Controls on Antimony Speciation and Mobility in Legacy Mine Tailings Environments: A Case Study of Mineral Occurrences in the Tintina Gold Province, Alaska and Yukon.

USGS Award MRERP 06HQGR0177

(Principle Investigator T.P. Trainor)

T.P. Trainor[1], S.H. Mueller[2,*], V. Ritchie[1], R.J. Goldfarb[2]
1.University of Alaska Fairbanks, Dept. of Chemistry and Biochemistry, P.O. Box 756160, Fairbanks, AK 99775-6160, Phone: 907-474-5628, Email: fftpt@uaf.edu
2. U.S. Geological Survey, Mineral Resources Program, Denver, CO 80225
* Present Address: Water Management Consultants Inc., 3845 North Business Center Drive, Tucson, AZ 85705, Phone: 520-319-0725

Research supported by the U.S. Geological Survey (USGS), Department of the Interior, under USGS award number 06HQGR0177. The views and conclusions contained in this document are those of the author(s) and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Government.

Introduction

In recent years, a great deal of progress has been made in the development of geoenvironmental models to predict the potential for environmental contamination associated with mineral resource development (c.f. du Bray, 1995; Plumlee and Logsdon, 1999). The application of such models to current, prospective, and legacy mining sites provides industry, public land managers, and environmental quality agencies an important tool for developing management and remediation strategies. An essential aspect of developing such models is access to high quality water, sediment, and soil chemistry data sets from well-characterized mineral deposits. These data sets can be used to predict the identity and levels of potentially toxic trace elements based on similarities in ore deposit mineralogy, host rock lithology, and other geo-environmental variables. It is also essential that the key physicochemical processes controlling trace element speciation (e.g. oxidation state, aqueous-solid phase partitioning, and mode of association with major/minor element phases) are understood in order to extend the geoenvironmental model concept to include prediction of downstream trace element mobility and potential bioavailability (Smith and Huyck, 1999), as well as to provide insights into the efficacy of potential treatment and remediation scenarios.

The focus of this project is to provide a detailed analysis of the chemical composition of waters and sediments associated with select mineral deposits in the Tintina Gold Province (TGP) of Alaska and Yukon. The specific aim of our work is to elucidate the factors that control the speciation of antimony (Sb), and co-associated arsenic (As), in deposits containing abundant stibnite (Sb_2S_3) and arsenopyrite (FeAsS). A number of geoenvironmental studies within the TGP have shown that acid mine drainage derived from oxidation of sulfide minerals is generally limited in extent as a result of either low sulfide content of ore materials or naturally high acid buffering capacity of waters (c.f. Goldfarb et al., 1995; Eppinger et. al., 2000; Mueller et. al., 2003; Plumlee et. al., 1999). In general, these studies have observed that surface waters draining natural mineral occurrences and legacy mining operations (e.g. abandoned tailings, adits, and other workings) contain concentrations of priority contaminant metals, such as copper, lead, zinc, and mercury, below EPA drinking water standards and typically at, or just above, background values (Goldfarb et. al. 1995). A notable exception is the common observation of elevated dissolved concentrations of Sb and As derived from the weathering of stibnite and arsenopyrite, respectively (Goldfarb et al., 1995; Goldfarb et. al., 1997, Eppinger et. al., 2000; Mueller et. al., 2003).

In order to extend our understanding of the factors controlling Sb and As mobility in the TGP we have focused our efforts on: 1) characterizing the primary antimony sulfide minerals and secondary oxides at each study area, 2) determine geochemical characteristics of surface waters draining the Sb-rich source materials, 3) examine the fine fraction of bed-sediments in stream channels downstream from antimony mineralization to determine the association with major/minor element (e.g. Fe, Mn, Al, Si) secondary precipitates, and 4) compare the geochemical behavior of antimony with arsenic at various locations across the TGP, particularly relative to variable mineral deposit type, associated sulfide minerals, and host rock composition. Our conventional water and sediment characterization is coupled with detailed analysis of Sb/As speciation in order to extend the data set to provide results on the dominant chemical processes controlling elemental mobility. These results are particularly relevant to enhancing the predictive power of descriptive geoenvironmental models, as the elemental speciation is a

predominant factor controlling trace element mobility and bioavailability. Our work also provides information regarding the hydrogeochemistry of a number of mineral deposits throughout Alaska and Yukon that to date lack detailed geoenvironmental study. This latter point is of particular relevance to management issues within Denali National Park and Preserve (location of two of our sites) which has been the main focus of our work covered under this funding.

Background

Antimony is commonly associated with syngenetic and epigenetic metallic mineral deposits throughout the northern Cordillera and, along with arsenic, is one of the primary contaminants of concern for current and legacy mineral resource developments in the TGP. The occurrence and chemical behavior of antimony is similar to arsenic, and, like arsenic, is considered highly toxic (EPA maximum contaminant level for antimony in drinking water is 6 ppb). Antimony typically occurs as the sulfide mineral stibnite (Sb_2S_3) in ore deposits. Oxidative weathering of primary antimony sulfides most likely results in the formation of stibiconite ($Sb_3O_6[OH]$) or other oxide and sulfosalt weathering products along with soluble Sb(III) and Sb(V) oxyanions (Filella et al. 2002 a).

In contrast to metals such as mercury, arsenic, and lead, far less research effort has been focused on understanding the geochemical behavior of antimony. The fate of antimony in natural waters is presumably controlled by both the oxidation state and formation of solution complexes, as well as association with secondary (hydr)oxide phases of Fe-, Mn- or Al- or natural organic matter. Furthermore, the potential bioavailability and risks for human and wildlife exposure depend directly upon antimony speciation, as Sb(III) is believed to be more toxic than the Sb(V) form (Bencze, 1994). However, the relative importance of the various species and partitioning mechanisms controlling the environmental fate and mobility of antimony are poorly understood. In a recent review, Filella et al. (2002a,b) point out several shortcomings in our current understanding of the environmental behavior of antimony, including a lack of fundamental knowledge on: 1) the speciation of antimony in natural waters, 2) the partitioning of antimony between aqueous and solid phases, and 3) the effects of organic matter on the behavior of antimony in natural environments. The widespread occurrence of this metal in ores, coupled with the lack of fundamental understanding of physicochemical controls on antimony behavior, suggests that further detailed analysis of antimony speciation and transport is critical to improving geoenvironmental models applicable to a large metallogenic belt in Alaska and Yukon that is an important focus of present exploration and development.

Antimony Occurrence and Site Descriptions

Numerous deposits throughout Alaska and the Yukon contain massive, late stage, stibnite veining and pods. Such deposits are particularly common within the Tintina Gold Province of interior Alaska and Yukon (**Fig 1**), several of which served as a primary source of antimony ore throughout World Wars I and II. In the current study, we have chosen four historically mined vein or disseminated style deposits that contain significant antimony mineralization and are located across the TGP. These are the Brewery Creek gold mine in central Yukon, Scrafford antimony mine in the Fairbanks district, and the Stampede mine and Slate Creek mines in the Kantishna Hills district within Denali National Park and Preserve, Alaska. These sites were chosen in part because previous reconnaissance-level hydrogeochemical investigation by the

U.S. Geological Survey established prior results that we can build upon. Below we provide brief description of the deposit geology, and significant hydrogeochemical findings associated with the study areas.

