pyrite. That is consistent with observations made here, which moreover indicate that the Cu minerals may also have replaced interstitial bitumen (Fig. 5c), as suggested by Thorson and MacIntyre (2005). In most samples examined in this study the Cu and Cu-Fe sulfides display a variety of complex intergrowth and replacement textures (Fig. 5d) that preclude the evaluation of a detailed paragenetic sequence. They are widely reported to be argentiferous and are probably the source for the silver found in the supergene zones, which attracted the initial mining attention (Emmons, 1906). Pyrite is scarce in the high-grade zone but becomes more common towards the edges of the deposits. Thorson and MacIntyre (2005) reported a general zonation from chalcocite-dominated ores near the fault to chalcopyrite on the periphery.



Fig. 5. Petrography of Cashin and Cliffdweller samples from the Wingate sandstone. A: Chalcopyrite, surrounded by covellite and digenite, replacing cement and detrital grains (UT16-C5). Note ragged edges of remaining quartz grains. B: Cross-nicols photomicrograph of part of a large, tightly cemented sandstone clast in the carbonate matrix of a breccia (UT16-C11). C: Chalcopyrite, chalcocite, and bituminous globules filling interstices in sandstone (UT16-C8). D: Complex textures of bornite, chalcopyrite, covellite, and hematite growing on a euhedral quartz overgrowth, which has been partly dissolved (UT16-C11).

Near the surface the ores are altered to malachite and azurite, along with supergene covellite and chalcocite at greater depth. Native Cu has been reported since Emmons (1906) and is still found on the existing dumps (Thorson, writ. commun., 2018). Chalcopyrite, bornite, and whatever pyrite remained yielded Fe oxides, mainly limonite, when oxidized by supergene fluids. Most of the supergene minerals were apparently formed by oxidation in situ, with little long-distance mobilization. MacIntyre (2008) attributes this to the abundance of dolomite in the rock, which would quickly have neutralized any metal-bearing sulfuric acid produced by weathering sulfides and have induced reprecipitation of the metals.

Paragenetic assessments of the Wingate Cu deposits vary. Fischer (1936) worked out a paragenesis for the Cashin deposit that began with early pyrite formation and continued with a lengthy ore stage. This ore stage successively produced chalcopyrite; galena and sphalerite with more chalcopyrite; then bornite, chalcocite, tennantite, and an unidentified metallic mineral, with a final pulse of chalcopyrite again at the end; and finally dolomite, luzonite, covellite, and more chalcopyrite. Barite was found being replaced by dolomite, but Fischer considered its exact paragenesis uncertain. MacIntyre (2008) also made a paragenetic sequence for the Cashin deposit, which differs significantly from Fischer's and contains more detail. This paragenetic sequence begins with diagenetic reddening of the Wingate through hematite precipitation, followed by dolomite and quartz overgrowth formation. Hydrocarbon-induced bleaching came after this and included partial dissolution of feldspar, dolomite, and quartz, hematite dissolution and replacement by pyrite, and kaolinite precipitation. Copper minerals then precipitated in the bleached areas along the faults, along with additional barite and further dissolution of feldspar and dolomite. The last episode was supergene alteration of the copper minerals. The observations made in this study are generally consistent with this paragenesis, except that some of the carbonate overgrows the Cu ore minerals and is therefore definitely late in the sequence (Fig. 6).

The timing of bleaching and mineralization remain uncertain. Gray et al. (1996) estimated the timing of fluid flow events along the Cashin fault (and presumably copper mineralization) as Paleocene to Eocene based on paleomagnetic dating of chemical remagnetization. MacIntyre (2008) places hydrocarbon migration and bleaching in the Laramide and Cu mineralization in the late Tertiary just before the recent uplift. This is based on the burial history worked out by Nuccio and Condon (1996) and receives some support from the saddle textures observed in the barite and dolomite veins, which indicate deformation (Thorson and MacIntyre, 2005). However, ongoing Re-Os dating of chalcocite by Jason Kirk at the University of Arizona suggests a significantly earlier time for bleaching and/or mineralization. Further work will be required to substantiate this.



Fig. 6. Paragenetic sequence for Wingate-hosted Cu deposits, based on Fischer (1936), MacIntyre (2008), and the present study.

Uravan Belt U-V (Stops 3-1 through 3-4)

The Uravan belt of western Colorado is an east-convex arc of U-V deposits hosted in the Salt Wash member of the Morrison Formation (Chenoweth, 1981; reprinted, this volume). Mined extensively for radium in the 1900s-1920s, vanadium in the 1920s-1940s, and for uranium in the postwar era, Uravan produced some 32,000 t U and close to 150,000 t V through 2007 (Dahlkamp, 2009). The ratio of $V_2O_5:U_3O_8$ varies from 1:1 to 14:1 within the belt (Carter and Gualtieri, 1965). For this study, 35 thin sections from the Slick Rock and Monogram Mesa districts were examined.

Petrographically, the Salt Wash sandstones at Uravan are well-sorted quartzarenites with <10% feldspars and illite-dominated lithics, all well-rounded (Fig. 7). Coalified plant trash is rare but present. Minor to trace detrital phases include fluorapatite, barite, ilmenite, rutile, zircon, monazite, and chromite. Cements are varied: calcite and dolomite are common, clay is rarer, and quartz overgrowths and vanadian chlorite and vanadian mica both help cement the rock in and near ore zones. Limited SWIR analysis of 16 samples identified most of the clay as kaolinite. Where calcite cements the rock it is nearly pure, with no detectable Fe and minimal Mn. By contrast, dolomite cements commonly contain nearly 1 mol % Fe and lower, but detectable, Mn.

Many of the rocks in the Uravan belt are bleached, most noticeably the ore-hosting Salt Wash. The bleaching type is mixed, as the Fe is reduced and some of it is removed (Carter and Gualtieri, 1965). Paired whole-rock analyses show a drop in $\[MegaPol]{Fe_2O_3}$ from 3.6 to 1.2%, but the rocks contain pyrite and abundant ferroan carbonates or their limonite pseudomorphs (Shawe, 2011; I. Barton, unpub. data). In one thin section from the hard, white sandstone above the Opera Box mine at Monogram Mesa, Fe also occurred as highly crystalline, Al-poor jarosite, potentially hypogene.

The pyrite is typically fine-grained and dispersed through the rock, although some nodules have been observed. In sandstones in which the quartz is sutured together, pyrite crystals appear to be caught in the sutures, suggesting that pyritization preceded pressure-solution. The pyritic samples also contain trace to accessory galena, sphalerite, acanthite, and chalcopyrite. The galena and sphalerite have generally similar textural and distribution characteristics to the pyrite and appear coeval but chalcopyrite consistently overgrows the pyrite. Acanthite (or argentite) was observed in only one sample as an inclusion in pyrite. All the metallic minerals, except the supergene ones, form inclusions in carbonate cements. Barite and gypsum both occur as accessory phases and are paragenetically relatively late, overgrowing pyrite and vanadian minerals but forming substrates for supergene Cu and V minerals.

