PROJECT SUMMARY

The mining and processing of metal-bearing ores has left a legacy of contaminated mine wastes across the gold, silver, and mercury deposits of the north-central Mojave Desert located in southern California. In addition to the primary metals being mined at these sites, a host of other minor and potentially toxic elements (e.g. As, Cr, Pb, Sb) is naturally enriched and released concomitantly during the mining process, introducing significant fluxes of elements that pose threats to both human health as well as the local and regional environments surrounding the mines. The variety in geologic origin of the primary ores and the different processing methods applied to extract metals from them have resulted in chemically complex, heterogeneous mine wastes in which the distribution and composition of metal-bearing species present can be difficult to determine. Furthermore, weathering and dispersal of mine wastes redistributes metals and can (e.g. through oxidation, dissolution, sorption, and secondary mineralization) change their chemical forms, which may alter their bioavailability to organisms.

Few known studies have systematically addressed the effects of particle size on the concentration, speciation, distribution, and reactivity of toxic metals in mine wastes, despite the fact that size distribution is one of the governing variables controlling the transport of such materials to surrounding regions. We hypothesize that the bioaccessibility of arsenic and mercury in mine waste materials is largely dependent on particle size-dependent properties such that bioaccessibility increases only slightly with decreasing particle size, despite much larger increases in concentration, due to offsetting changes in As and Hg speciation and distribution. We therefore propose the following systematic, integrated, multidisciplinary approach to determine the relationships between particle size and the physical and chemical properties of mine waste materials in order to better predict the distribution and bioavailability of As and Hg, involving: (1) field sampling of gold and mercury mine sites in the north-central Mojave and Orange County, CA, including mine tailings, waste rock piles, streambed sediments, background soils, and surface water runoff collected during storm events; (2) size separation and characterization of mine wastes to identify trends in elemental concentrations and distributions with particle size and constrain the physical/chemical processes that contribute to these trends; (3) bulk and micro-scale X-ray absorption, fluorescence, and diffraction analyses of selected mine waste size fractions to identify trends in speciation and distribution as a function of particle size; and (4) leach extraction tests to assess the release of As and Hg in selected size fractions exposed to water and simulated lung and gastric fluids. Results will also be supported and interpreted with the aid of geochemical modeling.

Intellectual Merit: The proposed research will reveal previously uncharacterized yet fundamental trends in elemental concentrations, speciation, correlations, and bioaccessibility as a function of particle size ranging from >2.783 mm down to 0.056 μm. Using both conventional analytical methods as well as novel (micro)spectroscopic techniques to identify the behavior of As and Hg and their relative correlations with other elements in different size fractions, new information will be generated regarding associations of As and Hg compatible with their presence as primary ore minerals, secondary minerals, sorbed phases, and/or mineral coatings. Since speciation in particular is recognized as a critical component of assessing the relative reactivity and potential toxicity of trace metals in contaminated samples, identifying and quantifying the effects of particle size on speciation and using them to better predict trace metal bioavailability in natural systems represents a potentially transformative contribution to our understanding of the environmental geochemistry of mine waste materials.

Broader Impacts: This project involves a fully integrated plan of research and education by generating opportunities for independent research and fieldwork to undergraduate students, providing undergraduates with experience at national synchrotron research facilities, and initiating collaborative partnerships between Chapman University, a primarily undergraduate institution, governmental agencies, and public school educators. High school science students from traditionally underrepresented groups will be recruited for summer research internships and exposed to the proposed research through poster presentations and other outreach activities, while schoolteachers will be brought to Chapman through a release program that provides them with the opportunity to learn about and participate in novel scientific research. Results will be disseminated to relevant stakeholders impacted by the mine sites and may also lead directly to the development of remediation strategies in areas where heavy metal contamination is cause for environmental concern.

PROJECT DESCRIPTION

INTRODUCTION

The mining and processing of metal-bearing ores has left a legacy of metal-contaminated mine wastes across the world's mineralized regions, including the gold, silver, and mercury deposits of the north-central Mojave Desert located in southern California. In addition to the primary metals being mined in this region, a host of other minor and potentially toxic elements (e.g. As, Cr, Pb, Sb) is naturally enriched and released concomitantly during and after the mining process. For example, arsenic, a serious environmental contaminant, is commonly associated with mercury ores, with a highly stable Hg-As-sulfide aqueous species proposed from quantum chemical studies [1] that may be responsible for the simultaneous transport of Hg and As in hydrothermal fluids; similarly, arsenopyrite and Hg-sulfide minerals are commonly found cogenetically with gold and silver quartz vein deposits in this region. Such exposed mine sites contaminated by both primary and secondary metal releases pose threats to both human health as well as the local and regional environments surrounding the mines [2].

The geologic diversity of these primary ore bodies and the various ore processing methods used over time, including stamp milling, calcining (roasting), and cyanide treatment, have resulted in chemically complex, heterogeneous mine wastes in which the distribution and composition of metal-bearing species present can vary markedly from their initial depositional state. Furthermore, weathering and dispersal of mine wastes redistributes metals and further changes their chemical forms (e.g. through oxidation, dissolution, sorption, and/or secondary mineralization), which can alter their bioavailability to humans and wildlife [3-5]. Therefore a clear understanding is needed of the macro- and molecular-scale mechanisms that contribute to significant dispersal pathways and transformations of potentially harmful metals and metalloids in highly concentrated mine waste materials. In addition, the effects of these processes on the actual availability of these metals must be carefully examined under conditions relevant to biological systems.

A number of factors influence the transport, distribution, speciation, and bioavailability of toxic metals in mine waste materials. One particularly important variable to consider in addressing metal mobility from mine wastes is the size distribution of the material itself. Particle size (by which we define a particle as a solid non-aggregated mineral(-like) grain) is a well-documented determinant of transport potential in the environment by both aeolian [6-10] and fluvial [11-16] means, while both the bulk chemical composition and mineralogy/speciation of mine wastes, natural soils and sediments have been shown to vary, sometimes dramatically, as a function of particle size [17-19]. Perhaps most significantly, although relatively unstudied at the field scale, particle size effects may substantially influence the reactivity of mine wastes, with finer-grained particles possessing higher available surface areas and therefore enhanced solubility in aqueous systems. As these smallest particles are also most prone to incidental ingestion and inhalation, such effects have substantial yet currently unknown implications for the bioavailability of hazardous metals in mine wastes.

Surprisingly, very few studies have systematically addressed the effects of particle size on the concentration, speciation, and reactivity of toxic metals in mine wastes, despite the fact that size distribution is one of the governing variables controlling the transport of such materials to surrounding regions. Further, trade-offs that we have either observed in preliminary studies or hypothesize will occur with declining particle size between surface area (which generally increases), trace metal concentration (which usually but not always increases), speciation (which we propose will shift to less soluble phases), and microscale distribution (which we propose will feature more surface-accessible metals and fewer encapsulated phases) mean that the actual risks posed by the fine-grained and airborne fractions of mine wastes are highly uncertain. Thus, we suggest that the reactivity of trace metal(loid)s, As and Hg in particular, in mine waste materials generally increases with decreasing particle size but is mediated substantially by changes in speciation that produce more stable and less soluble metal phases in the finer-grained fractions. Quantifying these size effects and using them to better predict trace metal bioavailability in natural systems has yet to be done and represents a potentially transformative contribution to our understanding of the environmental geochemistry of mine waste materials.