Brewery Creek

The Brewery Creek gold deposit is located 57 km east of Dawson City in central Yukon on the northeastern side of the Tintina Fault in the hanging wall of the Robert Service thrust fault. The dominant host rock lithologies are Paleozoic clastic sedimentary rocks of the Selwyn Basin that are described in Diment, (1996), Diment and Craig, (1999), and Lindsay et al., (1999). The orebodies, totaling 12 km in length and suggested to be either intrusion-related or Carlin-like deposits, consist of gold within quartz veinlets and disseminated arsenopyrite and pyrite are the most abundant phases coeval with the gold. Coarse-grained stibnite is also common and occurs in veins that appear to post-date gold deposition. A reconnaissance level study by the U.S.G.S and the Yukon Geological Survey of the post-mining hydrogeochemistry revealed that the surface waters draining the orebodies are slightly alkaline (pH 7.6-8.2), moderate to high conductivity (400-700 μS/cm) containing between 9-21 μg/L dissolved antimony and between 3-18 μg/L arsenic (Mueller et al., 2004). These concentrations are significantly higher than local background concentrations (<3 μg/L).

Scrafford

The Scrafford lode deposit is located approximately 18 km north of Fairbanks, in the Fairbanks mining district. The Scrafford mine was the second largest antimony producer in Alaska, producing a total of approximately 2 million pounds of antimony, with the majority of production occurring between 1915 and 1918 (Robinson, 1981). The property lies along the north side of Murphy Dome Road at the headwaters of Treasure Creek. The antimony ore in the form of massive stibnite is hosted within the heterogeneous greenschist facies rocks of the Fairbanks schist. Massive fibrous stibnite occurs along shear zones and within quartz stockwork veinlets. The stibnite was mined along an open trench and underground. All of the underground workings have since collapsed and all that remains at the surface are tailings piles and some of the open trench. Only two known water samples had been collected at the Scrafford mine prior to 2004; one sample was taken from a stream above the mine cut and tailings piles, and the other was taken immediately downstream of the tailings. The upper sample was had a pH of 7.2 and a low specific conductance (141 μS/cm) with low arsenic (5 μg/L) and antimony (4.8 μg/L) (Goldfarb et al., 1995). In contrast the same stream below the mine tailings had a pH of 8, specific conductance of 532 μS/cm, with significantly increased arsenic (92 μg/L) and antimony (200 μg/L) concentrations (Goldfarb et al., 1995).

Kantishna Hills, Stampede and Slate Creek

The Kantishna Hills gold and antimony mining district is located within the northwestern portion of Denali National Park and Preserve. This district contains a number of antimony lode deposits including Alaska's historically largest antimony producer, the Stampede mine, as well as occurrences along Slate Creek. The Kantishna district is made up of a number of polymetallic vein deposits that trend toward the northeast extending over a linear distance of 40 miles from Slate Creek in the southwest to Stampede in the northeast. The host rocks consist of Precambrian to Paleozoic metamorphic rocks of the Birch Creek schist, the Spruce Creek sequence, and Keevey Peak and Totatlanika Schist Formations (Bundtzen, 1981). The veins that

make up the bulk of the orebodies in the area are structurally controlled along faults and range in width from 8 cm to >9 m and range in length from 30 m to >500 m. The orebodies at both Stampede and Slate Creek are predominately composed of massive stibnite. Although no hydrogeochemcial study of Stampede is available, Eppinger et al. (2000) conducted a reconnaissance level environmental geochemical study of the Slate Creek deposit. They sampled naturally mineralized springs and streams, streams and pools that had contacted waste rock and mine tailings, and streams outside of the mined zone. They found the pH in the waters ranged from 3-8, specific conductance ranged from 130-1700 μS/cm, and antimony concentrations ranged from <1 μg/L to 190 μg/L. The highest antimony concentrations were found in water within the mine site; however, naturally mineralized samples also contained as much as 14 μg/L-dissolved antimony. Stream sediments were also sampled and revealed a wide range of relatively high antimony concentrations from 43-6000 ppm.

Because these locations show a wide range of antimony concentrations in both stream waters and sediments, wide ranges of pH, and varied host rock lithology, they provide an opportunity for a detailed examination of antimony behavior across a broad range of geo-environmental variables. Furthermore, characterization of the Slate Creek and Stampede sites located within Denali National Park and Preserve are of particular importance to current assessment and remediation efforts by the NPS as discussed below.

Sampling and Analysis Methods

The sampling and analysis protocol for our studies are outlined below. Our work during the 2006 and 2007 field seasons was primarily focused on the Stampede and Slate Cr. sites within the Kantishna District of Denali National Park. The Stampede site is of particular importance, since it is one of the major antimony localities within the TGP, and there is little or no previous hydrogeochemical study of this site. Furthermore, the NPS is considering remediation efforts at Stampede (P. Brease, personal communication) in order to limit impacts to Stampede Cr. Our work prior to site remediation has established current conditions, and will allow us to develop a data set that can be used in follow up studies for post remediation assessment.

Access to the Stampede site during 2006 was carried out with logistical support of Kantishna Air, who provided fixed wing transport from the Denali entrance to an airstrip adjacent to Stampede Cr.. Field work during the summer of 2007 was carried out at Slate Cr. and adjacent drainages within the Kantishna district of Denali NP. These sites were accessible from the Park road. In addition to field work a substantial amount of effort has been put into sample analysis, including the use of x-ray absorption spectroscopy (XAS) to characterize Sb and As speciation, and the development of LC-ICP-MS methods for analysis of soluble Sb species. The XAS work involved several trips to the Advanced Photon Source, Argonne National Lab for experimental time.

Sampling Design

Pre-selected streams draining mineralized areas, tailings and waste rock piles, as well as undisturbed background, were sampled for basic water and stream sediment analysis. The number of samples within a given drainage was based on stream flow, depth, accessibility, and stream course. In general, sampling was carried out from above identified impacted sites, through the course of a drainage in order to assess the changes in water chemistry relative to

background and the extent of trace element transport. Samples collected at each sites included primary ore minerals and associated secondary minerals, water samples, and stream sediment samples. A select subset of samples was subject to detailed speciation analysis.

Sample Collection

At each sampling point, in-situ measurements of pH, dissolved oxygen, Eh, and specific conductance were measured using standard probes (calibrated daily during the sampling period). Four water samples were taken at each location: 1) a 125 ml sample filtered using 0.45 μm capsule filter for dissolved major and trace elements preserved with 1% trace metal grade HNO_3 by volume; 2) one filtered 250 ml sample for anions and alkalinity; 3) one filtered 75 ml sample for iron, antimony and arsenic speciation preserved with 1% HCl by volume; 4) one 125 ml unfiltered water sample for total major and trace elements preserved with 1% trace metal grade HNO_3. In addition, at several sites we collected water samples for determining dissolved sulfide (preserved with Zn-acetate and sodium hydroxide). Samples were collected using a portable peristaltic pump fitted with pre-rinsed (diluted HNO_3) flexible, cured, 1/4-inch diameter silica tubing and rinsed with sample water prior to sample collection. All sample bottles are HDPE and rinsed with sample water prior to collection of the sample. Samples collected for speciation analysis are stored in dark sample bottles to prevent light exposure. All samples were kept refrigerated until analysis.

Sediment samples were collected at each site using a variation on the technique described in Shelton and Capel (1995). Material from the top few centimeters of bed sediment is collected using a teflon spatula or spoon and then homogenized in a Teflon basin. After homogenization, the composite sample will be wet sieved in the field into 1 L HDPE wide mouth bottles to obtain the < 0.63 μm size fraction. Samples are stored cold until analyzed.

