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# Reactivity of As and U co-occurring in Mine Wastes in northeastern Arizona

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#### ABSTRACT

The reactivity of co-occurring arsenic (As) and uranium (U) in mine wastes was investigated using batch reactors, microscopy, spectroscopy, and aqueous chemistry. Analyses of field samples collected in proximity to mine wastes in northeastern Arizona confirm the presence of As and U in soils and surrounding waters, as reported in a previous study from our research group. In this study, we measured As (< 0.500 to 7.77 µg/L) and U (0.950 to 165  $\mu$ g/L) in waters, as well as mine wastes (< 20.0 to 40.0 mg/kg As and < 60.0 to 110 mg/kg U) and background solids (< 20.0 mg/kg As and < 60.0 mg/kg U). Analysis with X-ray fluorescence (XRF) and electron microprobe show the co-occurrence of As and U with iron (Fe) and vanadium (V). These field conditions served as a foundation for additional laboratory experiments to assess the reactivity of metals in these mine wastes. Results from laboratory experiments indicate that labile and exchangeable As(V) was released to solution when solids were sequentially reacted with water and magnesium chloride (MgCl<sub>2</sub>), while limited U was released to solution with the same reactants. The predominance of As(V) in mine waste solids was confirmed by X-ray absorption near edge (XANES) analysis. Both As and U were released to solution after reaction of solids in batch experiments with HCO3<sup>-</sup>. Both X-ray photoelectron spectroscopy (XPS) and XANES analysis determined the predominance of Fe(III) in the solids. Mössbauer spectroscopy detected the presence of nano-crystalline goethite, Fe(II) and Fe(III) in (phyllo)silicates, and an unidentified mineral with parameters consistent with arsenopyrite or jarosite in the mine waste solids. Our results suggest that As and U can be released under environmentally relevant conditions in mine waste, which is applicable to risk and exposure assessment.

1. Introduction

The Southwestern US has numerous sites affected by mining legacy. The Claim 28 site in the Blue Gap Tachee community in northeastern Arizona is an example of a mine waste site (Fig. S1) in which the cooccurrence of arsenic (As) (20-40 mg/kg) and uranium (U) (110-6600 mg/kg) was previously reported (Blake et al., 2015). The presence of As (5.70-9.56 µg/L) and U (66.9-169 µg/L) was also detected in seeps proximate to these mine wastes (Blake et al., 2015). The mineralized uranium deposits at the Claim 28 site are within the Rough Rock Sandstone of the Cretaceous Mesa Verde Group, an arkosic sandstone composed of quartz, potassium feldspar, and clay minerals (Chenoweth, 1990). The U in these deposits is associated with U- and vanadium (V)-rich minerals, including carnotite (K<sub>2</sub>(UO<sub>2</sub>)<sub>2</sub>(VO<sub>4</sub>) 2. 3H<sub>2</sub>O), tyuyamunite (Ca(UO<sub>2</sub>)<sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>  $\cdot$  5-8H<sub>2</sub>O), and melanovanadite  $(Ca(V^{5+}, V^{4+})_4O_{10} \cdot 5H_2O)$  (Chenoweth, 1990). The presence of U-Vbearing phases similar to carnotite and As-iron (Fe)-phases were also observed in mine wastes from the Claim 28 site (Blake et al., 2015; Avasarala et al., 2017). A recent study reported that carnotite dissolution is a relevant process affecting the reactive transport of U and V in this site (Avasarala et al., 2017).

Geochemical processes such as complexation, sorption/desorption,

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solubility, and redox state affect the reactivity of As and U and can alter speciation and mobility of these elements. Sorption of As and U can occur when sediment grains contain clay minerals and Fe-oxides (Sylwester et al., 2000; Smedley and Kinniburgh, 2002; Blanchard et al., 2017; Uddin, 2017). Sorption on clay minerals occurs on the interlayer and edge sites which provide many reactive exchange and sorption sites because of the inherently large surface area and net negative surface charge at pH 6-9, the characteristic range of natural waters (Kipp et al., 2009). Iron oxides such as ferrihydrite, goethite, and hematite can play an important role in the adsorption of As and U under environmentally relevant conditions (Fendorf et al., 1997; Dixit and Herring, 2003; Nico et al., 2009; Ilton et al., 2012; Marshall et al., 2014; Massey et al., 2014: McBriarty et al., 2017). The desorption of As or U oxyanions from Fe-oxides can occur at high pH conditions (> 8.5) or in strongly reducing conditions at near-neutral pH (Smedley and Kinniburgh, 2002). Reduced and oxidized forms of As [e.g., As (III) and As(V)] and U [e.g., U(IV) and U(VI)] can adsorb on Fe or manganese (Mn) (oxyhydr)oxides and clay minerals by forming both inner-sphere and/or outer-sphere complexes (Cheng et al., 2009; Latta et al., 2014; Massey et al., 2014; Zhang et al., 2016; Blanchard et al., 2017). The reactivity of As and U, which can co-occur in the environment, depends on pH and redox conditions, and the two elements generally exhibit opposite behavior when present in similar redox conditions (Troyer et al., 2014a). For example, the oxidation of reduced U(IV) minerals can cause the oxidative dissolution and release of labile U(VI) (Ulrich et al., 2009; Cerrato et al., 2013), while the reductive dissolution of Fe(III)oxides associated with As can cause As to mobilize (Troyer et al., 2014a). Carbonate can compete with As oxyanions for sorbent sites on mineral surfaces allowing As oxyanions to stay in solution (Kim et al., 2000; Radu et al., 2005; Blake and Peters, 2015), and it can complex with U and calcium (Ca) to form ternary complexes (Dong and Brooks, 2006; Borch et al., 2010; He et al., 2018). Recent studies have reported that the stability of As and U complexes can occur with U to As ratios of 1:1 and 1:2 at a range of pH values. For instance, at pH 7 the 1:1 major species is UO<sub>2</sub>(H<sub>2</sub>AsO<sub>4</sub>)(H<sub>2</sub>O)<sub>3</sub><sup>+</sup> and at extreme alkaline pH ranges,  $UO_2(AsO_4)(H_2O)_3$  <sup>-</sup> is the dominant species (He et al., 2018).