Near the U-V deposits, detrital quartz grains commonly feature either ragged edges or overgrowths of euhedral quartz, both well known from the literature (e.g., Garrels et al., 1959; Shawe, 1976, 2011; Meunier et al., 1990). These overgrowths are characteristically well zoned in cathodoluminescence, but in most places are tightly held together by sutures that crosscut the zones in the quartz overgrowths. They help cement the rock, making it a very hard white sandstone with a sugary appearance in hand specimen – the so-called "sugar sand" used by prospectors as a criterion for U-V mineralization. Evidence from unmineralized, bleached Salt Wash sandstone in La Sal Creek Canyon suggests that the euhedral quartz overgrowths formed by ripening of precursor chalcedony rims (Fig. 7a). The overgrowths are typically thin compared to the diameter of the detrital grains and are interpreted as the results of pressure solution and local redeposition of silica. Between rims and overgrowths are tiny fluid and mineral inclusions (Fig. 7b, g). Mineral species identified in these inclusions are, in various samples, uraninite, montroseite, a Ca-U mineral, hematite, pyrite, chalcopyrite, and an unknown Ti-V oxide. The hematite is the rarest of the inclusions, noted only in a very few samples, and may represent original pyrite oxidized by groundwater seeping into fractures in the quartz grains.

Montroseite, coffinite, and uraninite are the principal hypogene ores and occur commonly as interstitial fillings or growths on detrital grains, primarily quartz (consistent with the descriptions by Northrop et al. (1990) of the Salt Wash U-V deposits in the Henry Basin). Locally, asphalt or bitumen replaces quartz grains and itself is apparently replaced by uraninite, coffinite, and rutherfordine (Fig. 7e-f, h). Plant coal, where present, is usually not thus replaced, but commonly has a fringe of primary U and V minerals. Vanadian chlorite, studded with inclusions of Ti-V and V-U oxides, occupies interstices and

forms a cement to some of the ore-bearing rocks. In places where it fringes some of the detrital quartz grains, textures indicate that the vanadian chlorite replaced the quartz overgrowths (Fig. 7c, which was also noted by Garrels and Pommer (1959) and Northrop and Goldhaber (1990).

Supergene alteration is extensive in several the samples examined and includes carnotite and tyuyamunite, easily recognized by their bright yellow and chartreuse colors. Other, less common supergene minerals observed have been tentatively identified as uvanite, tivanite, volborthite, tangeite, lyonsite, mottramite, and vesignieite. Chrysocolla, malachite, azurite, and pseudomalachite are locally abundant. In all cases these are found overgrowing detrital grains, overgrowths, carbonate cement, and primary ores.

Based on these textural relations, the following paragenetic sequence is inferred (Fig. 8). (1) Asphalt or bitumen entered the rock at an early stage, partly replacing the detrital grains in some areas and forming interstitial droplets in others. This must be considered tentative as the early timing of hydrocarbons is inferred from their replacement by U minerals, not from direct textural evidence. (2) Pyrite, sphalerite, and galena formed at approximately the same time as the primary uraninite, coffinite, and montroseite and accessory Ti-V and Ca-U minerals (including uvanite or whatever the unidentified U-V oxide is). Chalcopyrite formed only slightly after the pyrite. The U minerals were trapped by the hydrocarbons and replaced some of the asphalt, as well as taking advantage of reduced zones around plant coal. (3) This mineralizing episode was followed by the development of quartz overgrowths, which preserved inclusions of the ore minerals. (4) Both these events preceded pressure solution or compaction, which dissolved some of the overgrowths and sutured quartz grains and may have caused additional overgrowth development. (5) Roscoelite and the vanadian biotites and chlorites formed after this, cannibalizing some of the silica dissolved from the quartz and incorporating the earlier metallic minerals as inclusions. (6) Barite and gypsum precipitated afterward, overgrowing the vanadian sheet silicates. (7) The calcite/dolomite cementing the rock formed after the sulfates. (8) Supergene alteration happened later, producing carnotite, tyuyamunite, volborthite, tangeite, lyonsite, mottramite, vesignieite, and supergene Cu and Fe minerals.

This paragenesis is largely consistent with most of the more recent interpretations of Salt Wash mineralization (e.g. Shawe, 1976, 2011; Northrop and Goldhaber, 1990). It differs substantially from the paragenetic sequences developed by early (1950s-1960s) work, which typically placed primary U-V mineralization after the development of quartz overgrowths and which divided the ore stage into several

Fig. 7. Petrography of Salt Wash U-V deposits. A: Quartz overgrowths developing from chalcedony rims (brown) on detrital grains in altered but unmineralized Salt Wash guartzarenite in La Sal Creek Canyon (UT18-13a, 5x). B: Montroseite needles growing on the edge of a detrital quartz grain and forming inclusions in its euhedral overgrowth (UT18-MM5c, 50x conoscopic). C: Backscattered SEM image showing occurrence of uvanite(?) or mixed montroseite and uraninite as needles in a matrix of vanadian chlorite. D: Panchromatic cathodoluminescence photomicrograph showing that sutures between guartz grains terminate the zoning in guartz overgrowths (CO16-SR10). E: Backscattered SEM photomicrograph showing asphalt (black) with uraninite and coffinite (white spots) within it, replacing heavily corroded quartz grains (gray) The bright grains adjacent to corroded quartz rims are galena and pyrite (UT18-MM5). F: EDS elemental map of the area in Figure 11e converted to RGB by ImageJ (red = U, green = C, blue = Si). G: A ring of uraninite grains (bright) around the detrital core of a quartz grain, trapped in the guartz overgrowth and cut off where the quartz grain is sutured to a neighboring clast (CO16-SR21). H: Remains of a strongly corroded quartz grain amid a globule of bitumen (upper left) with a paisley pattern caused by partial replacement by uraninite; a different area of the same globule is shown in E-F. Pyrite and galena occur between quartz grains outside the bitumen globule (UT18-MM5).





Fig. 8. Paragenetic sequence for Salt Wash U-V, based on Carter and Gualtieri (1965), Shawe (1976, 2011), Northrop and Goldhaber (1990), and this study.

substages. In the first of these, roscoelite and vanadian mica and clays formed (with pyrite in some interpretations; Carter and Gualtieri, 1965; Shawe, 2011); in the second, uraninite, coffinite, montroseite, galena, sphalerite, chalcocite, and tennantite precipitated (with the pyrite entering at this stage in other interpretations; Garrels et al., 1959; Shawe, 2011). A continuation of the ore stage after this produced first chalcopyrite and clausthalite, then uraninite plus covellite (Carter and Gualtieri, 1965). This paragenesis was revised after further research, and later works invoke a single hypogene ore-forming episode that emplaced the U, V, Cu, Pb, and Zn minerals (Shawe, 1976, 2011; Northrop and Goldhaber, 1990). The principal disparity between these later paragenetic sequences and the one outlined above is the timing of dolomite formation, which Northrop and Goldhaber (1990) thought was contemporaneous with U mineralization but which the textures described above suggest was later. The late timing of dolomite and calcite is, however, consistent with the observations of Shawe (1976, 2011) at Slick Rock.