Water Sample Analysis

Water chemistry data includes determination of total dissolved cations, alkalinity, dissolved anions, and dissolved Fe(II) in order to assess the redox condition of the waters based on the Fe(II)/Fe(III) redox couple. The samples for dissolved major elements and trace metals were analyzed by a combination of ICP-MS and ICP-AES techniques at the U.S. Geological Survey in Denver, CO, and at the Advanced Instrumentation Laboratory, University of Alaska Fairbanks. The methods used are described by Lamothe, et al. (2002) and Briggs (2002a). Alkalinity values are determined using an autotitration preset endpoint technique as described in Theodorakos (2002a). Dissolved anion concentrations (including sulfate, chloride and nitrate) are determined by ion chromatography as described by Theodorakos et al. (2002b). Fe(II) concentrations are determined using the colorimetric technique described by Theodorakos (2002c).

Solid Samples

Splits of the stream sediment samples were characterized using multiple techniques to provide data on bulk composition, mineralogy, and trace element association. Bulk major and minor element composition were determined on centrifuged and air dried fractions of the stream sediments using wavelength dispersive x-ray fluorescence (XRF) at UAF. Samples were also analyzed by conventional powder x-ray diffraction to characterize mineralogy of the solid phase materials. Trace analysis of sediment samples was performed by total digestion followed by analysis with ICP-MS at U.S. Geological Survey in Denver, CO (Briggs and Meier, 2002). A

number of samples were also analyzed for total organic carbon at the USGS using a Shimatzu TOC analyzer, following standard procedures (Brown and Curry, 2002a, Taggart, 2002).

Sb and As Speciation

Liquid phase Sb speciation is being performed using a hyphenated liquid chromatography (LC) ICP-MS technique. In this method, aqueous samples are introduced to the ICP-MS through polymer-based anion-exchange column. The separation of Sb(III)/Sb(V) aqueous species can be accomplished using a mobile phase of 2 mM phathalic acid - 5 mM EDTA at pH 4.5 (Zheng, et al, 2000). Our preliminary work on adapting this method shows that Sb(III) and Sb(V) are easily distinguished at concentrations ranges typical of field samples (**Fig 2)**. A similar approach using a modified mobile phase is being used for analysis of As(III)/(V) species. The As speciation method is a well established standard technique (c.f. Agilent Technologies, 2000; Ficklin 1983). This work is being carried out by V. Ritchie as part of her MS thesis, and we anticipate that final results and interpretation to be completed in Spring 2008.

The solid phase characterization of Sb (and As) speciation has been carried out using x-ray absorption spectroscopy (XAS) (**Fig 3**). The advantage of this *in-situ* technique is that no sample alteration is required for analysis. For example, it is common to examine solid phase speciation by first performing an extraction procedure, followed by liquid phase separation and analysis. However, alteration of the elemental speciation and/or incomplete extraction are typical complicating factors associated with such methods, often leading to erroneous results. Furthermore, these approaches only give limited information on the mode of association of trace elements with the solid phase components (e.g. differentiation between adsorption and co-precipitation). Direct analysis of samples using XAS provides element specific speciation information including oxidation state, and the chemical coordination environment immediately surrounding the element of interest (c.f. Brown *et al.* 1999; Manceau *et al.* 2002). These results are particularly useful for distinguishing the predominant coordinating ligands (e.g. oxygen, sulfur, carbon or other elements), and to distinguish between co-precipitated Sb/As (i.e. bound within a three dimensional secondary phase matrix) versus adsorbed species bound to particulate surfaces.

Antimony and arsenic K-edge x-ray spectra of select tailings and sediment samples were collect at GSECARS beamline 13BMD. The beamline optics consist of a Si(111) double crystal monochrometer and a Pt coated focusing/harmonic rejection mirror. Sb K edge x-ray absorption near edge structure (XANES) spectra were collected from 30425 to 30650 eV using 1eV steps. Arsenic K edge XANES spectra were collected from 11840 to 12000 eV using 0.5eV steps. Antimony and arsenic X-ray absorption fine structure (XAFS) spectra were collected to 13-15$Å^{-1}$ using 0.5 $Å^{-1}$ steps. Data were processed using Ifeffit (Newville, 2001).

Samples for XAS analysis were to be representative of the overall sample population based on major composition, trace element composition, and sample environment. Samples were analyzed under ambient conditions; using, original wet pastes with no sample pre-treatment. Samples were stored in the dark at 4°C prior to analysis to prevent sample alteration.

Results and Discussion

Across the sites investigated the stream waters ranged in pH from 2.5-8.5, with specific conductance from 17-2980 μS/cm. The majority of waters can be described as Ca-HCO_3 type waters (**Fig 4**). Dissolved (<0.45 μm) Sb concentrations range from <0.3-665 μg/L, dissolved As concentrations range from <1 to 384 μg/L (**Fig 5**). In general the concentrations of other priority trace metals are below EPA drinking water standards, or rapidly decline as a function of distance from the source environments. In contrast we observe elevated antimony concentrations up to several kilometers from source materials, suggesting the Sb remains highly mobile in the well buffered, circum-neutral pH waters characteristic of our sampling localities. For example, in **Fig 6** we show a subset of data from the Slate Cr. drainage within Denali National Park and Preserve. Sb concentrations near the source region are as high as 665 μg/L and remain elevated throughout the drainage, still nearly an order of magnitude above EPA drinking water standards at the confluence of Moose Cr.. This same trend is observed at other sites, notably the Stampede Cr. drainage (**Fig 7**) and Scrafford Mine sites show highly elevated Sb levels and evidence for extended metalloid transport.

Stream sediment concentrations of Sb and As are also elevated downstream of mineralized zones. The <63 μm stream sediment samples downstream of exposed waste-rock and tailings piles show Sb concentrations ranging broadly from 4 to 7230 ppm. In general Sb concentrations were an order of magnitude higher in both sediments and waters when draining exposed waste-rock or tailings compared to natural mineralization exposures. The solid phase Sb concentrations are well correlated with As concentrations (**Fig 8**), suggesting similar patterns in mobility. The Sb and As concentrations also correlate well with Fe and Al, suggesting that secondary precipitates of Fe- and Al-(oxy)hydroxide precipitates are the predominant sink via either adsorption or co-precipitation processes.

X-ray absorption spectroscopy analyses have been completed on select stream sediments and tailings samples. Our results indicate that the secondary weathering products associated with the primary sulfide phases (stibnite) appear to be a Ca/Na rich Lewisite ($(Ca,Na,Sb(III))Sb(V)_2O_6(OH)$) (e.g. **Fig 3** and **Fig 9**). Lewisite is structurally similar the mixed Sb(III)/Sb(V) oxide stibiconite ($Sb(III)Sb(V)_2O_6(OH)$), the main difference being substitution of Ca/Na for Sb(III). Structural analysis of the secondary phases (**Fig 10**) confirms a local structure consistent with the lewisite, indicating that direct weathering products of stibnite that we have analyzed are highly oxidized (predominately Sb(V) oxides).

XAS analyses of the <63 μm fraction stream sediments show that antimony is predominantly in the form Sb(V) and adsorbed/co-precipitated with iron hydroxide (**Fig 11**). In contrast, As has been observed as both As(III) and As(V) in the stream sediments, indicating that Sb and As are not behaving in a chemically similar manner. An example of the comparative speciation behavior of Sb and As is shown in **Fig 12**. These samples from the Scrafford mine site consist of stream bed sediments and a 12 cm core sample taken from a tailings pond. The XAS results measured sequentially through the tailings pond core sample show that Sb(V) remains the predominant species while As is present as both As(III) and As(V) in varying proportions. These results suggest that Sb and As behave differently within the reducing sediment environment. This observation has important implications for understanding the transport, and potential

toxicity of both Sb and As species under variable physicochemical conditions of stream and pond sediment environments.