Although the presence of As and U in environments affected by mining has been extensively reported (Blake et al., 2015; Borch et al., 2010; Kipp et al., 2009), the specific mechanisms affecting the reactivity of As and U co-occurring in mine waste sites remain unknown. For example, sequential extraction studies on fine grained sediments collected from mine wastes in South Dakota reported that U became labile at acidic, reducing and oxidizing conditions; however, As was mostly released under reducing conditions (Kipp et al., 2009). Differences in As and U reactivity were also observed in soils collected at various distances from a mine waste site in South Dakota (Troyer et al., 2014a). Sequential extraction results from this study show that U is released as an acid extractable fraction (suggested to be carbonate related) and the As is released through the reductive dissolution of iron oxy(hydr)oxides (Troyer et al., 2014a). A previous study from the Claim 28 mine reported that As and U were mobile at pH 3.8 and 8.3, but the specific mechanisms affecting the release of these elements was unclear (Blake et al., 2015). A laboratory experiment showed that the reaction of As and U with mackinawite (FeS) under reducing conditions can result in uranyl-arsenate precipitation (Troyer et al., 2014b). Additional research is necessary to better understand the geochemical processes affecting the release of As and U under environmentally relevant conditions.

The objective of this study is to investigate the reactivity of As and U co-occurring in mine wastes by integrating laboratory batch experiments, sequential extractions, spectroscopy, microscopy, and electron microprobe analyses. This study builds on previous findings from our group reporting that As–Fe phases co-occur with U–V phases (Blake et al., 2015; Avasarala et al., 2017). However, the interaction between As, Fe, and uranyl vanadate minerals in this system is not entirely understood. The approach used in this study made use of new information

about aqueous and solid speciation of metal mixtures after exposure to different reactants to identify relevant mechanisms affecting the release of As and U from mine wastes. The results from this study have important implications for risk assessment, remediation, and resource extraction applications.

# 2. Materials and methods

### 2.1. Materials

Sediments and waters from the Claim 28 mine site located in the Blue Gap Tachee community in northeastern AZ and surrounding areas were collected for analysis (Fig. S1). A previous study from our research group focused on the U minerals and associated reactivity with vanadium (Blake et al., 2015; Avasarala et al., 2017). This study focuses on the reactivity of co-occurring As and U at the site. Additional water (n = 10) and sediment (n = 6) samples were collected for analysis in this study. Water was sampled from springs, a seep, a stock pond and wells in the area. Water samples were put in coolers with ice for immediate transport to the University of New Mexico Analytical Chemistry Laboratory (UNM). At UNM, the samples were filtered with 0.45 µm polypropylene filters and acidified for analysis by Inductively Coupled Plasma or left unacidified for alkalinity titrations and Ion Chromatography. Sediment samples were collected from the top 50 cm of the surface with care taken to avoid collecting the sediments that were directly at the surface and therefore more weathered. Samples were transported in bags back to UNM and dispersed to appropriate laboratories for analysis. Four sediment samples were evaluated in sequential extraction experiments and are labeled MW1, MW2, MW3, and BRS where MW stands for mine waste and BRS stands for background reference soil. Two sediment samples (MW3 and MW4) were evaluated in batch leaching experiments. Sample MW1 was mapped by electron microprobe, sample MW3 was evaluated by Mossbauer spectroscopy, and sample MW5 was analyzed with X-ray photoelectron spectroscopy (XPS). Sediment samples MW4 and MW5 were evaluated by X-ray absorption near edge spectroscopy (XANES). Samples MW1, MW2, and BRS were used in the arsenic speciation experiment. The methods used are described below.

#### 2.2. Solid characterization

Mine waste samples (MW1 – MW5) were analyzed using X-Ray Fluorescence (XRF), Electron Microprobe, XPS, XANES, and Mössbauer spectroscopy. XRF pressed pellets were prepared using 9g of sample mixed with 1g of the binder "spectroblend". The homogenized sample was pressed at 25 tons per square inch. Solid samples were analyzed for bulk elemental and oxide composition using an XRF Rigaku ZSX Primus II Wavelength dispersive instrument.

Qualitative X-ray mapping of epoxy-mounted polished mine waste samples was performed on a JEOL 8200 electron microprobe. Maps were acquired at 20 kV accelerating voltage and 30 nA beam current utilizing stage mapping at 2 mm steps (pixel) and 100 ms dwell time per pixel. The K- $\alpha$  X-ray lines for V and Fe; the L- $\alpha$  line of As; and the M- $\alpha$ line of U were mapped on 5 separate wavelength dispersive spectrometers (2 passes per map area) simultaneously with the K- $\alpha$  lines for aluminum (Al) and silicon (Si) on an energy dispersive spectrometer. A backscattered electron image was also acquired for each map area.

An XPS was used to acquire the near surface (< 10 nm) elemental composition and oxidation states. This analysis was performed on MW5 prior to and after reaction with  $HCO_3^-$  to compare surface behavior. Sulfur, iron, magnesium, arsenic, and uranium composition and oxidation states were evaluated. A Kratos AXIS-Ultra DLD XPS was used to acquire the near surface (5–10 nm) elemental composition and oxidation states by using monochromatic Al K- $\alpha$  source operating at 225 W. Survey spectra were acquired at 80 eV and high resolution at 20 eV pass energy. Three areas per sample were averaged to obtain each data

Sequential extraction method.