We propose a systematic, integrated, multidisciplinary approach to determining the relationships between particle size and the physical and chemical properties of mine waste materials in the north-central Mojave desert in order to better predict the distribution and bioavailability of metal(loid)s including As and Hg and to provide a sound scientific basis for the development of effective remediation strategies to control metal fluxes from these mine sites. Such an approach necessarily utilizes a combination of field studies, macroscopic analyses of both physical and chemical properties of mine wastes, spectroscopic studies, and simulated bioaccessibility (defined as the fraction of a substance that is released from solid particles into solution during processes such as digestion) extraction tests. We propose the following field, laboratory, and spectroscopic studies: (1) field sampling of gold and mercury mine sites in the north-central Mojave and one site in Orange County, CA, including mine tailings, waste rock piles, streambed sediments, background soils, and surface water runoff collected during storm events; (2) size separation and characterization of mine wastes to determine trends in elemental concentrations and distributions with particle size and constrain the physical/chemical processes that contribute to these trends; (3) bulk and micro-scale X-ray absorption, fluorescence, and diffraction analyses of selected mine waste size fractions to identify trends in speciation and distribution as a function of particle size; and (4) leach extraction tests to assess the release of As and Hg in selected size fractions exposed to water and simulated lung and gastric fluids. Geochemical modeling will be employed to interpret the experimental results in the context of mineral stability, solubility, adsorption, and aqueous speciation. The proposed studies are represented schematically in **Figure 1** to show the logical, integrated, and sequential order in which the studies build upon one another to address the central hypothesis and scientific goals

Figure 1. Flowchart of work proposed. Black rectangles indicate proposed studies, gray ovals indicate information obtained.

defined above and in the following sections. Throughout the proposed work, related education and outreach efforts will enhance both the scientific experience for the students and teachers involved as well as the impact and visibility of the research within the broader scientific and civic communities.
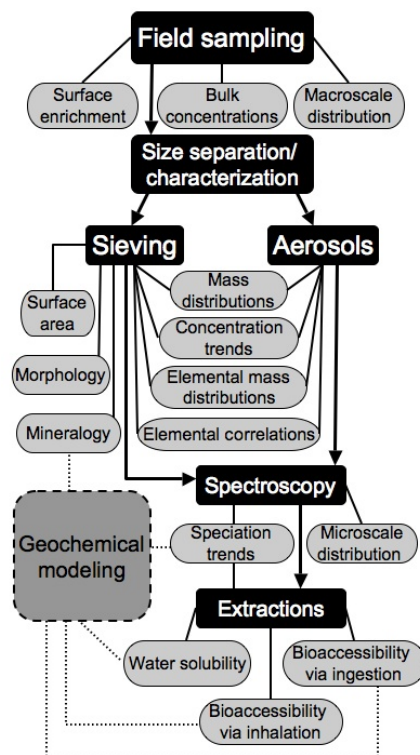
PLAN OF WORK

1. Field sampling of gold, silver, and mercury mines in Southern California (Yrs 1-3)

Purpose: Collect samples at gold, silver, and mercury mines to assess As and Hg enrichment and dispersal into surrounding regions, characterizing generally the extent/rate of mobilization through erosional weathering, airborne transport and isolated storm events. Use these results to identify locations and materials most appropriate for detailed size, spectroscopic, and bioaccessibility analysis.

Background

The dominant proportion of US mining activity took place in the western states, particularly in California which hosts some of the largest gold and mercury deposits in the North American continent. These ores are located in a variety of lithologic terranes and were deposited at different crustal depths by hydrothermal systems with differing chemical characteristics; for example, mercury is found both in high-T Si-carbonate deposits formed in altered serpentinite bodies and in low-T, near-surface hot spring deposits [20], while gold and silver ores can occur in near-surface quartz-carbonate-chalcedony veins, massive sulfide deposits, and placer deposits [21]. At mercury mines, the primary Hg ore represents the greatest risk in terms of human health, while at both gold and mercury mines several trace elements including As are enriched and also pose potential health hazards.

2

Weathering and dispersal of mine tailings along with unprocessed "waste rock" materials from mine sites throughout the state of California are of considerable concern to regulatory agencies and have prompted studies of mine waste transport documenting the ability of metals to travel extensive distances via surface water supplies, often several km from the source [22, 23]. Additionally, intermittent storm events can dramatically increase surface runoff and transport of mine waste materials in relatively brief time frames such that most of the metal transport in a watershed occurs during a few isolated events [22, 24]. However, in low rainfall regions such as the Mojave desert (average 5-6" rain/year), windborne movement of fine-grained material can play a substantial role in the distribution of hazardous metals over great distances [10, 25]. Subsurface transport of particles through porous media, while also a potentially important pathway of metal dispersal [26-30], is not known to be a significant process in this region and is not a primary focus of this proposal.

The concern regarding the widespread distribution of mine waste materials over broad regions is exacerbated by continued urban growth in increasing proximity to formerly remote mine site locations as well as visitors to these areas for recreational purposes (off-road vehicle usage, hiking, horse-back riding), further enhancing potential exposure to contaminant-bearing dusts, soils, and sediments. In certain locations in Southern CA, such as the Red Hill mercury mine in Orange County, regions around the mine have been highly developed, with suburban developments directly bordering the waste piles themselves. Surprisingly, few known studies of metal distribution, transport, or availability have been conducted in these developed regions as part of the urban planning process. The potential for elevated levels of exposure to mine wastes is expected to increase over time with continued population growth and (sub)urban development, providing an important social context to the fundamental studies proposed.

Research and Educational Objectives

The distribution of primary and associated metals from mine sites is an issue of significant concern, yet in the mines of the north-central Mojave desert, no known comprehensive sampling studies have been undertaken to resolve the degree and extent of metal contamination. Additionally, field sampling must be conducted to collect representative samples for the subsequent size separation, spectroscopic, and extraction experiments planned. Therefore, the following studies are proposed:

1. *Measure the concentrations of heavy metal(loid)s including As and Hg in and around selected mine sites, including background regions, to determine the spatial extent of contamination and the rate of dispersal from the initial point source locations*
2. *Quantify the degree of windblown As and Hg enrichment as a function of distance and depth*
3. *Collect streambed water samples during periods of strong rainfall to measure the extent of particulate runoff and subsequent metal mobilization during isolated storm events*
4. *Utilize initial concentration data to collect bulk samples representative of different media including mine tailings, waste rock, streambed sediments, and background materials for more detailed size-dependent analyses*

To complete these tasks, the PI will work with colleagues in the Bureau of Land Management (BLM) and the U.S. Geological Survey (USGS) to secure access to the desired mine sites and approval to conduct sampling. This work is expected to involve between 4-6 undergraduate students during the academic year, adding 2 high school research interns during summer sampling periods. During the rainy season, which begins in the fall, undergraduate students from the PI's fall semester courses (ESCI 111: Physical Geology and ESCI 101: Intro to Environmental Sciences; enrollments 40-80 students) will also be offered the opportunity to travel to field sites and collect samples during storm events, as such trips are by necessity scheduled on short notice, pending weather conditions, and research group members may not be available. All students will receive appropriate safety and sampling training prior to participating in fieldwork.

Experimental Methods

Table 1 lists the mines currently targeted for sample collection; more may be added over the duration of the grant based on progress and priority issues with the BLM. The sites in the Randsburg and Soledad mining districts of the north-central Mojave desert were selected for the highly elevated As and

Hg concentrations recorded (1000-13000 mg/kg, or ppm), the relatively undisturbed nature of the mine locales, the low-precipitation climate regime which is representative of dozens of other mines in the region, and accessibility (2-3 hour drive). For comparison, the Red Hill mine site was selected due to its highly developed suburban location, the elevated levels of As and Hg (300-1500 ppm), and a location (10 minute drive) that will

Mine	Deposit Type	Media to Sample
Cactus	High sulfidation Au-Hg	Bkgd soils, tailings
Kelly	Hot-spring Ag/Au/Sb	Bkgd soils, tailings, sediments, res. soils
Golden Queen	High sulfidation Au-Hg	Bkgd soils, tailings
Red Hill	Silica-carbonate Hg	Calcines, waste rock
Tropico	High-sulfidation Au-Ag	Bkgd soils, tailings, residential soils
Yellow Aster	Low-sulfide Au-quartz	Bkgd soils, tailings

Table 1. Mines targeted for sampling, type of ore deposit, and media to sample at each site.

facilitate the involvement of students from the PI's courses in field sampling.