Absolute age constraints are lacking. As with the Chinle ores, attempts at U-Pb dating of the U-V mineralization have resulted in a range of ages from 46 to 118 Ma for the hypogene suite (Ludwig et al., 1984). A histogram of all available U-Pb dates for primary ores in the Morrison and its equivalents shows a definite mode from 100 to 120 Ma, with far fewer dates thereafter (the dates were filtered to include only those concordant to within 10 Ma). Although far from conclusive, this seems to indicate that ore was emplaced in the Salt Wash shortly after the unit was deposited, which would be consistent with the precipitation of U-V minerals prior to the development of quartz overgrowths.

Burro Canyon-Hosted Copper (Stop 3-5)

The sandstones and conglomerates of early Cretaceous strata contain economic Cu mineralization at the northwest and southeastern extremes of the Lisbon Valley anticline. Most of the ore is hosted in the Burro Canyon formation, with accessory mineralization in the overlying Dakota sandstone. Minor, uneconomic copper is also present in the Hermosa, Cutler, Chinle, Wingate, Kayenta, Navajo, and Entrada formations in the area of the major deposits (Weir and Puffett, 1960; Kennedy, 1961, J. Thorson, unpub. data). The

Burro Canyon-hosted mineralization at the anticline's northwest tip, which had been mined by the Anasazi in ancient times, was organized in 1892 and was well into production by 1900 as the Big Indian mine (Weir and Puffett, 1981; Hampson, 1993). Major production from the deposit at the southeastern tip began in 1908 from what was then called the Blackbird mine, now the site of the Lisbon Valley mine (Hahn and Thorson, 2005). The mining area over the entirety of the anticline was then referred to as the Big Indian district and included both the Cu deposits and the as-yet-unknown U-V orebodies. Mining at both Big Indian and Blackbird continued intermittently over most of the next century under various auspices, and continues today at the Lisbon Valley mine. The Big Indian mine ceased production of metallic Cu by 1974, but reopened as a specimen mine for azurite in 1981 (Hampson, 1993). Hahn and Thorson (2005) and Thorson (2018) review the resource and mining history of the Lisbon Valley mine.

The distribution of alteration and mineralization is controlled by the Lisbon Valley fault and its associated strands, which parallel (strike ~045°) and cut the anticline and dip about 58° NE (range from 25 to 60° in various places). The maximum displacement is normal and >1200 m, and the fault trace extends for several tens of km across southeastern Utah. The large displacement corresponds to a fault zone up to 10 m wide with extensive brecciation and nearby fracturing. Within the fault zone the rocks are sheared, locally strongly silicified, and bleached, with some asphalt and a few small concentrations of copper minerals along fractures (Jacobs and Kerr, 1965). The normal chlorite, illite, and montmorillonite clays have been altered to kaolinite and dickite in the fault zone and to kaolinite up to 100 m away in claybearing strata. Silicification extends up to 18 m away from the fault, and bleaching for up to 5 km; it is especially prominent in sandstones of the Dakota and Burro Canyon (Jacobs and Kerr, 1965; Merin and Segal, 1989). Movement along the fault is recent and occasional detections of seismic activity indicate that it may be ongoing (Hahn and Thorson, 2005).

Mineralization shows a strong structural control, occurring only near the Lisbon Valley fault and its strands. Economic concentrations of copper are confined to five sandstone beds in the Dakota and one (the richest) in the Burro Canyon. Both are similar in depositional facies. The Burro Canyon is about 80 m thick at Lisbon Valley and consists of fluvial sandstone and conglomerate facies intermixed with shales, grading upward into mudstone and limestone. It is in unconformable contact with the overlying Dakota sandstone, which is about 40 m thick and consists of similar rocks.

Bleaching alteration is found in multiple strata at Lisbon Valley, from the upper Cutler to the Burro Canyon. Its distribution is largely controlled by the Lisbon Valley fault, and most of it is due to the action of hydrocarbons, which still reside in the strata as disseminated bitumen spots, as vitrinite, and as large gas fields in the Paradox Formation (Jacobs and Kerr, 1965; Merin and Segal, 1989). Petrographic evidence such as tiny hematite crystals preserved by quartz overgrowths around detrital grains indicate that the Burro Canyon sandstones at Lisbon Valley were once red beds, and have been bleached since (Altinok, 1998). The exact type of bleaching is uncertain. Nodules and disseminated grains of pyrite are very common in the Burro Canyon around the ore deposits, in fact considerably more abundant than in comparably bleached Wingate. However, it is not clear whether the pyrite resulted from the reduction of hematite by sour gas or entered the rock with the Cu-mineralizing fluid. Either is possible; the local Lisbon Valley oil field contains several wt % H₂S (Adkins et al., 2011). Ordinarily the type of bleaching could be inferred by measuring the pyrite content of bleached Burro Canyon sandstones away from the ore zone, but the lack of exposure and drilling in the Burro Canyon outside the mineralized area precludes this. Thus, it remains possible that either the bleaching reduced the Burro Canyon hematite to pyrite, or that the bleaching removed the Fe from the rock and the influx of metal-bearing fluid during the ore stage restored it.

By contrast with the Burro Canyon, petrographic and geochemical evidence indicates that the Dakota sandstones never underwent diagenetic reddening and have been pale-colored since they formed. The reasons for this are uncertain, but may be related to the rapid deposition of 1000+ meters of Mancos Shale above the Dakota. As described above, diagenetic reddening is thought to result from repeated wetting and drying of sandy layers with consequent oxidation and destruction of ferroan detrital components (e.g., Walker, 1976, 1989), and the quick burial of the sandstones under a large thickness of shale would not provide these conditions.

Petrographically, the ore-bearing sandstones are quartz-dominated arenites with subsidiary feldspar and lithic clasts, most of which are argillites or chert, as well as trace biotite. Coalified plant remains are erratically distributed and locally abundant. The detrital quartz grains are commonly overgrown by euhedral rims, which enclose mineral inclusions not yet identified (Fig. 9). In the ore zones, detrital grains appear corroded and many of them are sutured together; Hasenohr (1976) attributed this to pressure solution. Most of the cement is carbonate of varying grain size, but clay is also present as interstitial fillings and chalcedony has been observed. In some high-grade samples, azurite and malachite help to cement the rock.