Summary and Future Studies

Our preliminary findings, point out that Sb is highly mobile in near neutral, oxidizing environments. At several sites both dissolved (<0.45 mm) and bed-load (< 63 mm) concentrations are significantly elevated at significant distances downstream (~2 km) from the source. Our results also show that XAS provides a detailed characterization of the solid phase speciation of Sb and co-associated As in tailings and downstream sediments. These results, coupled with the aqueous phase Sb speciation results via LC-ICP-MS and the conventional water and sediment analysis provide a comprehensive geochemical data set that can be used to assess the various chemical and geo-environmental variables that control Sb speciation and transport. In particular these results allow us to develop a preliminary model of the pathways controlling Sb speciation and transport (**Fig 13**). Future work focused on elucidating additional details of these pathways are on going using model system (laboratory scale) studies, as well as plans for additional field work.

Publication/Presentation Resulting From This Work:

T.P. Trainor, S.H. Mueller, V. Ritchie, A. Ilgen, M. Newville, R. Goldfarb (2007). Antimony Mobility Associated with the Oxidation of Stibnite-bearing Waste Rock from the Eastern Tintina Gold Province, Alaska and Yukon. In preparation for submission to Applied Geochemistry.

T.P. Trainor, S.H. Mueller, V. Ritchie, A. Ilgen, M. Newville (2007). *Invited Keynote Address*. Antimony Mobility Associated with the Oxidation of Stibnite-bearing Waste Rock from the Eastern Tintina Gold Province, Alaska and Yukon. Presented at *Frontiers in Mineral Sciences 2007*, Cambridge University, U.K., June 26-28, 2007.

S.H. Mueller, T.P. Trainor, V. Ritchie, M. Newville (2006). *Talk*. Antimony Mobility Associated with the Oxidation of Stibnite-Bearing Waste Rock From the Eastern Tintina Gold Province, Alaska and Yukon. *Geological Society of America Cordilleran Section 102nd Annual Meeting*, Anchorage, AK, May 8-10, 2006.

S.H. Mueller, T.P. Trainor, V. Ritchie, R.J. Goldfarb, C.J.R. Hart (2005). *Poster*. Antimony Speciation and Transport in Mine Tailings and Sediments from Alaska and the Yukon. *American Geophysical Union 2005 Fall Meeting*, San Francisco CA, December 5-9, 2005.

Acknowledgements

We gratefully acknowledge the financial support of the U.S. Geological Survey through Grant MRERP 06HQGR0177. A. Ilgen, S. Petitto, E. Marsh, J. Scherzinger, P. Brease, L. Tyrell provided support for field work.

References Cited:

Agilent Technologies, 2000, Separation and Analysis of Toxic Arsenic Species Using LC-ICP-MS. Application Note 5980-0262E.

Bencze, K., 1994 Antimony. *in* Seiler, H.G., Sigel, A., Sigel, H. (Eds.), Handbook on Metals in Clinical and Analytical Chemistry. Marcel Dekker, New York, pp. 227-236.

Briggs, P.H., 2002, The determination of twenty-seven elements in aqueous samples by inductively coupled plasma-atomic emission spectrometry, *in* Taggert, J.E. ed, Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey, Open-file Report 02-223, p F1-F11.

Briggs, P.H. and Meier, A.L., 2002, The determination of fourty-two elements in geological and botanical samples by inductively coupled plasma-mass spectrometry, *in* Taggert, J.E. ed, Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey, Open-file Report 02-223, p. I1-I14.

Brown, G.E., Jr., Foster, A.L. and Ostergren, J.D., 1999 *Mineral surfaces and bioavailability of heavy metals: a molecular-scale perspective.* Proceedings of the National Academy of Sciences of the USA, **96,** p. 3388-3395.

Brown, Z. and Curry, K.J., 2002a, Total carbon by combustion, *in* Taggert, J.E. ed, Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey, Open-file Report 02-223, p.R1-R4.

Brown, Z. and Curry, K.J., 2002b, Total sulfur by combustion, *in* Taggert, J.E. ed, Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey, Open-file Report 02-223, p. Q1-Q4.

Bundtzen, T.K., 1981, Geology and mineral deposits of the Kantishna Hills, Mount McKinley Quadrangle, Alaska: Fairbanks, Alaska, University of Alaska Fairbanks, M.S. Thesis, 238 p.

Diment, R., 1996, Brewery Creek Gold Deposit, *in* Yukon Exploration and Geology, 1995, Exploration and Geological Services Division, Yukon Region, Indian and Northern Affairs Canada, p.57-66.

Diment, R. and Craig, S., 1999, Brewery Creek Gold Deposit, Central Yukon, *In* Yukon Exploration and Geology, 1998, C.F. Roots and D.S. Emond (eds). Exploration and Geological Services Division, Yukon Region, Indian and Northern Affairs, Canada, p. 225-230.

du Bray, E.A. (ed), 1995, Preliminary Compilation of Descriptive Geoenvironmental Mineral Deposit Models. U.S. Geological Survey Open File Report 95-831.

Eppinger, R.G., Briggs, P.H., Crock, J.G., Meier, A.L., Sutley, S.J., Theodorakos, P.M., 2000, Environmental-Geochemical Study of the Slate Creek Antimony Deposit, Kantishna Hills, Denali National Park and Preserve, Alaska, *in* Studies by the U.S. Geological Survey in Alaska, 2000, F.H. Wilson and J.P. Galloway (eds). U.S. Geological Survey Professional Paper 1662, p 123-141.

Ficklin, W.H., 1983, Separation of arsenic(III) and arsenic(V) in ground waters by ion-exchange, Talanta, v.30, no.5, p. 371-373.

Filella, M., Belzile, N., Chen, Y.W., 2002a, Antimony in the environment: a review focused on natural waters I. Occurrence, Earth-Science Reviews, vol. 57, p. 125-174.

Filella, M., Belzile, N., Chen, Y.W., 2002b, Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry, Earth-Science Reviews, vol. 59, p. 265-285.

Goldfarb, R.J., Taylor, C.D., Meier, A.L., d'Angelo, W.M., O'Leary, R.M., 1995, Hydrogeochemistry of Mine-Drainage Waters Associated with Low-Sulfide, Gold-Quartz Veins in Alaska, *In* Geological studies in Alaska by the U.S. Geological Survey, 1995, J.A. Dumoulin and J.E. Gray (eds). U.S. Geological Survey Professional Paper, 1574, p. 3-17.

Goldfarb, R.J., Farmer, G.L., Cieutat, B.A., Meier, A.L., 1995, Major-element, Trace Element, and Strontium-Isotope Systematics of Natural Waters in the Fairbanks Mining District: Constraints from Local Geology. *In* Geological studies in Alaska by the U.S. Geological Survey, 1997, K.D. Kelley (ed).U.S. Geological Survey Professional Paper, 1614, p. 139-150.

Hart, C J R, McCoy, D T, Goldfarb, R J, Smith, M, Roberts, P, Hulstein, R, Bakke, AA, Bundtzen, T K, 2002, Geology, Exploration, and Discovery in the Tintina Gold Province, Alaska and Yukon. *In*

Integrated methods for discovery: global exploration in the twenty-first century. Society of Economic Geologists, Special Publication 9, R J Goldfarb and R L Nielsen (eds), p 241-274.

Lamothe, P.J., Meier, A.L., Wilson, S.A., 2002, The determination of forty-four elements in aqueous samples by inductively coupled plasma-mass spectrometry., *in* J.E. Taggart (ed). Analytical methods for chemical analysis of geological and other materials, U.S. Geological Survey. U.S. Geological Survey open-file report 02-223.