Mechanism	Extractive reagent	ctive reagent Reagent:Sample Ratio		Reaction temp °C
Easily labile	18 MΩ DI water, pH 7	15:1	1	Room temp
Pulls off outer sphere complexes (cation exchange)	0.4 M MgCl <sub>2</sub> ,pH 5	15:1	1	Room temp
Oxidizer	5–6% NaOCl,	15:1	1	96
	pH 7.5			
Mild acid	1.0 M NaAc in 25% HAc, pH 4	15:1	4	Room temp
Reducer	0.04 M NH <sub>2</sub> OH · HCl, pH 2	15:1	5	Room temp
Corrosive	Aqua regia	2.5:1	1	90

value. Charge compensation was accomplished using low energy electron at standard operating conditions of -3.1 V bias voltage, -1.0 V filament voltage and a filament current of 2.1 A. Gold powder was deposited on each sample, and Au 4f spectra were acquired for calibration purposes. All spectra were processed using CasaXPS (CasaXPS, 2018). Atomic percentage content was calculated by using sensitivity factors provided by the manufacturer.

We collected X-ray absorption near edge (XANES) spectra for iron. The X-Ray absorption spectra (XAS) data were collected at the Advanced Photon Source (APS), at Argonne National Laboratory, at the beamline 20-ID (XOR). The 20-ID beamline is equipped with a Si(111) monochromator. An uncollimated X-ray beam was used and the monochromator was detuned by 15%. The monochromator was calibrated using metal reference foil for K-edge at 7112 eV. The monochromator step size was 10 eV in the pre-edge, 0.5 eV in the XANES region, and 0.05 Å-1 in the XAFS region. Fluorescent counts for iron Kedge spectra were collected using a Vortex Si Drift solid state 4 element detector. The samples were kept at a temperature of 22 K (-250 °C), using a Displex liquid helium cryostat. Standards for Fe(III) and Fe(II) were iron (III) oxide Fe<sub>2</sub>O<sub>3</sub>, and iron (II) sulfate FeSO<sub>4</sub>. The XAS data were processed using the Athena interface to the IFEFFIT program (Newville, 2001). The background subtraction (AUTOBK algorithm) (Newville et al., 1993), and normalization were conducted as described in Kelly et al. (2008). The Fe K-edge XANES spectra were analyzed by linear combination fitting by using Fe(III), and Fe(II) standards. XAS measurements for As were performed at Beamline 11-2 at the Stanford Synchrotron Radiation Laboratory. Samples were measured at the As K Edge in fluorescence mode using a 100 element Ge detector and a double crystal Si(220) Monochromator, calibrated at the first inflection point of, and Au metal foil absorption at, 11919.0 eV. Measurements were performed at room temperature in a LN Cryostat with samples attached to the cold finger and kept under vacuum through the measurement. No change was observed through consecutive scans, nor changes observed in the absorption when first and last scans of the series were compared, ruling out beam damage during the measurement. Samples sets were reduced and analyzed by using Athena and Artemis (Ravel and Newville, 2005).

The sample for Mössbauer spectroscopy was prepared by lightly pressing 100 mg of the < 63  $\mu$ m powder into a disk within a 3 mm thick acrylic plastic holder and sealed in place with two pieces of polyimide tape. <sup>57</sup>Fe Mössbauer spectra were collected in transmission mode with a constant acceleration drive system (SEE Co., Inc) and a <sup>57</sup>Co(Rh) source. Samples were mounted in a Janis gas-exchange closed cycle cryostat capable of maintaining a sample temperature of 18 K. The Mössbauer source was at room temperature. Data were calibrated with an  $\alpha$ -Fe foil at room temperature. Spectra were fitted with the Recoil software package using Voigt lineshapes with an intrinsic line width fixed to that of the instrumentally-determined width of the inner lines of the Fe foil (0.13 mm/s) (Lagarec and Rancourt, 1998). Unless otherwise noted, spectra were fitted with all parameters allowed to float during the fitting routine.

# 2.3. Inductively Coupled Plasma Optical Emission and Mass Spectrometry

Water samples and extracts from the acid digestion of the solid samples were measured for elemental concentrations using a PerkinElmer Optima 5300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), with a detection limit of 0.5 mg L<sup>-1</sup>. Trace elemental concentrations were measured with a PerkinElmer NexION 300D (Dynamic Reaction Cell) Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), with a detection limit of 0.5 µg/L. Both ICPs were calibrated with a 5-point calibration curve and QA/QC measures including blanks, calibration check standards, and an internal standard on the ICP-MS were taken to ensure quality results.

# 2.4. Sequential extractions

Four samples were part of the sequential extraction based upon Tessier et al. (1979) (Table 1): background reference soils (BRS) (low U concentration), Mine Waste 2 (MW2), Mine Waste 3 (MW3), and Mine Waste 4 (MW4). Total bulk samples (heterogeneous) were used in the sequential extraction and the samples were not sieved. Each sample was split and run in triplicate aliquots with 2 g of sediment per aliquot (Schultz et al., 1998). In between each extraction step, samples were centrifuged for 10 min at 2000 RPM followed by a rinse with 18 M $\Omega$  DI water to remove residual reagent and centrifuged an additional 5 min at 2000 RPM (Table 1). The pH of each reagent was adjusted using dilute NaOH or HNO<sub>3</sub><sup>-</sup> depending on the initial pH of the solution. All extraction solutions were diluted and analyzed by ICP-OES for As, U, V, S, P, Fe, Mn, Ca, K, Si, and Cr. ICP-MS was used to analyze As, U, and Mn present at trace concentrations.