The Cu ores are dominantly oxides and supergene chalcocite near the surface. Reported oxides (sensu lato) include malachite, azurite, cuprite, and tenorite; native copper is scarce but not absent (Hasenohr, 1976) and chalcotrichite forms on exposed surfaces in the mines. Aurichalcite, conichalcite, clinoclase, olivenite, tyrolite, chalcophyllite, cornwallite, and wulfenite are also reported (Hampson, 1993). The oxides occur as interstitial fillings, grain coatings, and veinlets, and in areas where they replace carbonate cement they form small, pea-sized nodules. Below about 50 m depth, hypogene sulfides remain and their abundance increases downward, although many of them show partial replacement by malachite and the other supergene minerals. The sulfides occur as nodules within the sandstone, as cements and interstitial grains, disseminated, and as the matrix to fault breccias (Hasenohr, 1976). In at least some instances they have been found in association with precursor pyrite, plant coal, and bitumen (Adkins et al., 2011), and



Fig. 9. Petrography of Lisbon Valley samples. A: Disseminated malachite in Burro Canyon sandstone in interstices between euhedral overgrowths on detrital quartz grains (UTMM-LV2, 10x). B: Deformation textures in sutured detrital quartz grains offset trains of secondary fluid inclusions and affect crystallite orientation in crossed nicols (UT16-LV3, 20x). C: Fragments of plant coal embedded in coarse calcite from Burro Canyon (UT17-LV3, 5x); note that epoxy is blue. D: Disseminated pyrite in bleached Burro Canyon sandstone (UT17-LV3, 5x).

textures observed in this study suggest that some of the Cu sulfides replaced interstitial bitumen. Chalcocite and digenite dominate the sulfide assemblage, sometimes intergrown with covellite, and chalcopyrite, enargite, tennantite, and sphalerite have also been observed (Fig. 9; Hasenohr, 1976). Detailed XRD analysis has shown that most of the chalcocite-group minerals correspond in composition to djurleite (Schmitt, 1968). The Cu sulfides are weakly zoned from chalcocite in the center of the deposits to distal pyrite in the poorly mineralized halo, with bornite and chalcopyrite zones between (Adkins et al., 2011).

Chemical analysis of ore samples by Kennedy (1961) and Hasenohr (1976) detected consistent significant enrichment in Ag (up to 724 ppm) and Mo (10s of ppm). Otherwise, no metal other than Cu was consistently anomalous, although about half the samples in the study contained >5 ppm Co and >10 ppm Zn. The Zn is presumably housed in the trace sphalerite observed, but the speciation of the Co and Ag is uncertain. No Ag minerals have been observed at Big Indian or Lisbon Valley, and analogy with the Wingate-hosted Cu mineralization at the Cashin and Cliffdweller mines suggests that the Ag may exist in solid solution in the Cu sulfides. Irregular and minor U enrichment around the Cu mines was detected, but does not correlate with Cu mineralization (Kennedy, 1961). Adkins et al. (2011) review the use of these and other elements as geochemical vectors to mineralization around Lisbon Valley.

The paragenesis of the Lisbon Valley and Big Indian ores can be pieced together based on observations from several sources. Thorson (2004), Hahn and Thorson (2005) and Adkins et al. (2011) divide alteration at Lisbon Valley into two stages. Flow of hydrocarbons and an oil-field brine during the first stage reduced the Burro Canyon red bed sandstones, leaving bitumen and pyrite that trapped Cu from the chloride brine that arrived in the second stage. Altinok (1998) worked in altered Burro Canyon sandstones outside the Cu deposits at Lisbon Valley and did not discuss ore formation but defined an alteration paragenesis for everything else. His began with the diagenetic reddening of the sandstone, followed by calcite cementation, then development of quartz overgrowths, and then more calcite. This was followed successively by pyrite, siderite, clays, more quartz overgrowths, precipitation of calcite and dolomite, and then weathering. By contrast, Hasenohr (1976) worked out a paragenesis for both Big Indian and Lisbon Valley that includes only the ore minerals. According to this sequence, the oreforming episode began with pyrite and continued with chalcopyrite, tennantite, and enargite. Sphalerite, digenite, covellite, and contemporaneous chalcocite and djurleite overlapped pyrite formation in time, but continued to form well after its precipitation ceased. This hypogene episode imperceptibly became supergene as native Cu, cuprite, tenorite, malachite, and azurite are shown starting to precipitate before the hypogene mineral suite has finished forming.

The observations made in this study are consistent with some of these events. A combined paragenetic sequence, adjusting these published paragenetic sequences in accordance with textural evidence gathered in the present work, is presented in Figure 10. It differs from Hasenohr's (1976) sequence in separating hypogene from supergene episodes and in attributing pyrite to the bleaching episode, and from Altinok's (1998) sequence in having only a single episode of quartz overgrowth formation. Current petrographic data are insufficient to evaluate the detailed paragenesis of the hypogene ores, so the precipitation of Cu sulfides is presented as a single event without differentiation. The absolute timing of bleaching and mineralization remains unknown but may be elucidated by ongoing efforts at Re-Os dating of chalcocite (J. Kirk, unpub. data, May 2018). The paragenesis of Cu mineralization in the Burro Canyon and Dakota formations closely resembles the sequence of events depicted in Figure 6.

Big Indian U-V (Stops 3-6 and 3-8)

The Big Indian district covers most of the Lisbon Valley anticline in northern San Juan County, southeastern Utah. Of the 42,000 t U produced from Chinle ores of the Colorado Plateau, roughly 75% came from Big Indian (Dahlkamp, 2009), making it one of the largest single districts on the Colorado Plateau judged by U production. The district includes the famous Mi Vida deposit, whose 1952 discovery by Charlie Steen precipitated an American prospecting frenzy second in scale only to the California gold rush. The V/U ratio varies, but generally increases from northwest to southeast and updip (Kennedy, 1961; Huber, 1980).



Fig. 10. Paragenetic sequence for Burro Canyon-hosted Cu deposits, based on Altinok (1998), Hahn and Thorson (2005), and this study. Compare with Figure 5.

Known U-V mineralization is mainly in the footwall block of the Lisbon Valley fault, which cuts the anticline along its axis. The major ore host is the Chinle formation just above its unconformable contact with the underlying Cutler formation, which also contains local mineralization (Weir and Puffett, 1981). Most of the Chinle ores occur in fluvial facies within the conglomeratic Shinarump member and the sandstone- and conglomerate-bearing Moss Back member. All of the various U-V mines in the Chinle of the Big Indian district are associated with a point bar facies, which apparently meandered considerably over the course of deposition (Huber, 1980). Notably, the ore deposits are confined to areas of the Chinle point bar facies above the stratigraphic pinchout of a friable, intensely bleached cross-bedded sandstone bed of the upper Cutler, termed the "sugar sand" for its sparkly appearance in hand sample (Fig. 11; Schmitt, 1968; Weir and Puffett, 1981). The sugar sand locally contains bitumen.