Sampling will be conducted at several locations within each mine region. At mine tailings piles, 0.5 kg of tailings will be collected per site for bulk analysis and 2-3 kg for size separation analysis, with the top several cm of surficial material removed to avoid sampling the most weathered material; this is done in order to determine the representative As and Hg concentrations and the relative As/Hg flux potential of each pile, which will aid both sample selection for subsequent experiments and regulatory priorities for eventual remediation. Where visible fluvial transport of tailings is observed, such as in washes (ephemeral drainages), comparable amounts of sediments will be collected at progressive intervals downstream, with the interval length and total distance from the tailings piles to be determined based on the geomorphology of each site and upon consultation with USGS and BLM collaborators; 100' increments have been utilized in preliminary samplings and have been found to adequately document dispersion trends away from the sources. In-field sieving of additional bulk samples to <250 μm will also be conducted at sites where size separation will be undertaken in order to guarantee sufficient quantities of very fine-grained material for later extraction experiments. To assess surface contamination of background and residential soils through windborne transport, as well as to establish true background concentrations in these regions, depth profiles will be conducted uphill of tailings piles with sampling depths determined based on soil properties or, if soil horizons are not clearly evident and/or soil development is poor, at 0-2", 2-6", 6-12", and >12" depth intervals. Similar depth profile sampling will be conducted in areas based on topography to be proximate to the transport path of mine wastes by fluvial processes. Sampling of these solid mine wastes and sediments will be conducted during the spring and summer prior to the advent of the rainy season, which removes soluble phases such as efflorescent salts from the wastes. GPS coordinates will be collected at each sampling location for plotting of results and overlaying of data.

During storm events, samples of runoff waters will be collected at intervals consistent with those of the sediment sampling conducted during the dry season. The purpose of this sampling is to quantify particulate mobilization during rain events to pair with subsequent size-separation studies and not necessarily to collect the first flushes at the start of the rainy season, recognizing that the latter represent the largest metal fluxes but are difficult to capture. Water samples will be measured for suspended solids concentrations and aliquots filtered using 0.45 and 0.2 μm filters to be consistent with USGS/EPA operationally-defined protocols characterizing the fractions of metals associated with the solid, colloidal, and dissolved fractions. However, ultrafiltration/centrifugation methods will also be employed to filter samples to 0.02 μm and compare with the other filtrates to assess whether colloidal/nanoscale particles are passing through the coarser filters. All solid samples will be collected as grab samples and stored in borosilicate glass jars with Teflon lids, while water samples will be collected and stored in HDPE bottles.

Following collection, splits of solid and water samples will be sent to ALS Chemex (a private analytical laboratory) or the USGS-Denver analytical lab, respectively, for inductively coupled plasma-mass spectroscopy (ICP-MS) analysis of a suite of 49 elements and cold vapor atomic fluorescence spectroscopy (CVAFS) analysis of Hg using standard QA/QC protocols. From the resulting data, concentration and depth profiles of selected metals will be generated on maps of the different mine areas using GIS software to provide graphical representations of metal distribution in the solid, colloidal, and dissolved

fractions. The extent of surface enrichment, determined through a ratio of the 0-2" sample and the >12" sample collected from the depth profile sampling, can also be plotted for selected elements to show the degree to which airborne transport contributes to mine waste dispersal. Comparisons between sites of different background geology, topography, and proximity to urban areas will then be made directly to assess the relative influence of these variables on metal distribution and transport, with findings and recommendations communicated to the USGS and BLM in formal reports to aid remediation efforts.

<u>Preliminary Results and Expected Significance</u>

Exploratory sampling trips to the Randsburg mining district, which contains gold and silver ores with elevated levels of associated As and Sb, reveal that As-contaminated mill tailings and waste rock averaging 1500-2000 ppm have been fluvially and atmospherically transported from several mine sites in the district. Initial depth profiles at selected housing lots located 1-2 km away from tailings piles show degrees of enrichment in the top 2" of soil by as much as 300% above background levels (**Figure 2**); enrichment factors as high as 1350% have been measured directly adjacent to the mine. This preliminary data indicates that surface contamination appears to be mostly limited to the top 6" of soil and that what can be deemed a "background" concentration varies from location to location around the site, a finding that will influence the degree of remediation necessary at each location.

Figure 2. Depth profiles from housing lots located adjacent to mine tailings in Randsburg, CA, demonstrating arsenic enrichment within the top 6 inches of soil sampled.

Two water samples were collected during a brief storm event in January 2008 from direct runoff associated with the Cactus gold mine heap leach pad and analyzed for solution composition (**Figure 3**); results show that total unfiltered As concentrations approached 100 mg/L, 90% of which was removed through filtration by 0.45 and 0.2 μm filters. However, the filtered As concentrations of ~10 mg/L exceed the EPA drinking water limits by 3 orders of magnitude, suggesting that high concentrations of potentially dissolved As are transported during intermittent storm events that may contaminate local waterways.
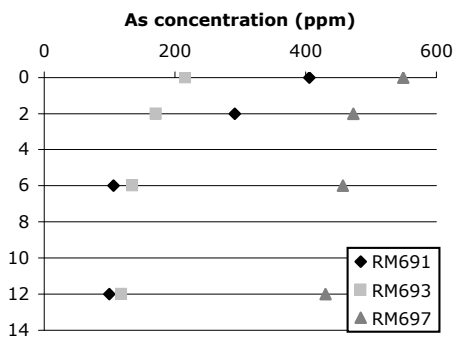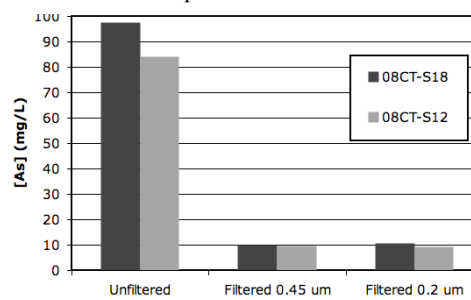

Figure 3. Filtered and unfiltered solution data for surface water runoff collected directly off the Cactus gold mine tailings pile.

2. Trends in metal concentrations/associations in mine wastes as a function of particle size (Yrs 2-4)

<u>*Hypothesis:*</u> *The concentrations of trace metal(loid)s including As and Hg are inversely related with particle size in mine wastes, suggesting that they are either concentrated as insoluble metal(loid) species into the finest size fractions or partitioned onto fine-grained iron (hydr)oxide coatings.*

<u>Background</u>

Particle size is a critical yet often overlooked variable governing metal transport and mobility in mine wastes. As mentioned, smaller particles are naturally more prone to airborne transport and can be carried for longer distances in surface water runoff. However, the chemical composition and mineralogy of such fine-grained particles may also vary as a function of size; for example, the PI and other investigators have observed dramatic increases in Hg concentrations with decreasing particle size in Hg mine tailings and sediments [17, 19, 31, 32], while other researchers have found variable trends in the composition of a wide variety of elements with particle size [33-44]. An inverse relationship between particle size and concentration, may be largely a result of physical weathering phenomena where mineral hardness dictates whether a certain metal is enriched in the smaller size range, as softer minerals will weather preferentially over other matrix phases and concentrate in finer size fractions. This is best exemplified by cinnabar (α-

HgS), which has a hardness of around 2.5 [45] but a K_{sp} value of 10^{-36} [46], resulting in rapid physical breakdown but slow chemical dissolution that enriches cinnabar in the finest size fractions (as observed spectroscopically by the PI [17]. Alternatively, more extensively weathered size fractions may feature a greater abundance of mineral coatings such as amorphous iron (hydr)oxides which serve as effective sorbents for metal(loid) ions [47-51].