# 2.5. Additional batch experiments for As, U, and Fe release

To better understand the reactivity of As, U and Fe in the sediments, a series of batch experiments were performed. Reagents used included 18 M $\Omega$  DI water, 0.4 M MgCl<sub>2</sub> and 1 mM HCO<sub>3</sub><sup>-</sup>. These reagents were chosen to emulate potential environmental conditions. The  $18\,M\Omega$  DI water is similar to rain water, with low specific conductivity and ion concentration, the 0.4 M MgCl<sub>2</sub> mimics an arid environment with abundant evaporites and can help to evaluate ion exchange, and the 1 mM HCO<sub>3</sub><sup>-</sup> shows the potential for release related to an oxyanion at a higher pH, which is possible in this environment. Two grams of each sample (MW3 and MW4) were weighed and placed in 50 mL centrifuge tubes in duplicate for each reagent. For each tube, 50 mL of reagent was added to the sample, and the tube was placed on a rotator arm. Each tube was then subsampled by pipetting 8 mL from the reagent every 30 min from time 0.5 h to 6 h. Each aliquot concentration was then multiplied by the remaining volume of reagent in the tube to account for the final concentrations over time.

#### 2.6. High Performance Liquid Chromatography-As speciation

Samples MW1, MW2 and BRS from the batch experiment were measured for As(III) and As(V) species by using High Performance Liquid Chromatography (HPLC) coupled with ICP-MS. Samples were kept cold until sample analysis time. The sealed vials were placed in a rack and samples were diluted at a 1:1 ratio with the mobile phase buffered at pH 7.00  $\pm$  0.05 SI Unit. The vials contents were mixed until homogenized by using a vortex and filtered (0.45 µm filter) into HPLC auto-sampler vials. The mobile phase was made of 146 mg Ethylenediaminetetraacetic acid (EDTA), 650 µL Tetrabutylammonium hydroxide (TBAOH), and 50 mL ethanol, buffered at pH 6.90 to 7.02.

Calibration standards for Arsenite (As(III)) and Arsenate (As(V)) were prepared similarly to the samples matrix by using the buffered mobile phase. The analytical mobile phase was buffered at pH 7.00 and brought to volume in 5% ethanol "HPLC Grade." A PerkinElmer Flexar HPLC was coupled to a NexION 300D ICP-MS through injection valve. The system was calibrated by using a blank and four-point calibration standards, then the samples were analyzed in automated mode. Chromatogram retention time was adjusted, peaks were identified, and the linearity of the calibration curves was verified for each species. The analytical data were reprocessed, validated, and then exported in Excel format. Specific parameters for the ICP-MS and HPLC are provided in the supplementary information (Table S1).

## 3. Results and discussion

# 3.1. Water sample analyses

Water analyses conducted in this study detected the presence of As and U in water sources close to the mine waste, confirming results reported in a previous study from our group (Blake et al., 2015). In the present study, additional locations were sampled to include a wider variety of water sources such as mine waste seeps, springs, stock pond water, and groundwater wells. Arsenic concentrations measured in these sources range from less than method detection limits  $(0.030 \,\mu\text{g/L})$ to 36.7  $\mu$ g/L, U concentrations range from 0.950 to 165  $\mu$ g/L and in situ pH values range from 3.54 to 8.71 (Table 2). The seeps are in direct contact with mine waste, while the Waterfall spring and White Clay spring are in contact with bedrock. The stock pond is approximately 1000 m downgradient from the Claim 28 mine site and the two wells sampled are even further downgradient (Fig. S1). Of the 14 water samples collected, only 1 well sample had an As concentration higher than the U.S. EPA maximum contaminant level (MCL) of 10 µg/L As (EPA, 2017). The As concentrations in the rest of the water samples were below the MCL of  $10\,\mu\text{g/L}$  As, showing a similar result to the seep and Waterfall spring concentrations reported previously (Blake et al., 2015).

The U concentrations in sampled waters were generally higher than the As concentrations. The U concentrations in 10 of the 14 waters sampled were higher than the MCL of  $30 \mu g/L U$ , whereas 4 of the water samples were below the MCL of  $30 \mu g/L U$  (EPA, 2015). Previously reported U concentrations in the seep and Waterfall spring samples

were both above the MCL of 30 µg/LU (Blake et al., 2015). The difference in As and U concentrations obtained in these water sources reflect the inherently complex hydrogeochemistry of the site. It remains unknown how much As and U in the water sources are from reaction with mine wastes or from naturally occurring mineral deposits. No previous studies have determined the source, and that determination is beyond the scope of this work. As evidenced by these aqueous concentrations, As and U do co-occur, but the relative amounts of As and U do not correlate, which means they are either from different sources or behave differently in the sediments and mine wastes. The mechanisms affecting the presence of As and U in these water sources remain unknown. Bulk sample analysis using an XRF and Electron Microprobe were conducted to identify the chemical composition of mine waste samples collected for this study and additional experiments were performed to better understand the chemical behavior of these co-occurring constituents.

# 3.2. Solid sample analyses

## 3.2.1. XRF and electron microprobe

Bulk sample XRF results for six mine waste samples (Table 3) have As concentrations that range from 20 to 36 mg kg<sup>-1,</sup> which is 5 to 6 times the average As concentration in continental sandstones (Smedley and Kinniburgh, 2002). Uranium concentrations from the mine waste samples were up to 3000 times the crustal average of U (U.S. EPA, 2008), ranging from < 60 to 6614 mg/kg (Table 3). The V concentrations in the mine waste samples ranged from 220 mg/kg to 17,000 mg/ kg, the Fe concentrations ranged from 3500 to 55,000 mg/kg, and the S concentrations ranged from 370 to 3400 mg/kg. The presence of U–V phases, As–Fe phases, and sulfide minerals identified at this site (Blake et al., 2015) indicate that the chemistry of V, Fe, and S may affect the distribution and mobility of As and U.