Lindsay, M.J., Baker, T., Oliver, N.H.S., Diment, R., Hart, C.J.R., 1999, The magmatic and structural setting of the Brewery Creek gold mine, central Yukon. *In* Yukon Exploration and Geology, 1998, D.S. Emond and L.H. Weston (eds). Exploration and Geological Services Division, Yukon Region, Indian and Northern Affairs Canada, p. 219-227.

Manceau, A., Marcus, M.A. and Tamura, N., 2002, *Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques.* Reviews in Mineralogy & Geochemistry, **49**, p. 341-428.

Mueller, S.H., Hart, C.J.R., Goldfarb, R.J., Munk, L.A., 2003, Post-mining hydrogeochemical conditions, Brewery Creek gold deposit, central, Yukon. . *In* Yukon Exploration and Geology, 2003, D.S. Emond and L.L. Lewis (eds). Yukon Geological Survey, Canada, p. 95-103.

Mueller, S.H., Trainor, T.P., Ritchie, V., Goldfarb, R.J., Hart, C.J.R, 2005, Antimony Speciation and transport in mine tailings and sediments from Alaska and the Yukon. American Geophysical Union 2005 Fall Meeting, Decemeber 5-9, San Francisco CA.

Newville, M., 2001, *IFEFFIT: Interactive XAFS Analysis and Feff Fitting*. J. Synchrotron Radiation, 8, 322-324.

Plumlee, G.S., Smith, K.S., Montour, M.R., Ficklin, W.H., Mosier, E.L., 1999, Geologic Controls on the composition of natural waters and mine waters. *In* The Environmental Geochemistry of Mineral Deposits. Part B: Case Studies and Research Topics. L.H. Filipek, and G.S. Plumlee (eds). Reviews in Economic Geology, Vol 6B, p. 373-432.

Plumlee, G.S., Logsdon, M.J. (eds), 1999. The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques and Health Issues, Reviews in Economic Geology, Vol 6A.

Smith K.S., Huyck, H.L., 1999, Geologic Controls on the composition of natural waters and mine waters. *In* The Environmental Geochemistry of Mineral Deposits. Part B: Case Studies and Research Topics. L.H. Filipek, and G.S. Plumlee (eds). Reviews in Economic Geology, Vol 6B, p. 373-432.

Taggart, J.E. 2002, Analytical Methods for chemical Analysis of geologic and other materials, U.S. Geological Survey. U.S. Geological Survey open-file report 02-223.

Theodorakos, P.M., 2002a, Automated preset endpoint (4.5) total alkalinity titration using the Orion 960 Autochemistry system. *in* J.E. Taggart (ed). Analytical methods for chemical analysis of geological and other materials, U.S. Geological Survey. U.S. Geological Survey open-file report 02-223.

Theodorakos, P.M., 2002b, Fluoride, chloride, nitrate, and sulfate in aqueous solution utilizing autosuppression chemically suppressed ion chromatography. *in* J.E. Taggart (ed). Analytical methods for chemical analysis of geological and other materials, U.S. Geological Survey. U.S. Geological Survey open-file report 02-223.

Theodorakos, P.M., 2002c, Ferrous iron (Fe^{2+}) from 0 to 3.00 mg/L for water, wastewater, and seawater utilizing the HACH DR/2010 spectrophotometer method. *in* J.E. Taggart (ed). Analytical methods for chemical analysis of geological and other materials, U.S. Geological Survey. U.S. Geological Survey open-file report 02-223.

Zheng J., Ohata, M, Furuta, N., 2000, Antimony Speciation in Environmental Samples by Using High-Performance Liquid Chromatography Coupled to Inductively Coupled Mass Spectrometry, Analytical Sciences. Vol 16, p 75-80.

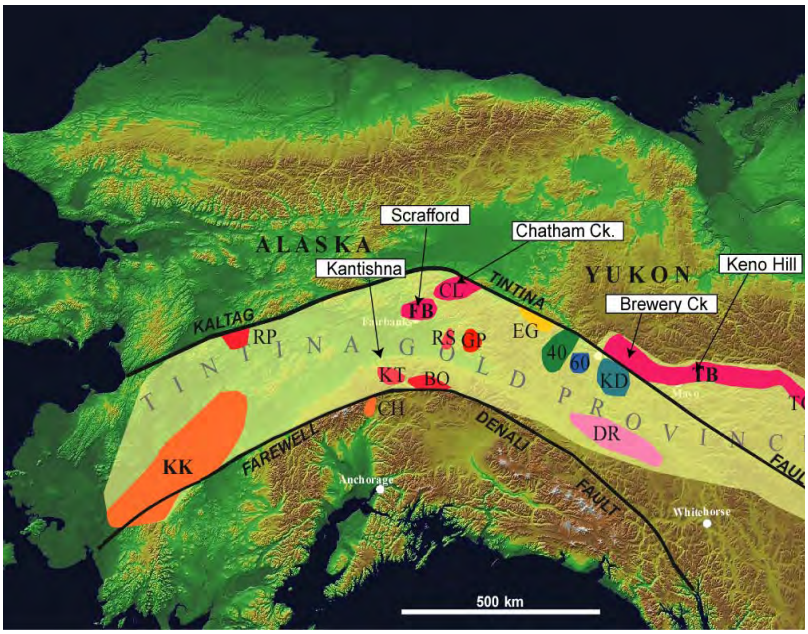


Figure 1. Map of the Tintina Gold Province(TGP) highlighting a number of the sampling localities covered in the current study. See text for detailed site descriptions. (after Hart et. al. 2002).

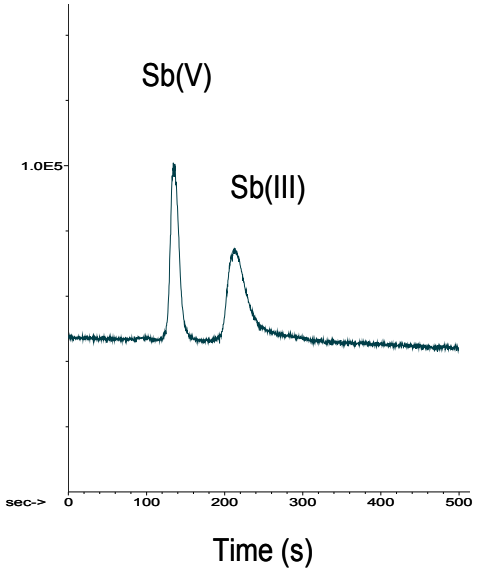


Figure 2. LC ICP-MS chromatogram of a mixed Sb(III)/(V) solution at approximately 10 ppb.