In other instances, metal concentrations may display a direct relationship (increasing with increasing particle size), a unimodal or bimodal relationship (one or two maxima in intermediate size fraction(s)), or what we have termed an inverse unimodal relationship (concentration minimum in an intermediate size fraction), each with multiple explanations for their development. Furthermore, elements which share the same size-dependent trends may be associated with one another in a number of possible ways, including co-existing in mineral form (e.g. $FeAsO_4$), as sorbed species (e.g. Cu sorbed to goethite (α-FeOOH) [52-54] or other mineral coatings), as (co-)precipitates (e.g. Zn-Al layered double hydroxides [49, 55]), or as substituted ions into other mineral structures such as clay minerals, sulfides, and other metal (hydr)oxides [56-59]. Despite the prevalence of such trends and correlations in natural systems, few known studies have explored them or their implications; the effects of changes in concentration with particle size, likely tied to changes in speciation as described above, on reactivity and bioaccessibility are poorly understood.

Research and Educational Objectives

The identification of metal concentration trends as a function of particle size has been underutilized as a diagnostic tool for predicting the mobility of metals from mine wastes and their potential bioavailability. The likely association of elements sharing similar concentration trends can also be used as a basis to determine the speciation of trace metals including As and Hg, an exercise that will be further supported by complementary analytical methods. Therefore, the following tasks are proposed:

1. *Conduct detailed size fractionations of selected samples from previous field sampling efforts using sieving and cascade impactor methods, and identify size-dependent concentration trends for elements including As and Hg*
2. *Conduct basic characterization of the separate size fractions using BET surface area analysis, scanning electron microscopy (SEM), and X-ray diffraction (XRD) to identify trends in surface area, particle morphology, and mineralogy with changing particle size*
3. *Use statistical analyses to identify the strongest correlations between As, Hg, and other elements*
4. *Apply bulk mass distribution and elemental concentration information to calculate the mass distribution of As and Hg and therefore identify size fraction(s) with the greatest potential for metal transport/release*

To complete these tasks, the PI will involve a minimum of 2 undergraduate students who will receive training in the proper use of the equipment and software required for the proposed work. In addition, shorter projects related to this study will be included as part of the PI's upper-level undergraduate courses (ESCI 301: Environmental Geology; CHEM 301: Inorganic Chemistry; CHEM 428: Advanced Environmental Chemistry; typical enrollment: 7-12 students) in order to provide students the opportunity to gain experience in current research methods and instrumentation.

Experimental Methods

Bulk samples collected from mine tailings, background soils, and distributed sediments in the previously-described field sampling efforts will be air-dried and weighed prior to size separation via the use of stainless steel sieves and a mechanical Rotap to generate 11 distinct size fractions (**Table 2**). The finest size fraction (<20 um) will then be passed through a rotating micro-orifice uniform deposit impactor (MOUDI) recently purchased by the USGS to further fractionate the materials into 11 finer size fractions relevant to the inhalation pathway. Each fraction for which sufficient quantities are collected will be weighed separately and a split sent to either the USGS or ALS Chemex for ICP-MS analysis of a suite of 49 elements and CVAFS analysis of Hg using standard QA/QC protocols. Selected size fractions will also be characterized using BET surface area analysis, SEM, and XRD using facilities located either at Chap-

Split #	Size range (μm)	Split #	Size range (μm)
S1	>2830	M12	18-20
S2	1700-2830	M13	10-18
S3	**1000-1700**	M14	5.6-10
S4	500-1000	M15	3.2-5.6
S5	250-500	M16	1.8-3.2
S6	**125-250**	M17	1.0-1.8
S7	75-125	M18	0.56-1.0
S8	45-75	M19	0.32-0.56
S9	**32-45**	M20	0.18-0.32
S10	20-32	M21	0.1-0.18
S11	**<20**	M22	0.056-0.1

Table 2. Particle size ranges of mine waste size separations by sieving (S) and by MOUDI (M). Fractions in bold will be selected for bulk EXAFS analysis to investigate the particle size dependency of Hg and/or As speciation.
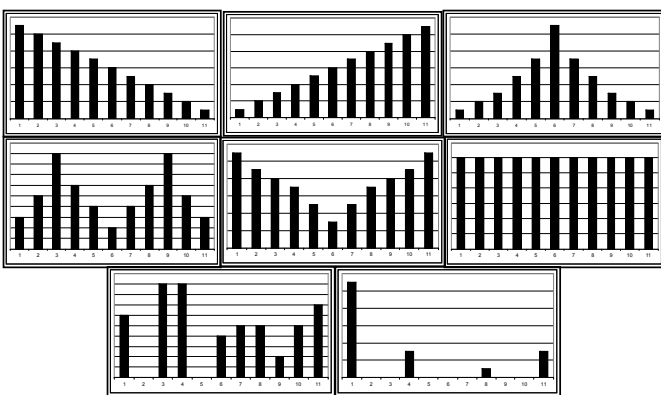

Figure 4. Schematics of concentration trend categories (L-R, top-bottom): direct, inverse, unimodal, bimodal, reverse unimodal, constant, poor, and below detection.

man (BET) or UC Irvine (SEM, XRD). This will provide additional contextual information regarding surface area, matrix mineralogy, and the morphology of the particles within each size fraction (e.g. to verify that size fractions are not substantially composed of aggregates).

Mass and concentration results will be represented in graphs showing the mass distribution, elemental concentration distribution, and elemental mass distribution within each sample as functions of particle size. The elemental concentration distribution graphs will be used to categorize elements based on their size-dependent behavior using a list of 8 possible trend categories (**Figure 4**). Finally, the JMP statistical analysis software [60] will be used to generate a 49x49 correlation matrix from the ICP-MS data, which can be sorted to determine the strongest correlations between elements as well as into subset pair correlation plots listing the relative strength of associations between one element and all others in the dataset. This information will help to statistically validate the category groupings generated, provide correlations rankings of elements most strongly correlated with As and Hg, and inform the selection of additional elements to study in later μXRF analyses.

Preliminary Results, Expected Significance

The methodology described above for analyzing and representing trends in metal concentrations as a function of particle size has been developed and refined as part of a prior research project funded by a USGS External Research Program grant and is the basis of a recently-submitted manuscript [61]. Examples of plots showing a sample mass distribution, As concentration distribution, and As mass distribution are shown in **Figure 5**; these results demonstrate the strong inverse relationship between As concentration and particle size as well as the influence of bulk mass distribution on As mass distribution. From the initial samples analyzed using this methodology, it is clear that a number of (although not all) trace metals in mine wastes show a similar inverse relationship between concentration and particle size, thus enhancing their potential mobility and the likelihood of dispersal through either windborne or fluvial transport. Importantly, SEM analysis of several size fractions confirms that the particles contained within each size fraction are present as coherent individual grains and not as aggregates of smaller particles; more detailed SEM studies will be undertaken to assess the presence of fine-grained mineral coatings at various size fractions, which may also increase in abundance with decreasing particle size. Preliminary BET results reveal that the surface area increases with decreasing particle size by a factor of approximately 5-10 in the mine tailings samples investigated.