Despite repeated efforts at U-Pb dating, the age of the Big Indian hypogene U-V deposits remains uncertain as the dates obtained for Chinle-hosted deposits range from 206 Ma (approximately the age of the host rock) to 91 Ma (Miller and Kulp, 1963). Geological evidence is similarly ambiguous. Neither V/U ratio nor any other known mineralogical feature of the rocks in the Chinle U-V deposits shows a relationship to the Lisbon Valley fault, unlike the Cu deposits in the district, whose grade and mineralogy are entirely controlled by the fault. Schmitt (1968) interpreted this to mean that the U-V deposition at Big Indian predates significant movement on the Lisbon Valley fault. No dates have been obtained on any ores from the Cutler-hosted U-V deposits, but geologic relations and U-Pb dates on other Cutler



Fig. 11. Pinchout of the Cutler sugar sand at Lisbon Valley, hyperspectral RGB image.

U-V mineralization along the extension of the Lisbon Valley fault zone are all early Tertiary (Miller and Kulp, 1963; Berglof, 1970). The Cutler deposits are widely interpreted as having been remobilized from deposits in the overlying Chinle, with whose locations they strongly correlate (Kennedy, 1961; Weir and Puffett, 1981). Paleomagnetic evidence from the Cutler near mineralized Chinle has suggested a Laramide (late Cretaceous to early Tertiary) age (Reynolds et al., 1985).

The U deposits occur mainly in bleached areas of the rocks, which are ordinarily a deep red color in both the Cutler sandstones and the Chinle (U-V deposits do occur in unbleached zones of the Chinle where they overlie bleached sandstone in the Cutler; Weir and Puffett, 1981.) Most of the bleaching in the Cutler formation consists of Fe removal, with %Fe₂O₃ decreasing from 2–3% in red to 0.5-1% in bleached sandstones (Thorson, 2018). In the Chinle much of the Fe appears to be immobilized in silicates, and bleaching decreases %Fe₂O₃ from 4.9 to 3.8% (I. Barton, unpub. data). The bleaching turns Chinle sandstones white and leaves more clay-rich units a gray-green color. The bleaching was likely related to hydrocarbon passage, which left traces such as trains of blue-fluorescing (in ultraviolet) secondary fluid inclusions in quartz grains (Fig. 12c). By contrast, Fe is strongly enriched in the Chinle sandstones just above the U-V ore horizon, where hematite locally cements the rock. These concretions commonly follow well-defined sedimentary structures in the sandstone and contain up to 60% hematite as cement in the rock. This hematite forms colloform coatings around detrital grains and is highly reflective, distinguishing it from the hematite typical of the ordinary sandstone, which is earthy, nonreflective, and forms small freestanding grains (Fig. 12). The boundary between the concretions and the ordinary red bed sandstone is typically very sharp.

The ore-hosting units are dominantly arkosic, with clasts of quartz, feldspars, and lithic fragments which are mainly argillite. Trace mica, almost entirely muscovitic, is present. The detrital grains are well rounded to subrounded and are well sorted in the sandstone, moderate to poorly sorted in conglomeratic hosts. In high-grade zones the edges of the detrital grains are conspicuously ragged, with textures suggestive of partial dissolution. Detrital quartz grans are commonly strained and fractured. Where plant coal is present, it occurs in a habit and size similar to the local lithic clasts. Plant coal and unidentified organic matter are common in the Chinle, but are nearly absent in the Cutler (Weir and Puffett, 1981). Cement makes up about 20% of the rock in most thin sections examined and is mainly a coarsely crystalline calcite with about 0.5-0.8% Mn and <0.1% Fe (I. Barton, unpub. data). Interstitial globules resembling bitumen are common, particularly where this calcite cement is absent. Trace ilmenite, zircon, monazite, and chromite persist among the detrital minerals, although the ilmenite has largely been replaced by rutile and hematite. Clays are not common but were identified by SWIR as illite and montmorillonite.

Ore mineralogy is principally uraninite and a U-silicate tentatively identified as coffinite; however, the presence of consistent detectable Ca with the U-silicate indicates some admixture of uranophane. Rutherfordine is present around the edges of the uraninite and U-silicate and may be a weathering product. Vanadian mica and montroseite are the main hypogene V minerals, and pyrite, chalcopyrite, galena, and sphalerite are common. The sphalerite is noticeably Cd-rich (up to 5 at. % Cd in the outermost zones of crystals) and contains no detectable Fe; it may be what Gross (1956) and Schmitt (1968) had identified petrographically and by XRD respectively as greenockite. This is consistent with the equilibrium co-precipitation of sphalerite and pyrite (Barton and Skinner, 1979), which is also indicated by the textures of both minerals (Fig. 12). They appear to partly replace barite, which is heavily embayed and which forms inclusions in the sphalerite. Pyrite and sphalerite grains are found fringing plant coal and growing off uranophane/coffinite, and small grains of pyrite are also scattered through cracks in plant coal. Pseudomorphs of Fe oxide after marcasite were observed, but not marcasite itself, although Schmitt (1968) reports it as an accessory mineral at Mi Vida and several of the other Big Indian U-V mines. Chalcopyrite overgrows both pyrite and sphalerite. Covellite and digenite occur as interstitial fillings that overgrow the ragged edges of detrital quartz grains, in similar fashion to the bituminous substance and pyrite but with no discernible textural relationships to the other sulfides (Fig. 12). Quartz overgrowths around detrital grains are rare, and no mineral inclusions were observed between cores and rims in the few specimens found. However, Gross (1956) found some quartz overgrowths on detrital grains in low-grade



Fig. 12. Petrography of Big Indian U-V deposits. A: Backscattered SEM photomicrograph showing complex textural relationships among ore-stage minerals in the Mi Vida hypogene suite (UT18-MV2a1). B: Reflected-light photomicrograph of plant material replaced by uraninite (lighter gray, in cell walls) and coffinite (darker gray, within cells) at Mi Vida (UT18-MV2a1). Galena and coffinite fill the cracks and two pyrite grains are visible growing on the edge of the coal in the lower right. C: Blue fluorescence in ultraviolet light of trains of secondary fluid inclusions crosscutting a quartz grain. Blue fluorescence indicates the presence of hydrocarbons (UTLS-MV04). This sample was taken from one of the sandstones with the hematite concretions just above the Mi Vida mine portal. D: General petrographic characteristics of the Chinle sandstone, showing arkosic composition and carbonate cement under crossed nicols (UT18-MV2c). E: Montroseite fringe (medium gray) around clastic grains (black). Galena (bright white) overgrows the montroseite. The matrix is a vanadian biotite (dark gray) (UT18-MV2a3). F: Reflected-light photomicrograph of euhedral chalcopyrite grains overgrowing the pyrite fringe on an ore-bearing clast (UT18-MV2a1).

zones in the Chinle sandstone at Mi Vida, and reports that montroseite needles fringing the detrital cores were trapped in the authigenic rims. All the metallic minerals, and the quartz overgrowths, are overgrown by the calcite cement.