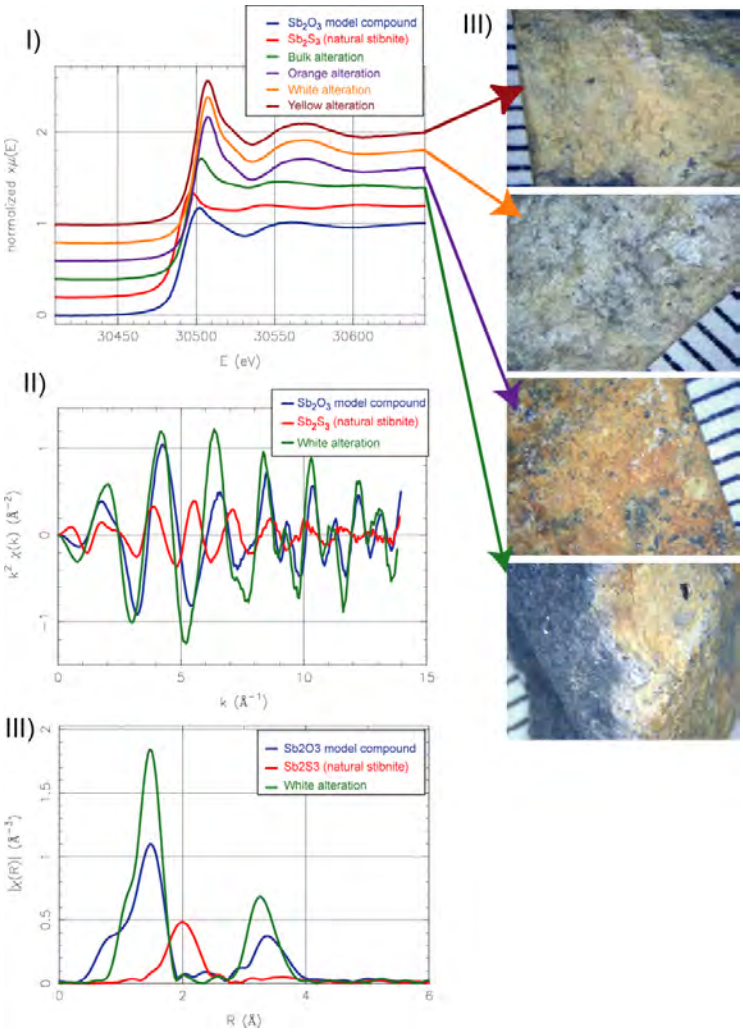


Figure 3. Antimony x-ray absorption spectra of stibnite (Sb_2S_3) and principle weathering products of a grab sample from the Scrafford tailings dump. (I) Near edge spectra (XANES) are highly sensitive to the oxidation state. XANES of the reduced Sb_2S_3 are shifted to >10 eV lower energy than the oxidized Sb(V) weathering products (white,

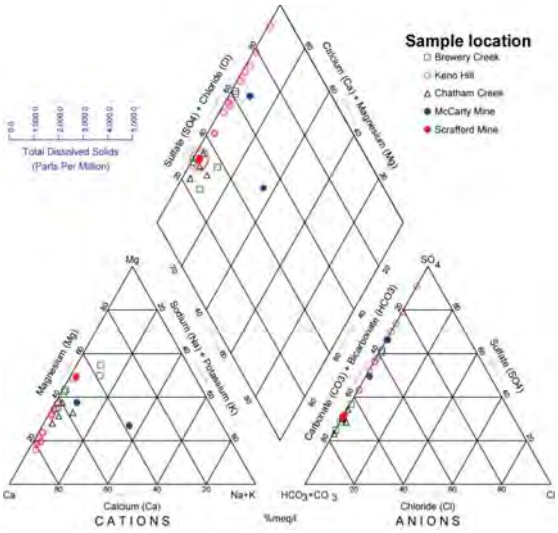


Figure 4. Piper diagram showing the major element and anion composition of stream water samples from select sample localities within the TGP (see Fig 1).

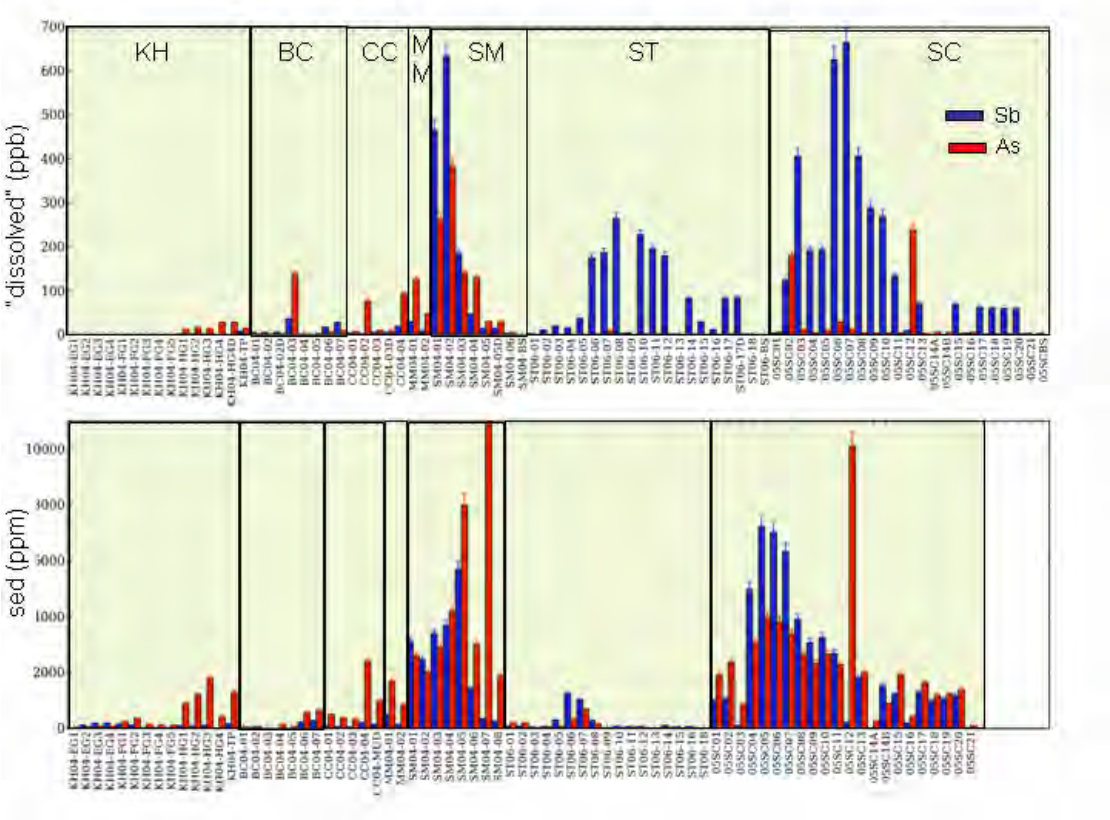


Figure 5. Concentration of dissolved (<0.45 micron) and sediment Sb and As at sampling localities within the TGP. KH=Keno Hill, BC=Brewery Cr., CC= Chatham Cr., MM = McCarty Mine, SM = Scrafford Mine, ST = Stampede, SC = Slate Cr.

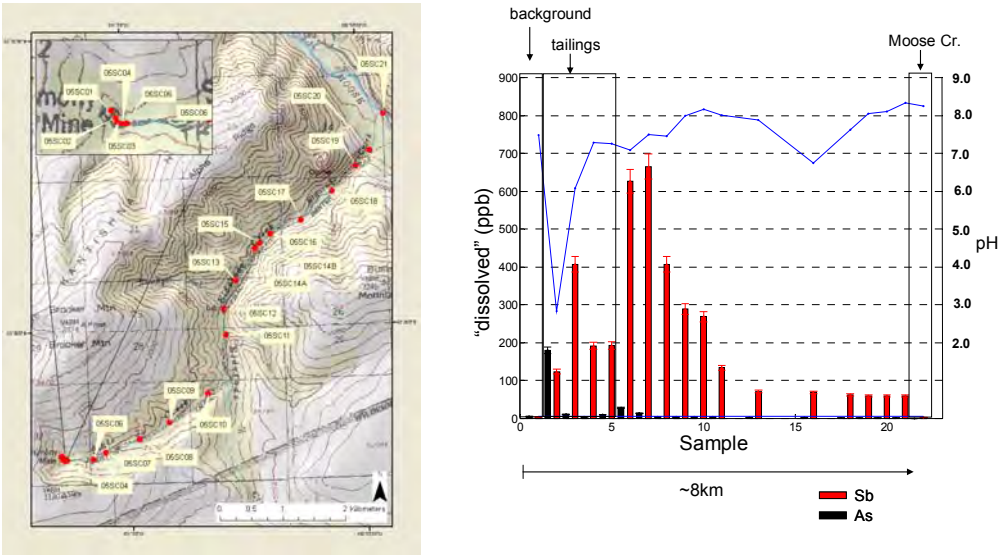


Figure 6. Sampling locations within the Slate Cr. drainage, Denali National Park and Preserve. Corresponding dissolved (<0.45 micron) concentrations of Sb and As showing the rise associated with tailings impacted areas and general dilution profile downstream.