These initial results hold considerable promise for the described approach as a way to rapidly obtain a sophisticated dataset of chemical compositions, concentrations, and mass distribution trends of mine wastes as a function of particle size. This data will be used to advise BLM and USGS regulators on which sites and size ranges are of greatest concern and suggest remediation strategies best suited to control further As and Hg dispersal. Importantly, such data will inform the subsequent research components

designed to determine the detailed speciation and bioaccessible fraction of As and Hg in the size-separated materials.
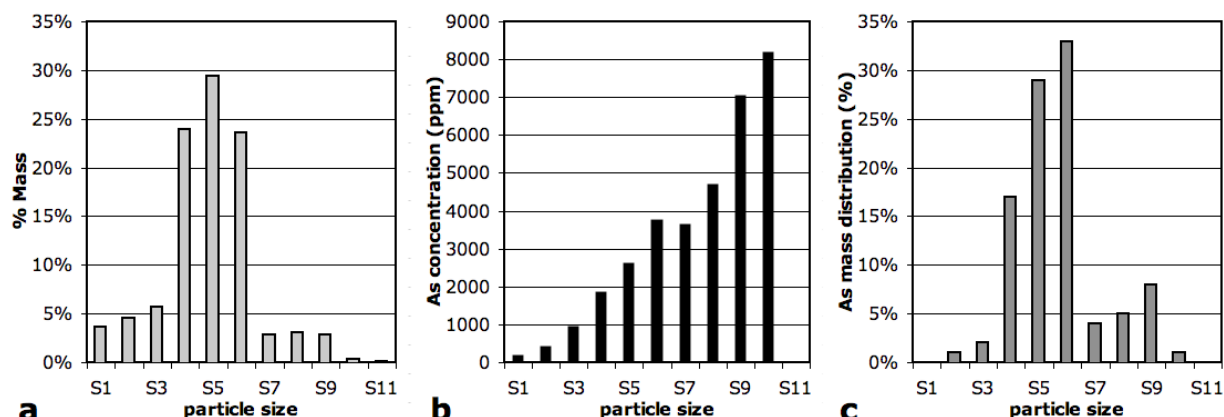

Figure 5. Size-separated data for a) mass distribution of bulk mine tailings from Randsburg, CA; b) arsenic concentrations in individual size fractions (demonstrating an inverse relationship between particle size and concentration), and c) percent mass distribution of arsenic within the sample. Refer to **Table 2** for size distribution ranges.

3. Trends in metal speciation and distribution in mine wastes as a function of particle size (Yrs 2-5)

Hypothesis: *The speciation of As and Hg in mine wastes changes with decreasing particle size such that the proportion of soluble phases declines and the proportions of insoluble and sorbed phases increases; also, the diversity of phases present increases due to secondary mineralization/sorption processes.*

Background

Speciation is now largely recognized as a critical factor in assessing the potential reactivity, transport, and bioavailability of toxic metal species [62, 63]. Different mineral forms of a single metal can vary by as many as tens of orders of magnitude in solubility, with corresponding impacts on the metal's mobility in the dissolved aqueous phase [2]. Thus trace metal concentrations must be regarded in the context of speciation when assessing their reactivity and potential hazard level.

While the concentrations of trace metals are often influenced by particle size, the relationship between particle size and speciation is less well known. Synchrotron-based X-ray analytical methods such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy have been proven to be of substantial utility in directly and non-destructively determining the speciation of metals in heterogeneous materials at relatively low, environmentally-relevant concentrations of 50-100 ppm or above [17, 58, 64-68]. At lower trace metal concentrations not feasible for bulk spectroscopy, microspectroscopic methods are more effective due to the ability to focus the X-ray beam to sizes as small as 2x2 μm on individual concentrated "hot spots" within the larger sample matrix, where micro X-ray diffraction (μXRD) and μEXAFS spectroscopy can then be applied. Microbeam methods can also be used to obtain a visual representation of trace metal distribution within a sample through micro-X-ray fluorescence (μXRF) mapping [69-73], and can further identify, both graphically and statistically, associations of metals with other elements throughout the sample.

Research and Educational Objectives

Trends in the speciation of heavy metals as a function of particle size have not been extensively documented, even though such trends may be highly influential in predicting the availability of metals when particle size and absolute metal concentrations are also known. Additionally, relatively new microspectroscopic methods can provide otherwise unobtainable microscale information regarding the distribution, speciation, and associations of metals in very low-concentration samples, increasing their applicability to mine-impacted soils and sediments. Therefore, the following tasks are proposed:

1) *Conduct bulk EXAFS analysis of selected size fractions of mine tailings, distributed sediments, waste rock samples, and airborne particulates to determine the speciation of As and Hg as a*

> *function of particle size*
> 2) *Conduct μXRF analysis of selected size fractions of mine tailings, distributed sediments, waste rock samples, and airborne particulates to determine metal distributions and characterize elemental correlations as a function of particle size*
> 3) *Conduct μXRD, uXANES, μEXAFS analysis at hot spots of (low-concentration) samples to generate speciation information inaccessible through bulk methods*

To complete this work the PI will involve 2-4 undergraduates throughout the academic year and 3-5 undergraduates along with 1 high school intern during the summer. Students will receive preliminary training, readings and practice using the data processing software prior to the synchrotron visits, which will be scheduled according to the undergraduate academic calendar to coincide with weekends, academic breaks, and winter/summer vacations. Since 2004, the PI has conducted all synchrotron research at the Stanford Synchrotron Radiation Laboratory (SSRL), Advanced Light Source (ALS), and Advanced Photon Source (APS) solely with the assistance of undergraduate students and has organized highly successful trips that both achieve the scientific goals of the allocated beamtime and provide a powerful educational experience for the participating students. The PI currently has three active 2-year proposals at SSRL and one active proposal at the APS, with a continuous record of allocated beamtime for the past 12 years. Undergraduate students will have the opportunity to conduct independent research at a national synchrotron facility and will participate in the collection, processing, and fitting of the data on-site with the assistance of the PI and synchrotron research support staff, with additional analysis to be conducted offline and back at campus. The continuously improving user interface and accessibility of synchrotron beamlines have greatly facilitated the use of such facilities by undergraduate students, as corroborated by SSRL Director Jo Stöhr (see Supplementary Documents,).

Experimental Methods

Following size separation and chemical composition analysis of bulk samples as described in the previous section, 4 size fractions (1000-1700 μm, 125-250 μm, 32-45 μm, and <20 μm) will be prepared for bulk Hg L_{III}-edge and/or As K-edge EXAFS analysis using the protocol reported by Kim et al. [74], contingent on their meeting the minimum concentration thresholds (typically 100 ppm) for such analysis. If sufficient quantities are available, size fractions collected from MOUDI separation will also be prepared for bulk EXAFS analysis. Data will be collected on beamlines 10-2 and 11-2 at SSRL or beamline 13-BM-C at the APS. Hg L_{III}-edge and As K-edge EXAFS spectra will be collected on the samples as dry powders at room temperature in the fluorescence-yield mode using a 30-element (SSRL) or 13-element (APS) high-throughput Ge detector [75]. Selected filters will be used to attenuate elastic scattering and minimize background matrix fluorescence.

The speciation of Hg and As in the unknown samples will be determined by comparison of their EXAFS spectra with those from Hg and As model compound spectral databases using EXAFS analysis software developed at SSRL [76]. EXAFS spectra of homogenous, well-characterized crystalline Hg, As(III), and As(V) compounds in addition to Hg(II) and As(III) or As(V) sorbed to a variety of crystalline and amorphous metal (hydr)oxide phases including goethite, hematite, and 2-line ferrihydrite have been collected by the PI and comprise the majority of the two databases. The latter database will also include existing published spectra of rare As phases donated by other investigators [64, 68, 77, 78]. The individual spectra of the model databases serve as unique fingerprints by which to identify component phases in a heterogeneous Hg- or As-bearing sample. Speciation is thus determined by deconvoluting the EXAFS spectrum of a natural sample containing multiple Hg or As phases using a linear least-squares fitting method into the sum of its individual components through direct comparison with the model compound spectra. Furthermore, determining the relative proportion of each model compound's contribution to the best possible linear combination fit allows quantification of the various phases present in a sample.

A larger subset of size fractions from the same mines including samples with concentrations too low to analyze using bulk EXAFS spectroscopy will be prepared for microspectroscopic analysis by both separately dispersing them onto Kapton tape and by embedding particles in epoxy and polishing them down to a thickness of a few microns; this will enable mapping of particle surfaces and particle cross-

sections, respectively, and allow for the investigation of the presence and role of surface coatings in As and Hg distribution. X-ray fluorescence mapping using a 2x2 µm beam spot will then be used to generate elemental distribution maps of a selected area within each sample, providing sufficient resolution to identify spots of As or Hg enrichment; due to current minimum beam dimensions, particles as small as 1 µm can be feasibly imaged. Map areas will be varied systematically in order to capture the same number of particles per map (approximately 150) for each size fraction. The µXRF maps will provide information at the micron scale on the distribution and correlation of selected elements including As and Hg based on the bulk chemical and correlation information obtained in the previous sections. Software developed at SSRL will be used for data processing [79].