The co-occurrence of As, U, V, and Fe in mine waste solids was confirmed by electron microprobe (Fig. 1). A closer look at the mine waste by microprobe image mapping shows areas in which U, As, and V are concentrated in a mineral grain. Vanadium and Fe co-occur adjacent to the grain, likely as an Fe oxide coating. This microprobe analysis indicates that As and U coincide in certain spots likely due to their association in a solid phase. In other microprobe maps, we observed the co-occurrence of As, U, V and Fe in the same spot (Fig. S2). In some mineral grains, U and As co-occur without the occurrence of V and Fe (Fig. S3). In other examples, V, Fe, and As co-occur with U on the edge of a predominantly Si and K grain (Fig. S4). Arsenic and U are also associated with Al, V, and some K, suggesting a clay coating on the edge of a quartz grain (Fig. S5). The specific mineralogy of these solid phases is currently unknown. Future research could identify the specific mineral phases in this mine waste. Further analyses of mine waste solids were conducted using Mössbauer spectroscopy to analyze Fe-solid

Table 2

Table 2				
Chemical analyses for U, As	s, and pH in water samples co	llected from different water so	ources in Blue Gap Tachee,	Northeastern Arizona.

	Sample ID	Description	Uranium (µg/L)	Arsenic (µg/L)	pH
June 2014	WS1	Mine waste seep	163	5.74	3.78
	WS2	Mine waste seep	169	5.71	3.79
	WS3	Waterfall spring	66.9	6.60	7.2
	WS4	Waterfall spring	135	9.56	7.4
March 2015	WS1	Mine waste seep	165	2.57	3.54
	WS3	Waterfall spring	84.0	0.717	-
	WS5	Stock Pond	12.6-19.0	BDL (< 0.030)	7.78
	WS6	White Clay Spring	55.7	1.67	-
July 2015	WS1	Mine waste seep	163	0.032	3.83
	WS3	Waterfall Spring	73.5–95.0	1.10-2.70	8.12
	WS5	Stock Pond	4.73	0.153	7.52
	WS6	White Clay Spring	68.8	0.739	7.48
	WS7	Well	1.94	36.7	8.71
	WS8	Well 4 K-388	0.950	7.77	8.05

#### Table 3

XRF Concentrations of mine wastes and background reference soil. Note that BDL means below detection limit. The detection limit for V is 200 mg/kg, for Mn is 100 mg/kg, for As is 20 mg/kg and for U is 60 mg/kg.

Sample	Na	Mg	Al	Si	Р	S	К	Ca	Ti	v	Mn	Fe	As	U
MW avg. conc. (mg/kg)	730	1470	84,300	262,000	438	1860	30,600	6990	4520	5500	717	26,200	30.1	1650
Std dev	546	917	27,800	79,000	222	1000	21,600	6080	1670	8080	331	18,000	9.24	2830
N	6	6	6	6	6	6	6	6	6	4	4	6	4	5
# BDL	0	0	0	0	0	0	0	0	0	2	2	0	2	1
BRS (mg/kg)	1440	3070	52,100	242,000	1120	1340	36,700	16,400	5340	BDL	566	26,700	BDL	BDL

speciation.

## 3.2.2. Mössbauer spectroscopy

The Mössbauer spectra of mine waste sample MW3 were collected as a function of sample temperature at 298 K, 140 K, 77 K, and 20 K (Fig. 2). At room temperature the Mössbauer spectrum consists of a broad, poorly defined feature (yellow) that can be fit as a collapsed sextet (Table S2) and two central doublets (doublets 1 and 2) with center shift (CS) and quadrupole splitting (QS) parameters of (doublet 1 (red): CS = 0.35 mm/s, QS = 0.52 mm/s; doublet 2 (green): CS = 0.35 mm/s, QS = 1.20 mm/s) (Table S2). QS is the quadrupole splitting parameter (distance between two doublets) and is an indication of the distortion of the electric field around the nucleus. The collapsed sextet is likely that of nano-crystalline goethite that is superparamagnetic at room temperature (298 K) and is magnetically ordered in low-temperature spectra (discussed below). The Fe(III) doublet 1 is consistent with octahedral Fe(III) in oxides, clay minerals, and rockforming silicates at room temperature (Dyar et al., 2006). The second Fe(III) doublet (CS = 0.35 mm/s) has a high QS parameter of 1.20 mm/s, which is not commonly seen for high-spin Fe(III) oxides, oxy-hydroxides, and clay minerals or phyllosilicates.

At lower temperatures the sextet increases in relative area from 50.5% at room temperature to 78.8% at 20 K and is consistent with loss of the doublet 1 area upon cooling. Together, the consistent decrease in area of doublet 1 with cooling, and growth of the sextet with Mössbauer parameters of CS = 0.38 mm/s,  $2\varepsilon = -0.23$  mm/s, and H = 45.5 T suggest that the sextet is because of the presence of nano-crystalline goethite. The ~15.8 to 17.5% relative area of doublet 1 at 77 K and 20 K is likely because of the presence of paramagnetic Fe<sup>3+</sup> in phyllosilicates/clay minerals or primary silicates.

Below 140 K, 2–3% of the spectral area is present as a doublet assigned to  $Fe^{2+}$  (CS = 1.24–1.28 mm/s, QS 2.75–2.96 mm/s) and has Mössbauer spectral parameters consistent with octahedral  $Fe^{2+}$  in silicate minerals. The low content of Fe(II) along with the poorly ordered



Fig. 1. Microprobe image mapping of mine waste sample MW1. The backscatter black and white image shows a bright grain, on which elemental mapping was done, shown on the right.