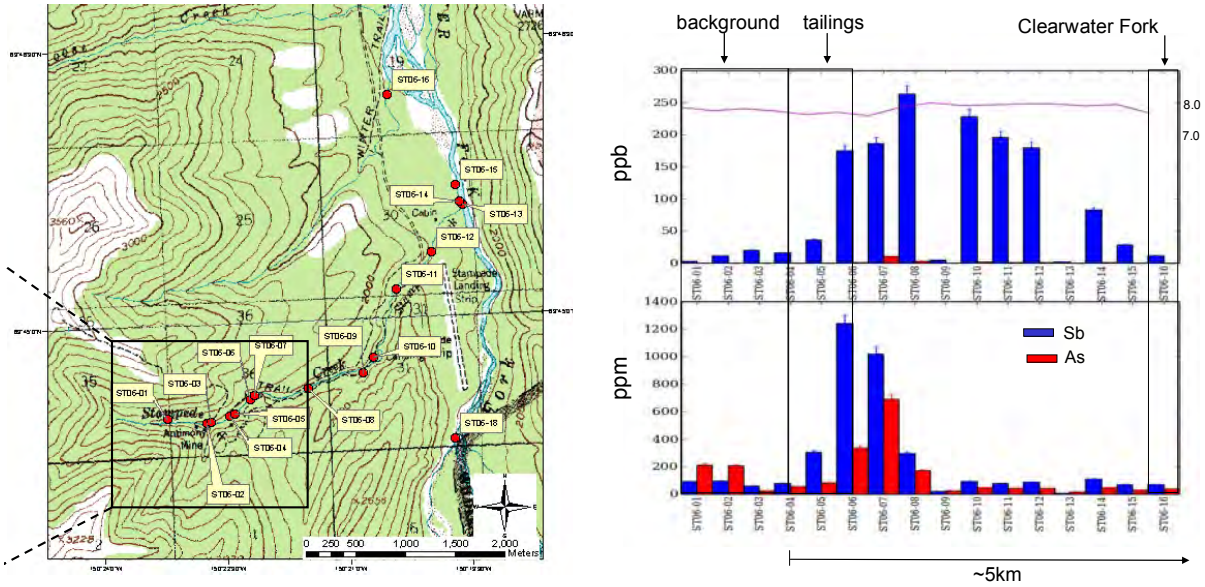


Figure 7. Sampling locations within the Stampede Cr. drainage, Denali National Park and Preserve. Corresponding dissolved (<0.45 micron, ppb) and sediment concentrations (<63 micron, ppm) of Sb and As showing the rise associated with tailings impacted areas and general dilution profile downstream.

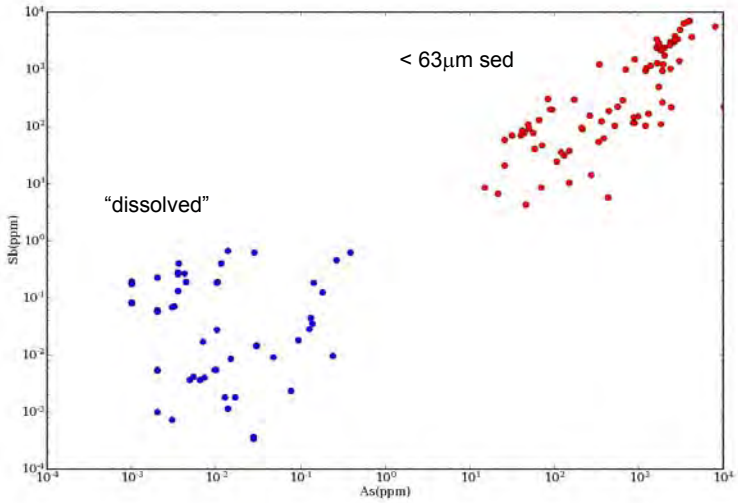


Figure 8. Correlation of dissolved (<0.45 micron) and sediment (<63micron) Sb and As concentrations at all sampling sites.

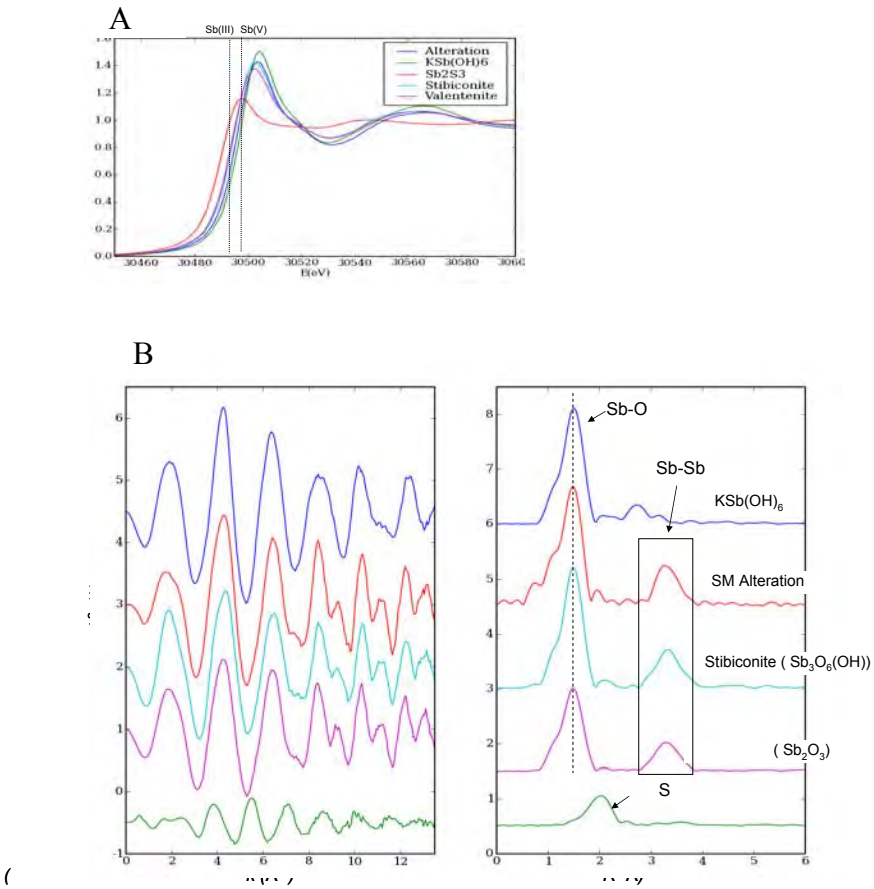
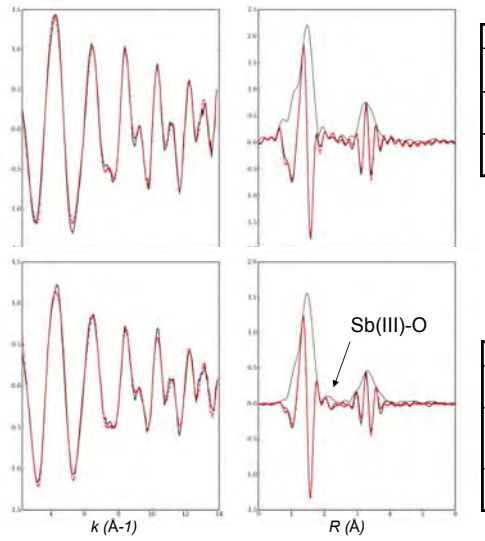