Data obtained will be expressed visually as µXRF maps to characterize the spatial distribution of each element at the microscale (e.g. as individual mineralized particles, as dispersed sorbed species, as encapsulated fragments within larger grains, within weathering rinds or mineral coatings) and used to establish correlation plots defining the statistical relationship between any two selected elements, e.g. As/Fe, Hg/S, etc. These plots will indicate more conclusively if As or Hg is consistently associated with a particular matrix phase. The presence of distinct correlation zones, presumably defining different types/ratios of associations of the same two elements, can help determine whether the correlated metals coexist within discrete particles and/or are more diffusely distributed. Where applicable, micro-X-ray diffraction (µXRD) will be conducted on specific grains to identify the specific As- or Hg-rich phases present or other matrix phases to which the metals may be associated (Fe-oxides, Al-oxides, clays, etc.).

High-resolution µXRF maps around any "hot spots" of consequent interest will be generated in order to locate optimal locations for µEXAFS data collection as needed. The µEXAFS spectra will be compared with the As and Hg model compound spectral databases to determine the speciation of the element through linear combination fitting methods as described earlier [17, 64, 67, 74, 80, 81]. Microbeam results will then be compiled for different size fractions of the same bulk sample in order to resolve trends in speciation and distribution as a function of particle size and as compared to our central hypotheses. While issues of statistical significance will be introduced by the microbeam method (i.e. analysis of only a few spots will be possible per sample, precluding any meaningful sense of the sample's representative speciation), the conclusive identification of discrete trace metal phases and potential associations of As and Hg with other elements/phases in the sample matrix will provide information previously unattainable for such low-concentration samples. Lowering the concentration threshold of samples that can be studied using X-ray spectroscopic techniques thus opens the door to a much wider range of previously-unstudied environments to better track As and Hg speciation trends in these areas.

Geochemical modeling of As and Hg mineral stability conditions will be conducted using The Geochemist's Workbench software package [82] for comparison with spectroscopic speciation results and field-collected data. Activity-activity and solubility diagrams (e.g. Eh-pH, $\log[As(V)]$-log fO_2, $\log[Hg(II)]$-pH) will be generated to determine thermodynamic stability fields for As or Hg minerals and evaluated against EXAFS-derived speciation findings as well as aqueous geochemical data collected during rainfall events from earlier sampling trips. This will help to support the experimental results and assess the equilibrium state of the samples and systems being studied.

Preliminary Results and Expected Significance

Bulk As EXAFS spectra were collected on the S7-S11 size fractions of mine waste samples from the Randsburg, CA mining district; fitting results suggest that subtle changes in speciation are indeed occurring as a function of particle size, with the fraction of arseniosiderite ($Ca_2Fe_3(AsO_4)_3O_3 \cdot 3H_2O$) declining and those of amorphous ferric- and Ca-arsenate increasing slightly as particle size decreases, suggesting solubility differences between these phases. Interestingly, this suite of samples does not appear to contain As in a sorbed form (i.e. to iron (hydr)oxides), as would be expected if mineral coatings were abundant; however, linear combination fits of spectra from ore, tailings, efflorescent salts, and soils in this area indicate the presence of As(V) sorbed to ferrihydrite in addition to variable amounts of scorodite ($FeAsO_4 \cdot 2H_2O$) and arsenian jarosite $[KFe_3[(S,As)O_4)](OH)_6$, (Rytuba et al., unpublished data), phases which are potentially soluble in lung or gastric fluids.

Micro-XRF analysis of separate size fractions of a single mine waste sample also reveals changes in metal distribution and associations as a function of particle size. As:Fe correlation plots for different size fractions of a background-contaminated region in Randsburg, CA (**Figure 6**) area-normalized to capture the same number of particles per map reveal an increase in the
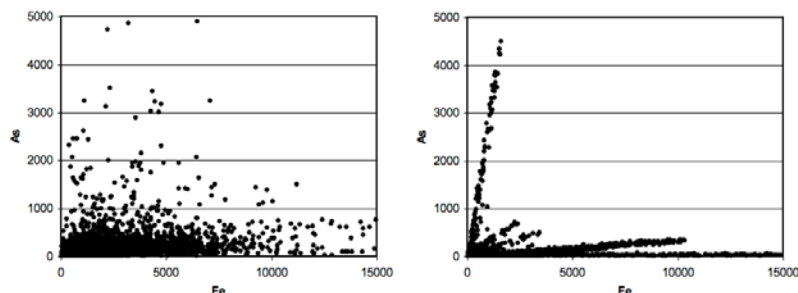

Figure 6. Correlation plots generated from area-normalized (i.e. the same number of particles/map) µXRF maps of a) 250-500 µm and b) <20 µm size fractions, comparing Fe (x-axis) fluorescence counts against As (y-axis) fluorescence counts.

resolution and number of discrete populations with constant As:Fe ratios (indicated by "fingers" of data points radiating from the origin) as particle size declines. This suggests an increasing diversity and more coherent particles of As-bearing species in the smaller size fraction, perhaps due to secondary mineralization or sorption processes that are more prevalent among smaller, more reactive particles. Such changes in speciation may be further confirmed by bulk EXAFS speciation analyses of the same size fractions.

4. Bioaccessibility of size-fractionated mine wastes via water and body fluid extractions (Yrs 3-5)

Hypothesis: *The bioaccessibility of As and Hg in mine wastes increases with decreasing particle size due to higher surface areas, greater concentrations, and more surface-accessible distribution (i.e. less encapsulation effects, more surface coatings), but these increases are offset by changes in speciation (i.e. more insoluble phases) that inhibit their mobilization in the extractant solution; additionally, the extractants' capacity to mobilize As and Hg will increase as follows: water < lung fluid < gastric fluid.*

Background

While the transport of hazardous metals from mine wastes dominantly occurs through the movement of solid particles, it is the short- and long-term dissolution of metal-bearing phases and subsequent leaching of metals into the aqueous phase that is often of greatest concern regarding potential health impacts to humans and wildlife. These processes are largely induced by exposure to surface water through precipitation and runoff, particularly in acid mine drainage regions [83]. Similarly, once solid particles are ingested or inhaled into the body, exposure to body fluids such as gastric acids and lung fluids can rapidly initiate particle dissolution and the conversion of metals from the mineral/solid form into the mobile/aqueous form, considerably increasing their potential toxicity [84].

The leaching of metals from mine wastes is influenced by a number of variables, with particle size again playing an important yet largely underexamined role. Since a particle's reactivity can be influenced by its surface area, the increased surface area available for exposure to the aqueous phase as particle size decreases suggests that the smallest particles, in addition to possessing the greatest transport potential, will also feature enhanced dissolution rates. Correspondingly, the higher proportion of surface-accessible material in small particles as a percentage of a particle's total mass suggests that encapsulation or "nugget" effects, wherein As- or Hg-bearing phases are entrained within larger particles and protected from solution, will also be less prominent for small particles, further increasing their mobilization. Of course, speciation of the metal(s) of concern must also be accounted for in this assumption, as fine-grained particles are also likely to be composed of highly insoluble phases that have withstood intense weathering over time; thus, the potential reactivity of smaller particles due to surface area and concentration effects may be substantially offset by changes in mineralogy and speciation, underscoring the importance of characterizing the speciation of metals as proposed in the previous research component.