Fig. 2.  ${}^{57}$ Fe Mössbauer spectroscopy temperature profile of mine waste sample MW3 with spectral fits shown.

nature of the sextet likely explain the rejection of an Fe(II) component at  $298 \,\mathrm{K}$  during fitting.

The second Fe(III) doublet "doublet 2" is difficult to assign to a mineral. Possible phases with similar Mössbauer parameters are jarosite  $(KFe_3(SO_4)_2(OH)_6, CS = 0.37 \text{ mm/s}, QS = 1.20 \text{ mm/s}), strunzite$  $(Mn^{2+}Fe_2^{3+}(PO_4)_2(OH)_2 \cdot 6H_2O, CS = 0.38 \text{ mm/s}, QS = 1.37)$ , or arsenopyrite (FeAsS, CS = ~0.30-0.47 mm/s, QS = 1.15 mm/s) (Deer et al., 2011; Dyar et al., 2006). The relative area of the Fe(III) doublet 2 decreases from 18% at 77 K to 5.3% at 20 K. The change in the spectral area may suggest that a magnetic ordering process occurs between these temperatures. If magnetic ordering occurs, then this likely rules out that the majority of doublet 2 is arsenopyrite, as at least at room temperature, arsenopyrite is diamagnetic (Vaughan and Craig, 1978). To our knowledge few, if any, publications exist on the low-temperature magnetic or Mössbauer properties of arsenopyrite. The dominant Fe oxidation state in arsenopyrite is Fe(II), which was found in XPS analysis of these mine wastes in Blake et al. (2015), in addition to Fe(III). However, because the Mössbauer parameters (CS  $\approx 0.5$  mm/s, QS  $\approx$  1.25 mm/s) are consistent with strunzite, jarosite, and arsenopyrite, Mössbauer spectroscopy is unable to confirm the identity of this mineral. In summary, the Mössbauer analyses of mine waste sample MW3 suggests that nano-crystalline goethite ( $\alpha$ -Fe<sup>3+</sup>O(OH)) is the dominant Fe(III) mineral, along with Fe(II) and Fe(III) in (phyllo)silicates, and an unidentified high QS mineral.

# 3.2.3. XANES and XPS of unreacted mine waste solids

The predominance of As(V) in mine waste and background soil samples was determined by linear combination (LC) fitting of XANES spectra. The spectra fitting results indicate that > 90% of the As was in the As(V) oxidation state for mine waste samples MW4 and MW5 (Fig. 3). A minor presence of As(III) (< 10%, which is within method detection error) was identified in these mine waste samples (Fig. 3a, b, and c). No evidence of arsenopyrite was found in the mine waste

samples with XANES. However, the presence of 84.8% As(V), 9.9% As (III), and 5.3% arsenopyrite was found in background soils (Fig. 3b and c). The predominance of As(V) in mine waste samples was confirmed by XPS analyses (Fig. 4a). The results of XANES analysis on MW3 shows that the dominant Fe species is Fe(III) (Fig. 3d and e), which further supports the findings from Mössbauer analyses. In a previous investigation of these sediments, reduced As was detected using XPS analyses in mine wastes from the Claim 28 site (Blake et al., 2015). The difference in the results obtained from the present study could be because of the heterogeneity of minerals present in mine wastes from this site. The predominant U species was reported as U(VI) by Blake et al. (2015). Additional sequential extraction and batch experiments were conducted to further assess the reactivity of these metals in mine wastes.

### 3.3. Sequential extraction

A 30 to 50% release (of the total extracted) of As (up to 94.0  $\mu$ g/L), likely labile or exchangeable As, was observed mostly after reaction with MgCl<sub>2</sub> (Fig. 5). The release of labile As may be indicative of the association with clay minerals, iron-sulfides, or calcite because of weak association with these solids (Ritchie et al., 2013; Sø et al., 2012; Gao et al., 2006; Bostick and Fendorf, 2003; Goldberg, 2002). The release of As and Fe by sequential extraction of mine waste solids was not linearly correlated (Fig. 6), indicating that As and Fe may have a strong inner sphere complexation (Sherman and Randall, 2003; Manning et al., 1998), where As bonds to iron oxide surfaces.

In contrast to the labile As, U release was observed mostly after reaction with NaOCl, NaAc, and Aqua Regia, suggesting that U on the surface of these mine waste sediments is not easily mobile because these reagents are stronger than DI water or MgCl<sub>2</sub> reagents (Fig. 5). However, there were low U concentrations (0.261 to 14.2 mg/kg) observed after reaction with DI water. It is likely that the U released after reaction under acidic conditions was because of the dissolution and subsequent release of mineralized U in these mine wastes. A linear correlation in the release of U and V after sequential extraction was observed (Fig. 6). A similar linear correlation in the release of U and V in batch experiments reacting mine waste with  $HCO_3^{-}$  (pH 8.3) and ascorbic acid (pH 3.8) was reported in a previous study from this site (Blake et al., 2015). The linear correlation in the release of U and V in these experiments suggests that the dissolution of U-V minerals is a key process affecting the release of these metals. This result is consistent with a recent study that integrated column experiments with mine waste solids from this site, and used reactive transport modeling to identify the relevance of the dissolution of U-V mineral phases similar to carnotite on the transport of U and V (Avasarala et al., 2017).