The primary U ore minerals occur as replacements of plant coal and of detrital grains, as interstitial fillings, and as veinlets that crosscut detrital grains, more rarely forming fine grains around the fringes of detrital material. Typically, they consist of masses rather than distinct crystals, and a detailed X-ray study of their crystallinity found that these masses consist of aggregations of crystallites <20 nm in size (Schmitt, 1968). Colloform textures are observed in some cases where the U minerals line the edges of preexisting grains, a feature also observed by Schmitt (1968). The V minerals are rarely found replacing detrital grains or plant coal but commonly fringe them instead, following the ragged edges where the grains are corroded (Fig. 12e). In one sample, the V-mica and the montroseite form the matrix to what resembles a breccia. In this rock, quartz-dominated clasts are cut by veinlets of coffinite or rutherfordine and galena, which terminate at the matrix. The clasts have a montroseite fringe, which is (in one place) overgrown by galena and which is engulfed by a biotitic vanadian mica throughout the sample. Textural evidence suggests that the vanadian mica, and some of the other ore minerals, cannibalized much or all of its component silica from preexisting, mainly detrital, grains.

The textures of the ore, shown in Figure 12, indicate a highly complex sequence of alteration events that cannot be adequately assessed from the limited number of ore samples available to this study, independent of other information. The paragenetic sequence given by Gross (1956) and corroborated by Schmitt (1968) begins with post-depositional precipitation of authigenic quartz, barite, clay, and calcite, followed by a lengthy ore-forming episode separated by an interval of minor deformation into two parts. The first part produced pyrite, chalcopyrite, V-clay (likely the V-mica observed in this study), coffinite, and uraninite. The second part produced corvusite, galena, and greenockite (likely the sphalerite observed in this study). Montroseite straddles both parts, beginning after U deposition started and continuing after it ended.

The mineralogy and textures observed in this study are generally consistent with that paragenesis, with a few exceptions. Firstly, the vanadian mica identified here as Gross's vanadian clay overgrows montroseite, the U minerals, and the pyrite and galena, indicating that it formed after they did. Secondly, the relationship of the montroseite to the pyrite and galena is ambiguous; the pyrite and galena seem to overgrow the montroseite, but have no consistent relationship to each other. Thirdly, the pyrite and sphalerite (probably what Gross called "greenockite") overgrow the U minerals, and therefore must postdate them, and are overgrown by the chalcopyrite, which must therefore have formed later. The corrosion of the quartz grains is not given in Gross's paragenetic sequence but must have predated the precipitation of montroseite since the montroseite fringes around detrital quartz grains follow the outlines of their ragged edges. Bitumen has not been conclusively identified, but hydrocarbons were plainly in the vicinity as local fluid inclusions fluoresce blue, and some of the ore mineral textures suggest they replaced bitumen. The paragenetic position of the bitumen or hydrocarbons could not be conclusively determined from the samples available, but they must have predated any sulfides that replaced them. Although this and some other aspects remain tentative, they are shown on the paragenetic sequence in Figure 13.

Other paragenetic sequences in the literature are not very detailed. Loring (1958) determined that pitchblende replaced pyrite, and that calcite accompanied the pitchblende. This obviously differs from the paragenetic sequence determined by Gross (1956) and modified here, and contrasts with textures such as Figure 10, which show pyrite overgrowing U minerals. Botinelly (1957, in Weir and Puffett, 1981) found that montroseite formed earlier than coffinite and uraninite, that chalcopyrite was later than the U minerals but barite was earlier than the U minerals, and that calcite had been repeatedly dissolved and reprecipitated.

Iron (and manganese) Mobility and Deposition

Concretions of Fe and Mn oxides in Paradox Basin sandstones are much discussed, both for their own sake and because of potential analogies to features observed by rovers on Mars (e.g., Chan et al., 2001,



Fig. 13. Paragenetic sequence for Mi Vida, based on Gross (1956), Schmitt (1968), and this study.

2013; Beitler et al., 2003; Loope et al., 2010; Reiners et al., 2014). Many types of concretions are known, ranging from hollow hematite pipes to large nodules to massive veins of Fe and Mn oxides. They tend to occur in widely spaced clusters in the quartzarenite sandstones of the Navajo and Entrada.

Although largely unreported, hematite concretions occur at Big Indian just a few meters above the U-V-bearing horizon. They are most noticeable outside the Mi Vida adit, where they fill sedimentary structures in the sandstone. Their characteristics are discussed above and resemble those described by Chan et al. (2000) from various hematite concretions around southeastern Utah. Fluid inclusions within 2 cm of the concretions fluoresce blue in ultraviolet light, indicating the presence of light hydrocarbons (I. Barton, unpub. data).

Additional fieldwork also turned up hematite concretions in the Kane Springs district, a group of U-V mines thought to have formed from the remobilization of U and V out of the overlying Chinle deposits along a fault (Davidson and Kerr, 1968). To the southeast of the Kane Springs district along the same fault is Flat Iron Mesa, home to large veins of Fe and Mn oxides hosted in the uppermost Navajo Sandstone (Garcia et al., 2018). The veins follow a set of regularly spaced faults with a few meters of normal offset apiece. All are subvertical and trend roughly 310°. Damage zones associated with the faults contain numerous small deformation bands, whose abundance decreases sharply a meter or two from each fault. Traces of the faults are visible across the highway into the Entrada sandstone. However, Fe and Mn oxide mineralization is confined to the uppermost Navajo, where veins reach up to 5 m wide (Fig. 14). They taper off rapidly with depth in the Navajo and are absent from the overlying Dewey Bridge. Veins occur in both bleached and red Navajo and do not appear to be related to the bleaching. The lowermost few meters of the Navajo are consistently bleached and recent field mapping discovered bitumen disseminated among the foresets just above the contact with the Kayenta (M. and I. Barton, unpub. data).

Petrographically, the concretions invade and partly replace the quartzarenite sandstone of the Navajo. Quartz grains are subrounded to rounded and many have euhedral overgrowths and considerable evidence of suturing. Close to high concentrations of Fe and Mn oxides, many of the quartz grains are shattered (Fig. 15). The oxides form a cement to the rock, filling interstices, making colloform linings around detrital grains, and veining the shattered quartz. Textural evidence shows that the several oxide minerals



Fig. 14. Schematic cross section of alteration and Fe-Mn oxide distribution at Flat Iron Mesa, from this study.

present formed in distinct, successive events (Fig.15). All are highly crystalline and reflective, and Reiners et al. (2014) noted that all are highly U-enriched as well.