Particle size is also a critical factor in assessing potential human exposure to mine wastes. Incidental ingestion of soils is often considered to be limited to particles less than 250 µm in size due to the adhesion properties of such particles to hands and food, increasing chances of ingestion [85], while particulate matter must be below 10 µm to enter the respiratory system, with a direct relationship between

size and penetration depth; for example, <2 μm particles can access the alveoli in the deepest regions of the lungs, whereas >10 μm particles are usually trapped by the nasal and oral cavities [86]. Combined with the inverse size-concentration relationship of As and Hg proposed earlier, these finest particles may represent the size fraction of greatest concern with respect to bioavailability. Therefore extraction tests designed to measure the solubility of metal-bearing phases under conditions relevant to environmental or biological systems are important in order to conclusively differentiate the relative importance of particle size, concentration, speciation, and extractant type on metal release from mine waste materials.

Research and Educational Objectives

As the field of medical geochemistry continues to expand, more linkages are being discovered between bioaccessible earth materials and human health responses. From this field has developed a number of methods to measure both the interactions of earth materials with, and their toxic effects upon, the human body, as reviewed comprehensively in Plumlee et al. [84]. However, the growing database of simulated bioleach and sequential extraction results [87-96] has not closely considered particle size as a key parameter of trace metal solubilization in different extractant media. The following studies are therefore proposed:

> 1) *Conduct water extraction tests for all size fractions within selected mine waste samples to identify trends in As and Hg release while accounting for particle size, initial metal(loid) concentration, speciation, and surface area*
> 2) *Conduct gastric fluid extraction tests for size fractions <250 μm from selected mine waste samples to identify similar trends in metal(loid) release upon ingestion*
> 3) *Conduct lung fluid extraction tests for size fractions <10 μm from selected mine waste samples to identify extent of metal(loid) release in finest size fractions upon inhalation*
> 4) *Explore the effects of extractions on the speciation of selected metals using XRD, EXAFS and microspectroscopic (μXRF, μXRD, μEXAFS) methods.*
> 5) *Apply geochemical modeling methods to interpret extraction results in the context of mineral solubility, adsorption, and aqueous speciation.*

This work is expected to involve 3 undergraduate students, one in charge of each extractant phase, during the academic year as well as the summer period. Students will be trained to conduct extraction experiments, prepare supernatants to measure the amounts of As and Hg released, and process and present their data in graphical format. In addition, shorter projects related to this study will be included as part of the PI's upper-level undergraduate courses mentioned earlier in order to provide students the opportunity to gain experience in current research methods and instrumentation.

Experimental Methods

Mine tailings and waste rock samples will be exposed to extraction tests using particle size fractions appropriate to each exposure pathway. The water extraction test will follow ASTM Designation D3987-85, a standard method for the shake extraction of solid waste with water [97]. Particles <2.783 mm (S2-S11) will be exposed to DI water maintained at pH 5.5 in a 4:1 liquid to solid ratio and agitated for 18 hours, followed by centrifugation, filtration of the supernatant through a 0.45 μm filter, acidification to pH<2, and analysis using atomic absorption (AA) spectroscopy at Chapman University for As, Hg, and other metals of interest including Fe, Al, Cu, and Zn. All samples will be run in triplicate and standard QA/QC measures taken during analysis, including calibration using standards prepared in the same solution matrices as the extraction tests, blanks, blank spikes, and duplicate samples, all analyzed at frequencies sufficient to ensure satisfactory QA/QC. Should AA spectroscopy be deemed insufficient for the analysis of certain metal(loid)s due to detection limits, samples will be sent to the USGS-Denver analytical lab for analysis using inductively coupled plasma-optical emission spectroscopy (ICP-OES), which typically features detection limits of over an order of magnitude lower than that of AA spectroscopy.

The simulated gastric fluid extraction tests will follow a procedure from Drexler and Brattin [98] which involves the preparation of a simulated gastric fluid adjusted to pH 1.5 and maintained at 37°C. Again reflecting the particle size range that is most likely to be ingested into the gastrointestinal system,

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<250 μm particles (S6-S11) will be used in the gastric fluid extraction tests. A 100:1 liquid to solid ratio will be obtained and the particles exposed for a period of 1.5 hours under constant agitation. The pH level will be measured following the extraction step and the test modified as necessary to avoid increases in pH of greater than 0.5 units, which may induce the (re)precipitation of relatively insoluble phases to which released metals may adsorb. Samples will be centrifuged and supernatants filtered and acidified as described for the previous extraction tests prior to AA or ICP-MS analysis as described above.

The simulated lung fluid extraction tests will follow a procedure established by Twining et al. [99] which involves the preparation of a simulated lung fluid that has been pH-adjusted to 7.19 and maintained at normal body temperature (37°C) throughout the extraction step. Consistent with the particle size range that can access the respiratory system, <10 μm particles will be generated by configuring the MOUDI apparatus to yield particles in this size range. Particles will be exposed to the simulated lung fluid in a 20:1 liquid to solid ratio for a period of 6 days with constant agitation and daily readjustment of pH as necessary. Supernatants will be prepared for AA or ICP-OES analysis as described earlier.

Based on extraction results, bulk XRD, EXAFS and/or μXRF analysis will be used to examine the solid phases both before and after the leach tests, with focus placed upon procedures that mobilize the greatest extent of metals. Linear combination fitting of the samples analyzed by EXAFS spectroscopy will identify the specific phases removed, while μXRF will explore changes in the distribution and associations of metals with one another as a result of the extractions. Complementary geochemical modeling using Geochemist's Workbench will utilize the solution conditions of the three extractants and the basic mineralogy of the samples to create basic reaction path models as progressively more dissolved As and Hg is added to the systems, characterizing mineral saturation indices, aqueous species distributions, and sorption reactions onto mineral surfaces (specifically hydrous ferric oxide to simulate mineral coatings) using a standard two-layer surface complexation model [100]. Thus an integrated framework incorporating geochemical modeling and the prior studies on concentration, elemental distribution, speciation, microscale distribution, and bulk mineralogy can be used to interpret the bioaccessibility results and establish predictive, informed risk assessments for As and Hg in mining systems of the Mojave Desert and comparable environments.

Preliminary Results and Expected Significance

Water and gastric fluid leach tests of size-separated tailings from the Cactus Mine ($[As]_T$ ranges from 2710-8540 ppm) near Mojave, CA show dramatically different degrees of As mobilization as a function of the extractant type. While water released only between 0.6-1.1% of the available As over the size ranges (S1-S9) examined, gastric fluids released between 5.8-46.4% of the initial As present (**Figure 7a**), with As release increasing steadily with decreasing particle size. This latter fact is notable because the absolute As concentration trend for this sample is unimodal (see **Table 2**), maximizing in the S7 fraction, indicating that surface area plays a significant role in As

Figure 7. Percentage of As mobilized in gastric fluid extraction test as a function of particle size, both with (a) and without (b) surface area normalization.

bioaccessibility, as shown by replotting As mobility after normalizing for BET-measured surface area (**Figure 7b**). Normalization greatly diminishes the effect of particle size on As release, but notably does not cancel it out entirely, suggesting that other factors including speciation, encapsulation effects, and possibly surface coatings play additional roles in the release of As to solution.