Arsenic and U chemical speciation is strongly dependent upon pH (Dixit and Herring, 2003; Kipp et al., 2009). For instance, chemical equilibrium analyses of water at pH7 indicate that As(V) could be present as negatively charged  $H_2AsO_4^-$  or  $HAsO_4^{2-}$ , whereas U could form positive hydroxyl complexes such as  $(UO_2)_3OH_5^+$ and (UO<sub>2</sub>)<sub>4</sub>OH<sub>7</sub><sup>+</sup>. At pH 5 (MgCl<sub>2</sub> reagent), As(V) would still be mostly present as negatively charged  $H_2AsO_4^-$  and U would be present as the positively charged UO<sub>2</sub>OH<sup>+</sup>. At pH 2 (NH<sub>2</sub>OH·HCl), As(V) would be either mostly present as neutrally charged  $H_3AsO_4$  or as  $HASO_4^{2-}$  while U will mostly be the positively charged uranyl ion,  $UO_2^{2+}$ . The differences in charge between As and U can affect the mobility and reactivity of aqueous species of these elements in solution. For instance, chemical aqueous species and solids of similar charge would repel due to electrostatic interactions and cause the stability of these aqueous complexes in water. Thus, additional batch experiments were conducted to better understand the release of As and U over time after reaction of mine waste solids with specific reactants of interest at pH conditions relevant to the site.





C.

Standards	MW4	BRS	MW5
FeAsS%	0	5.30	0
As(III)% Fh	9.80	9.90	5.10
As(V)% Fh	90.2	84.8	94.9

Ε.

Standards	MW5		
Fe(II)%	0		
Fe(III)%	100		

Fig. 3. XANES spectra (A) and linear combination fitting component weight (B and C) of MW4, MW5, and BRS samples. D and E show Fe XANES results. Sediment size of samples was  $< 63 \,\mu m$ .

# 3.4. Batch experiments

#### 3.4.1. Solution analyses

The release of As concentrations ranging from 24.1 to  $959 \,\mu\text{g/L}$  was observed after reaction of mine waste solids with each of the following reagents: DI, MgCl<sub>2</sub>, and HCO<sub>3</sub><sup>-</sup>. However, the highest release ( $959 \,\mu\text{g/L}$ ) was observed after reaction with HCO<sub>3</sub><sup>-</sup>, suggesting that anion competition is occurring between HCO<sub>3</sub><sup>-</sup> and As oxyanions (Fig. 7).

Most of the As released was As(V) as shown by HPLC-ICP-MS speciation analyses (Fig. 8). The As in the unreacted sample was also As(V) as shown by XPS results (Fig. 4). The results obtained from individual batch experiments were consistent with those obtained from sequential extractions reported in the previous section in which As was mobile after reaction with DI water and MgCl<sub>2</sub>. This suggests that As is easily labile and can be released because of exchangeable sites with MgCl<sub>2</sub>. These results indicate that As(V) is susceptible to mobilization under



Fig. 4. A. XPS spectra on unreacted samples, and samples following the reaction with HCO<sub>3</sub><sup>-</sup> for mine waste sample MW5. B. Sulfur standards showing binding energy locations. C. The table shows the percent of each element analyzed.

environmentally relevant conditions.

There was less variability in the range of U concentration released after reaction of solids with reagents DI, MgCl<sub>2</sub>, and HCO<sub>3</sub><sup>-</sup> compared to As release concentrations. (Fig. 7). The fact little difference was observed between the U susceptible to ion exchange with MgCl<sub>2</sub> versus complexation with HCO<sub>3</sub><sup>-</sup> indicates that there is some labile U. This outcome is consistent with the results from sequential extractions in which there was some labile U and little difference in release between the U mobilized from DI compared to MgCl<sub>2</sub> extractions. These additional batch experiments with HCO<sub>3</sub><sup>-</sup> are relevant because the pH and dissolved inorganic carbon concentration of the reagent are comparable to conditions measured in the field (Table 2). However, little additional release of U was observed with reaction with HCO<sub>3</sub><sup>-</sup>, indicating a limited portion of the U present in the solids is susceptible to complexation with HCO<sub>3</sub><sup>-</sup>.

The release of U was observed in all reactors after reaction with  $MgCl_2$  at concentrations as high as  $3800 \,\mu g/L U$  over the course of the batch experiment. However, the amount of U released in the replicate

sediment samples was different, indicating the variability associated with the heterogeneity of these samples. For example, after 30 min, MW3-1 released 369 µg/LU, MW3-2 released 1900 µg/LU, MW4-1 released 3300 µg/LU, and MW4-2 released 799 µg/LU. When reacted with HCO3<sup>-</sup>, the concentration of U released increased slightly over time up to 2500 µg/L. This trend was also observed for one of the mine waste samples reacted with DI water for the first 120 min, though the overall concentration was lower than in the HCO3<sup>-</sup> leachate. These results indicate that U in these mine waste sediments was mobile under environmentally relevant conditions, but reactions vary, depending on the reagent. The release of U during batch experiments reacting bicarbonate with mine wastes was reported in previous studies from our group (Blake et al., 2015; Avasarala et al., 2017). At the 8.3 pH value of the  $HCO_3^{-}$  solution, U is known to complex with  $CO_3^{\,2-}$  (Dong and Brooks, 2006), which is the likely mechanism occurring here. As previously mentioned, the concentrations of U in the mine waste samples collected for this study were lower than the concentrations observed in the previous study by our group (Blake et al., 2015). This shows the



Fig. 5. Sequential extraction results for As, Fe, U, and V of samples MW1, MW2, MW3, and BRS. Results are reported as percent of total extracted. Each extraction was analyzed in triplicate with the standard deviation shown.

inherent heterogeneity of mine waste solids. However, the concentrations of U released into solution are one to two orders of magnitude higher than the  $30 \,\mu g/L$  MCL for U.