The various oxides observed are a nearly pure Mn oxide that may be pyrolusite; goethite; a mixed Fe-Mn oxide; and a barian cryptomelane. The paragenesis is uncertain but in general the goethite and mixed Fe-Mn oxide are overgrown by the cryptomelane, which is overgrown and partly replaced by the pyrolusite. This would indicate early Fe followed by later Mn oxide precipitation, which is consistent with the textural relations and spatial sequence from proximal Fe to distal Mn oxides found by Garcia et al. (2018). The high Ba content of the cryptomelane is significant as it means that the geochemical system, though highly oxidized, was devoid of sulfate, which would have stabilized barite. The bitumen-bearing samples have not yet been studied, but further work is expected to elucidate the relationship between hydrocarbons and the Fe and Mn oxides.

Discussion

1. Metallogenetic models for Colorado Plateau Cu and U-V depositsl

The results of this study support the two-stage metallogenetic model developed by Thorson (2004), Hahn and Thorson (2005) and Thorson and MacIntyre (2005) for Colorado Plateau Cu deposits. In this model, initial flow of hydrocarbons and associated brines through a fault first-bleached permeable rock units nearby, usually by pyritization. At a later stage, a Cu-bearing brine flowed up the same fault and precipitated Cu ores at the redox and sulfide trap thus formed. Although many of the details remain to be worked out, the petrographic and geochemical evidence cited above is compatible with this general model.

Furthermore, the evidence presented above suggests that hydrocarbons played a similar role in the formation of the U-V deposits on the Colorado Plateau. Like the Cu deposits, U and V occurrences correlate closely with bleached rocks, and bleaching alteration in both the Chinle and the Salt Wash sandstones is associated with remnant bitumen in the rocks and with hydrocarbon-bearing fluid inclusions. Uraninite and coffinite are found partially replacing asphalt (Fig. 12) and are found around the fringes of pristine, unreplaced plant coal. All these imply that the U and V ores precipitated where the oxidized,



Fig. 15. Petrography of Flat Iron Mesa samples. A: Boundary between Navajo sandstone and a hematite concretion in reflected light (UT18-FIM1a, 10x). B: Shattering of detrital grains near a large Mn-Fe oxide vein, with pyrolusite cementing the rock (UT18-FIM1b, 5x). C: Colloform hematite rims (gray) around quartz clasts (black), overgrown by pore-filling barian cryptomelane (white). D: EDS elemental map of part of a mixed oxide concretion, converted to RGB by ImageJ (red = Mn, green = Fe, blue = Si).

U- and V-bearing fluid met either a mobile hydrocarbon in the rock, or the pyrite and bitumen that it left in passing. This is consistent with recent work on the geochemistry of U in relationship to organic matter (reviewed in Cumberland et al., 2016), and it does not preclude some of the other features observed, such as U precipitation on non-petroliferous organic matter such as coal.

This model departs from most metallogenetic inferences about the formation of U and V deposits (reviewed by Cuney, 2009; Kyser, 2014). Initial work specifically on the Salt Wash and the Chinle U deposits attributed U mineralization to reduction of dissolved U^{6+} by coal or plant trash in the sandstone (e.g., Garrels and Pommer, 1959; Garrels et al., 1959; Carter and Gualtieri, 1965). Later sedimentological information, particularly the inference that alkaline lakes had been present in the region, led to the suggestion that the U trap was not the plant matter itself but was humic acid or humate produced by its decomposition (Shawe, 1976, 2011; Turner-Peterson, 1978). Turner-Peterson (1978) and Thamm et al. (1980) invoked the reducing power of humates, whereas Shawe suggested that humic acid could lower the pH of an already reduced U-bearing solution enough to destabilize uranyl-carbonate complexes and induce precipitation (Shawe, 1976). Hansley and Spirakis (1992) implicated an unidentified "amorphous organic matter" as reducing agent. By contrast, Northrop and Goldhaber (1990) attributed U precipitation to reduction by aqueous biogenic H₂S, and Shawe (2011) to an unspecified altering fluid interacting with a

U-rich humate formation water. However, all of these models predict that ore grade should correlate with the abundance of the plant remains that supplied the coal, plant-derived humate or humic acid, or biogenic H_2S (Weir and Puffett, 1981).

Although the idea that hydrocarbons were the main reductant for Colorado Plateau U-V deposition is relatively new (Thorson, pers. commun., 2016), a detailed examination of the historical record turns up a subtle but lengthy series of suggestive observations. Shawe (2011), going back over his many decades of work at Slick Rock, speculated that the hydrocarbons he observed there could have been involved in U-V precipitation. Many of the mid-20th century articles on other U-V deposits of the Colorado Plateau refer to an unidentified organic substance in the rock, which Weeks et al. (1959) summed up as "interstitial insoluble carbonaceous matter that is isotropic and does not show any cell structure." This is similar to the "amorphous organic matter" of Hansley and Spirakis (1992). Weeks et al. also observed that the quartz grains surrounding this matter were heavily corroded. This strongly implies that it was asphalt or bitumen present in a texture similar to Figure 12. Thus, although the interpretation of U-V metallogenesis given here is not explicit in most of the historical work on the Colorado Plateau deposits, the key observations have been around for a long time.

Hydrocarbon reduction could explain two of the peculiar features of Colorado Plateau U-V ores that have puzzled geologists for decades. One is the variation of V/U ratio from as low as 1:1 to more than 15:1 without any apparent differences in V mineralogy, chemical characteristics, or inferred metallogenesis, since U and V behave similarly in aqueous systems. Analyses of different types of hydrocarbons show that they are commonly enriched in V by several hundred ppm, sometimes in concentrations ranging up to 1500 ppm (Manning, 1986). Such concentrations are more than sufficient to make a mobile hydrocarbon body a V-mineralizing fluid, capable of precipitating vanadium ore minerals irrespective of whether or not it meets a U-bearing fluid. The variable V/U ratios observed therefore reflect varying amounts of V not only in the U-bearing oxidized fluid, but in the hydrocarbon itself. The second peculiar feature is the contorted geometry of the Salt Wash orebodies, mapped in detail by Shawe et al. (1959) and Shawe (1976, 2011) and reviewed by Dahlkamp (2009). These orebody shapes, which do not correlate well with the abundance of plant coal, are difficult to reconcile with reduction by that or any other stationary solid or with a fluid derived therefrom (e.g., humates, humic acid, H₂S). However, it would be natural for the interface between two fluids in a heterogeneous medium to have an irregular shape and to move over time, producing the sinuous orebody geometries observed in the Salt Wash rolls.

Thus the Cu and U-V deposits of the Paradox Basin have disparate characteristics, but may reflect the same fundamental metallogenesis at work: reduction of a rock by hydrocarbons, followed by precipitation of ore at the reduced and/or sulfidized zone left or by interaction with the hydrocarbon body. It remains to consider whether this similarity is coincidence.