STATEMENT ON INTEGRATION OF RESEARCH AND EDUCATION

The proposed research represents a fully integrated plan of research and education. Providing undergraduate students with opportunities to conduct independent research is a key goal at Chapman Uni-
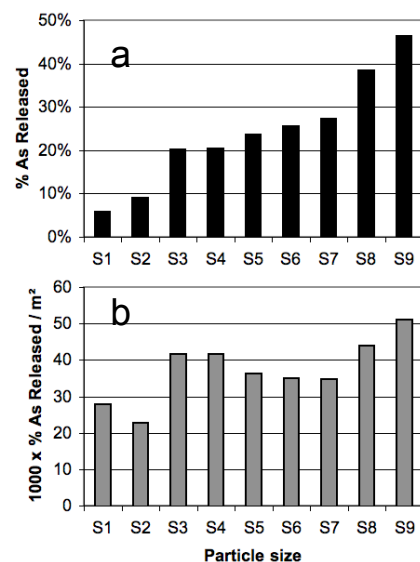
versity, a primarily undergraduate institution, and a clear benefit to the students, PI, and collaborators involved in this project. The proposed research will offer chemistry, environmental science, and biology undergraduates exposure to a range of current geochemical lab and field research methods, advanced analytical instrumentation, specialized spectroscopy techniques at national research facilities, and BLM and USGS collaborators. In particular, synchrotron-based spectroscopic methods, long the domain of graduate or post-doctoral level research, are now accessible (and sufficiently user-friendly) to students at the undergraduate level; one of the goals of this proposal is to increase the relationship between synchrotron centers and undergraduate-based research. We anticipate presenting our results at internationally-recognized scientific conferences and publishing our work in peer-reviewed journals in accordance with the expectations of the NSF-EAR Data Policy; this both provides students opportunities to discuss their work and ensures that it will reach a broader scientific audience. Thus far, undergraduate students in the PI's lab group have been lead authors on 13 presentations at national ACS and GSA meetings, synchrotron users meetings, and the international V.M. Goldschmidt geochemistry conference.

The PI has historically had between 6-10 undergraduate students working in his lab during the academic year (who either work for independent research credit, course credits in environmental science/chemistry research, or volunteer as research assistants) and 3-7 students working over the summer. In addition, for the past two years 1-2 lab members have elected to work full-time in the PI's lab following graduation, serving as mentors to new students and committing time and effort to their research comparable to that of graduate students (in fact, many such full-time research assistants have continued on to top-level graduate programs). Components of the proposed research will also be incorporated into the PI's lower- and upper-class undergraduate courses in the form of field sampling opportunities and class research projects. This method has served as an effective recruiting mechanism for new undergraduate group members in the past and insures that a high degree of research productivity can be maintained with undergraduates performing the majority of the research and analysis.

The PI and senior research students from his lab will participate in quarterly "Open House" town hall meetings convened by the BLM for residents of the three towns comprising the Randsburg mining district to receive updates on recent findings from the BLM, USGS, Department of Toxic Substances Control (DTSC) and Chapman University regarding As- and Hg-related research. These meetings, which draw between 30-60 local citizens, property owners, mining stakeholders, and mining employees, allow attendees the opportunity to learn about ongoing work and ask questions relevant to their concerns, and represents an important avenue by which to communicate scientific research to the public. Similarly, results from the Red Hill mercury mine in Orange County, CA will be communicated in formal reports to the California EPA for distribution to local homeowners and concerned citizens.

High school students from Orange and Troy High School will be recruited to take part in summer research internships in the PI's lab. Troy High School has a 150-hr unpaid summer internship program that the PI has participated in for the past 4 years, mentoring 5 incoming high school seniors during that time period; a similar program will be established with Orange High School under this grant. Troy research interns present their work in poster format in the school's spring Troy Tech Fair, which serves to inform the high school community of their experience as well as recruit new interns to the lab. In addition, outreach activities will be organized between the Advanced Placement Environmental Sciences (APES) class of Orange High School and Chapman in the form of poster presentation days, where Chapman students present their results from class research projects to the Orange High students who have the opportunity to ask questions of and interact with the Chapman students. These poster days, conducted on a limited basis for the past two years, are highly successful and particularly useful to the high school students as a means of learning more about applying to college and pursuing degrees in the sciences.

Public school teachers from the Centralia, La Habra, Magnolia, Orange Unified, Savanna, and Westminster School Districts will be identified through the California Mathematics and Science Partnership Grant (CaMSP) and Chapman University's Science Teaching and Research (STAR) Institute and recruited to participate in a substitute release day program in conjunction with the PI's lab. This program will allow teachers to obtain a substitute for a day during the academic year in order to visit the environmental geochemistry lab, learn about the scientific research being conducted, and develop ideas for new

teaching modules to use in the teacher's own classroom. A full day of organized lectures, poster presentations, demonstrations of lab techniques and instrumentation, and hands-on opportunities to participate in basic laboratory research will be offered during these release days. Teachers will then each develop a mini-lesson related to environmental research appropriate to their own classrooms with input and feedback from the PI, allowing teachers to translate what they have learned into a form they can use with their own students in their classrooms. These lessons will be uploaded onto a section of the PI's group website and shared publicly among teachers from the participating school districts. Teachers will also complete surveys before and after the release days to gauge their effectiveness and adjust their content to improve future release day programming. We anticipate 10 teachers ranging from primary, middle, and high school levels will participate in this program each year based on the PI's working relationships with CaMSP and the STAR Institute and interactions with teachers from both of these programs.

The research opportunities, internships, and outreach activities described are likely to increase the participation of underrepresented minorities in science; the Troy High student body is composed of 38% Asian, 32% Caucasian, 16% Hispanic, 5% Filipino, 5% Asian Indian, 1% African-American, and 3% other, while, the Orange High student body is comprised of Hispanic (68%), Caucasian (20%), and Asian (7%) students. Demographics of the Centralia School District, from where the majority of teachers would be recruited for the planned release days, are 43.6% Hispanic, 20.4% Caucasian, 15.1% Asian, 6.0% Filipino, 4.0% African-American, 1.5% Pacific Islander, 0.5% Native American, and 9.0% Multiple/No Response. The other school districts targeted have comparable demographics and can be accessed through the Education Data Partnership website [101]. Letters of collaboration have been obtained from representatives of the institutions referred to above to verify their commitment to the proposed outreach and internship activities (see Supporting Documents).

RESULTS OF PRIOR NSF SUPPORT

<u>NSF award number, amount, period of support:</u> NSF-EAR-0618217, $150,223, 1/1/07-12/31/09
<u>Title:</u> RUI: Heavy Metal Sorption/Co-precipitation Interactions with Nanoscale Iron Oxyhydroxides
<u>Summary of results of completed work, contributions to human resources:</u> A combination of macroscopic uptake studies to investigate the adsorption behavior of As(V), Cu(II), Hg(II), and Zn(II) onto nanoparticulate goethite (α-FeOOH) during aggregation through temperature, pH, and ionic strength changes reveal the effects that uptake has on growth and vice versa. Increasing uptake and changes in the speciation of these metal(loid)s with time imply shifts in the mode of uptake with time, with metal(loid)s transforming from surface-sorbed species to more structurally incorporated forms. This mode of incorporation has implications for the long-term fate and mobility of metals in contaminated regions. The completed work represented the direct research efforts of undergraduate research assistant Chris Lentini (Ph.D. candidate, Harvard University). Other recent graduates who have contributed to this and other ongoing work related to this grant include Brian Reinsch (Ph.D. candidate, Carnegie-Mellon University), Megan McKee (M.D. candidate, Marshall University), and Reyn Ono (R&D Scientist, Watson Pharmaceutical Laboratories, Inc.). Current students include James Dale and John Stegemeier, chemistry majors at Chapman.
<u>Publications resulting from the NSF award:</u> Kim, C.S., Lentini, C.J., and Waychunas, G.A. (2008) Synchrotron-based studies of metal adsorption and structural incorporation with iron oxyhydroxide nanoparticles. In <u>Adsorption of Metals By Geomedia II: Variables, Mechanisms, and Model Applications</u>, Barnett, M. (Ed.), Elsevier Academic Press, 478 pp.

<u>NSF award number, amount, period of support:</u> NSF-EAR-0651597, $33,613, 5/1/07-4/30/09
<u>Title:</u> Acquisition of a Surface Area Analyzer for Undergraduate Research and Teaching in the Earth Sciences
<u>Summary of results of completed work, contributions to human resources:</u> A Beckman-Coulter BET SA3100 surface area analyzer has been purchased and several projects completed or underway on 1) changes in surface area of goethite nanoparticles under variable aggregation conditions and 2) surface area trends in natural samples as a function of particle size range. This work has thus far involved the efforts of 4 Chapman undergraduates and 2 high school summer interns from Troy High School.
<u>Publications resulting from the NSF award:</u> None

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