The concentrations of As and Fe released to solution were high (400 to  $958 \,\mu\text{g/L}$  As and up to  $900,000 \,\mu\text{g/L}$  Fe) at the early stages of the experiment, but decreased over time after reaction with DI water,  $MgCl_2$ , and  $HCO_3^-$  (Fig. 7). This suggests that As and Fe re-adsorb onto the solids during the experiment. The solids likely have positive and negative charged surfaces depending on the mixture of grain sizes and mineralogy. As reported in Blake et al., 2015, the primary mineralogy of the mine waste solids is quartz, potassium feldspar, and kaolinite.

Kaolinite has been identified as an active clay constituent in regard to sorption and mobility of As(V) (Mohapatra et al., 2007). Arsenic is often found in the environment as an oxyanion, which can adsorb onto metal-oxides, and Fe could adsorb onto clay minerals (Blake and Peters, 2015). Depending on the charge of aqueous species and solid surfaces, As and Fe could re-associate to these solids because of electrostatic interactions that could facilitate adsorption processes. Additionally, the results of analysis from the leachate from the  $HCO_3^-$  batch experiment of MW3 and MW4 reveal that 475 to 958 µg/L of As was mobilized in the initial 30 min of the experiment. After 180 min, the concentration of the leachate was lower (72.9 to 115 µg/L). While the concentration of



Fig. 6. Sequential extraction comparison of As and Fe and U and V. Results are reported in micromol per kilogram.



Fig. 7. Batch experiments results for As, U, and Fe of extractant solution over time.



Fig. 8. As speciation after sample reaction with HPLC mobile phase for 15 min.

As on the surface of MW4 prior to leaching was low as determined by XANES, the concentration of As mobilized during the batch experiment was well above the drinking water standard of  $10 \,\mu$ g/L (EPA, 2017).

Additional XPS analyses were conducted to identify changes in As and Fe content and speciation in the near surface of the solids before and after batch reactions with  $HCO_3^{-1}$ .

# 3.4.2. XPS analyses of reacted samples

XPS analyses on the surface of MW5 prior to reaction with  $HCO_3^$ and after reaction with  $HCO_3^-$  show that As(V) was the predominant species on the unreacted sample (0.12%), but not detected on the reacted sample (Fig. 4). The detection of As(V) in solution after reaction with  $HCO_3^-$  explains the limited As detected on the solids in the reacted sample. Although some As was re-adsorbed onto the solid at the end of the experiment, the concentration of As in the solid phase was below the detection limit of XPS. This may be related to exchange between  $HCO_3^-$  and As oxyanions on the surface of the mine waste solid.

We detected 1.0% Fe on the surface of the unreacted sample and 1.3% on the reacted MW5 sediment sample. Further inspection of the oxidation states of Fe revealed that the percentage of Fe(II) was 29.3% and Fe(III) was at 70.7% in the unreacted sample (Fig. 4). On the reacted sample, Fe(II) and Fe(III) were detected at 14.3% and 85.7% respectively. Fe(II) could be complexed with HCO3<sup>-</sup> and be released in the solution which would reduce the amount of Fe(II) on the surface, so the percent Fe(III) would be increased. The percent Fe from the unreacted measurement to the reacted measurement increased by 0.3%, which is likely within measurement error. A shift to a higher binding energy was observed for S2p XPS spectra of reacted compared to unreacted samples. The highest peak was observed in the unreacted sample close to 168 eV which is typical for sulfate. However, the highest peak for the reacted sample was observed close to 171 eV which could be because of surface complexation of metals bound to sulfur functional groups in the surface as suggested by other studies (Bostick and Fendorf, 2003; Becker et al., 2001; Bebie et al., 1998).

The data reported in the present study indicate that arsenopyrite and jarosite are present in unreacted samples which also contained sulfate as reported by XPS and Mossbauer. This indicates that the binding of As to these minerals is relevant to understand As reactivity as reported in other studies (Deng et al., 2018; Johnston et al., 2012; Asta et al., 2009). As reported in the literature (An et al., 2017; Zhang et al., 2016; Troyer et al., 2014b), Fe and S are present in subsurface environments as iron-sulfide minerals such as pyrite and mackinawite. After these solids have been exposed to the surface because of mining activities, Fe and S can oxidize, resulting in the formation of Fe(III) oxides and sulfate. However, the reacted samples in this study show the absence of sulfate and the predominance of sulfide ( $S^{2-}$ ) in the solids. It is likely that the sulfate present in the unreacted samples was released into solution after reaction with HCO<sub>3</sub><sup>-</sup>. Future research is necessary to better understand sulfur speciation after reaction of the solids with HCO<sub>3</sub><sup>-</sup> and its relationship with As and Fe in these solids.

#### 4. Conclusions

The co-occurrence of As, U, V, and Fe in water and mine waste solids was confirmed by aqueous chemistry, batch extractions, sequential extractions, microscopy and spectroscopy. Based on sequential extraction and batch experiments, we identified water soluble and exchangeable As(V) and U in these sediments. Although U was extracted in batch reaction with  $HCO_3^-$ , the concentration was only 2 to 3-fold higher than that extracted with DI water and MgCl<sub>2</sub>. The presence of As (V) in the mine waste solids was confirmed by XPS and XANES which is consistent with the release of As(V) to aqueous solutions. Nano-crystalline goethite (a-Fe<sup>3+</sup>O(OH)), Fe(II) and Fe(III) in (phyllo)silicates, and an Fe mineral consistent with several phases including jarosite and arsenopyrite were observed by Mössbauer spectroscopy. These Fe minerals could play an important role on As binding in the mine waste solids. Our results suggest that As and U can mobilize under environmentally relevant conditions in mine waste from this site. For instance, the reaction of carbonate with uranium in solids can also affect the mobility of As. Future studies are necessary to better understand complexation and solubility reactions that could affect U and As mobility in mine waste sites. This information has important implications for risk and exposure assessment in this community.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2019.05.024.

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