2. Links among U, V, Cu, and Fe-Mn mobility and deposition in the Colorado Plateau

Most mining districts of the Colorado Plateau contain either U-V or Cu deposits. Very few have both, making it difficult to study the potential links between them. No U-V minerals are known from Cu deposits (Weir and Puffett, 1981; Shawe, 2011). Only one deposit, the Woods mine in the Cutler Formation near the southeast end of the Lisbon Valley anticline, contains major concentrations of both Cu and U minerals. The Woods mine is largely unstudied, and both the Cu and U therein may be exotic ores derived from supergene mobilization of metals from the nearby U-V and Cu deposits (Kennedy, 1961). The U-V deposits in both the Chinle and the Salt Wash contain minor Cu, which in primary ores speciates as chalcopyrite. It is almost certainly a part of the ore stage, occurring within quartz overgrowths in the Salt Wash deposits at Slick Rock and overgrowing the ore-stage pyrite in the Chinle deposit at Mi Vida. It is also reported from other mines in the Big Indian district and from several Uravan deposits and high Cu contents are considered a vector to mineralization (Gross, 1956; Shawe et al., 1959; Motica, 1968; Weir and Puffett, 1981). Some of the early work on the Colorado Plateau ores suggested a common source for the U and the Cu (Wright, 1955).

The geochemistry of Cu, U, and V suggests the reason for the difference (see the Preface by M. Barton). Copper solubility depends mainly on chloride content, whereas the solubilities of U and V are

largely independent of chloride concentration and are controlled by redox state (Barton and Skinner, 1979; Romberger, 1984; Wanty and Goldhaber, 1992). Oxidizing fluids may mobilize Cu, U, and V from a source rock that contains all three, if it has enough chloride to complex the Cu adequately. The difference lies in the trap: a reducing environment that causes U and V to precipitate will only trap Cu if it contains sulfide (Fig. 16). By contrast, any environment containing sulfide is able to trap U and V as well as Cu, because any environment that contains sulfide is ipso facto reducing enough to convert U^{6+} to U^{4+} and $V^{4+/5+}$ to V^{3+} . In the context of the metallogenetic models discussed above, any hydrocarbon would be capable of reducing dissolved U and V to their insoluble lower valence states, but only one with a high concentration of sour gas (H₂S-rich) would be able to trap Cu as well. And sour gas should be able to trap U and V from an oxidized fluid as well as Cu.

The presence of accessory Cu in the Uravan and the Big Indian U-V deposits indicates that the reductant did contain sulfide. This could have been sour gas associated with the hydrocarbons, or could have been derived from the breakdown of plants and other organic matter found in the rock. However, the relative scarcity of Cu compared to U and V, and the absence of U and V from the Lisbon Valley, Big Indian, and La Sal copper deposits, suggests that other factors, such as Cu, U, and V concentrations in the fluids and source rocks, are at work. Further research will focus on identifying and characterizing the various factors likely to be involved.

3. Connections between bleaching, Fe mobility, and U-V mineralization

A genetic connection has been postulated above between bleaching alteration of red rocks and U-V and Cu deposition, whether or not the U-V and Cu are themselves related. This leaves the question of where the Fe goes. Although much of the bleaching alteration at the sites described here is reductive, it typically involves some loss of Fe, which creates a mass balance problem. Here, the common association of



Fig. 16. Eh-pH diagrams for Cu, U, and V minerals. Modified from Garrels (1960).

hematite concretions with U-V systems, seen at Big Indian and Kane Springs as well as at other sites in the Paradox Basin (e.g., Temple Mountain), becomes significant, as does the absence of observed hematite concretions from the vicinity of Salt Wash U-V deposits.

Iron is mobile under reduced but sulfide-poor conditions, in contrast with both Cu and U-V solubility (see Barton, Preface). The lack of any evidence of a sulfide precursor for the hematite in the concretions at Big Indian, Kane Springs, and Flat Iron Mesa indicates that the hematite precipitated directly from solution, not as replacements for earlier sulfides. Thus, it is probable that the Fe was mobilized in a reducing, S-poor solution, moved, and precipitated once it reached an oxidizing regime. Bearing this out, all the observed hematite concretions associated with U-V deposits occur in red, unbleached sandstones.

The U-V mineralizing system at Big Indian clearly contained some sulfide, since it precipitated galena, sphalerite, pyrite, and chalcopyrite. But sulfides are relatively scarce among the ores, and H₂S availability may have been limited compared to the amount of metal mobilized. This would enable Fe dissolved from the bleached zone by the incoming hydrocarbons to travel until it reached an oxidized trap, such as unbleached sands, and precipitate. At Big Indian, this trap may have been the red Chinle sandstone just above the ore-hosting layer; at Kane Springs the reduced Fe-bearing solution might have traveled several kilometers along the fault before encountering a likely trap. Evaluating this hypothesis of Fe mobility linked to hydrocarbon movement and U deposition will be a topic for future work.

Conclusions

The Cu and U-V deposits of the Paradox Basin represent the activity of a diverse range of altering and mineralizing fluids. Although many details of their nature, sources, and timing remain without adequate constraint, examination of mineralogical and geological field data can help to elucidate their metallogenesis and their possible relationships to each other and to other geological phenomena.

Work presented here in preliminary fashion makes clear the intimate connection of both Cu and U-V deposits with bleaching alteration. This bleaching either reduces hematite to pyrite while conserving total Fe or reduces hematite and dissolves Fe²⁺, carrying it out of the rock. Both types of alteration are widespread in the Paradox Basin rocks and are ubiquitous in the vicinity of U-V and Cu deposits. The remnants of bitumen in pore spaces in the sandstones, the blue fluorescence of fluid inclusions from reduced areas, and analogy with a modern bleaching system at the Sinbad Seep suggests that hydrocarbons are likely responsible for both types. A sour gas or H₂S-rich hydrocarbon could pyritize a red bed sandstone; a sulfide-poor one could remove the Fe from it.

Petrographic and field geological evidence indicates that such bleaching is integral to the formation of both Cu and U-V deposits in the Paradox Basin. It has been demonstrated before that Cu deposition in the sandstones of the Wingate, Burro Canyon, and Dakota formations is the result of a two-stage mineralizing process of which hydrocarbon-induced bleaching was the first stage (Thorson, 2004; Hahn and Thorson, 2005; Thorson and MacIntyre, 2005). Hydrocarbons flowed up faults and spread out through permeable, dominantly sandstone strata, bleaching them and leaving pyrite and bitumen that acted as a reducing and sulfide trap for later Cu-bearing fluids. The U-V deposits in the Salt Wash and Chinle formations likely resulted from a similar process, with U and V entering the rock as oxidized aqueous species and precipitating after being reduced by pore-filling hydrocarbons or by the pyrite and bitumen they left behind. This process may have transiently mobilized and moved Fe, resulting in the formation of massive Fe oxide concretions near U-V deposits. Future work will focus on further elucidating these relationships.

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