Figure 9. Antimony x-ray absorption spectra of primary sulfide mineral (stibnite), oxide model compounds (valentinite, stibiconite, and $KSb(OH)_6$) and the alteration product associated with weathered stibnite ore materials (SM Alteration). (A) Near edge spectra (XANES) of the reduced Sb_2S_3 are shifted to ~10 eV lower energy than the oxidized Sb(V). The SM Alteration shows an edge shift near that of the Sb(V) model, suggesting its highly oxidized. (B) The extended x-ray absorption spectra and Fourier transforms show distinct spectral features between sulfide (Sb_2S_3) and oxide coordination. The scond shell (Sb-Sb) correlations are similar among the oxides stibiconite, valentinite and SM Alteration suggesting similar local structure.



SM Alteration

	R (Å)	N	σ^2
Sb-O	1.96 (1.97)	~5.6 (6)	0.002
Sb-Sb	3.63 (3.63–3.64)	~3 (6)	0.002
Sb-Ca	3.6 (3.63)	~3 (6)	0.009

- Sb(III) substitution in the A sites of Lewisite yields $R_{Sb\text{-}Sb}$~3.27, absent from alteration spectra

Stibiconite

	R (Å)	N	σ^2
Sb-O	1.97 (2.01)	~5 (6)	0.003
Sb-O	2.50 (2.22) (2.49)	~1 (2) (6)	0.002
Sb-Sb	3.63 (3.63)	~4 (12)	0.002

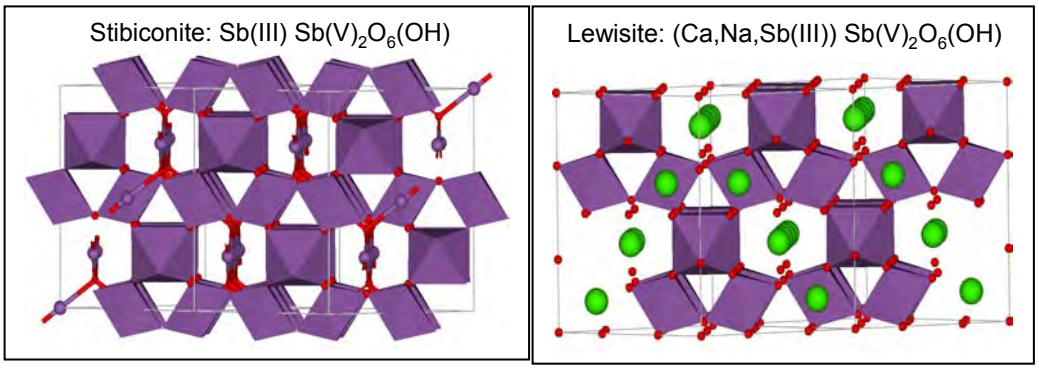
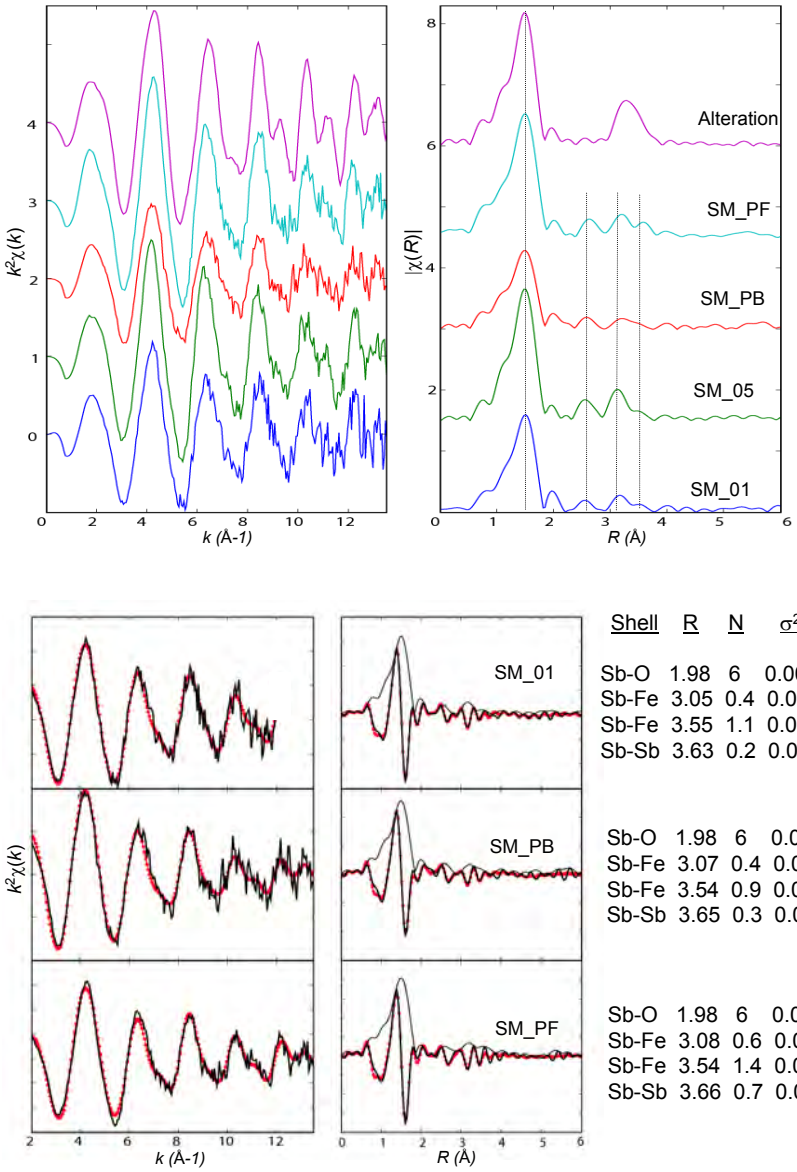


Figure 10. Structural analysis of SM Alteration and Stibiconite. The best fit shows similar coordination among the two minerals, however, the absence of the 2.50 Å Sb-O distance and the presence of Ca suggests the Lewisite is Sb(III) deficient, corroborating the XANES analysis.



Shell	R	N	σ^2
Sb-O	1.98	6	0.003
Sb-Fe	3.05	0.4	0.002
Sb-Fe	3.55	1.1	0.002
Sb-Sb	3.63	0.2	0.003
Sb-O	1.98	6	0.003
Sb-Fe	3.07	0.4	0.002
Sb-Fe	3.54	0.9	0.002
Sb-Sb	3.65	0.3	0.003
Sb-O	1.98	6	0.003
Sb-Fe	3.08	0.6	0.002
Sb-Fe	3.54	1.4	0.002
Sb-Sb	3.66	0.7	0.003

Fig 11. Antimony XAFS and FT results from a select set of <63 micron stream sediments. Fitting results (bottom panel) indicate that the local coordination environment is consistent with Sb(V) adsorbed to iron (hydr)oxide phases, due to the 1.98 Å Sb-O distance and the presence of Fe neighbors at 3.07 and 3.54 Å. The presence of the Sb-Sb correlation suggests that the adsorbed Sb is forming multinuclear complexes, or more likely there is a small fraction of the alteration product (Lewisite) present in the sediments.

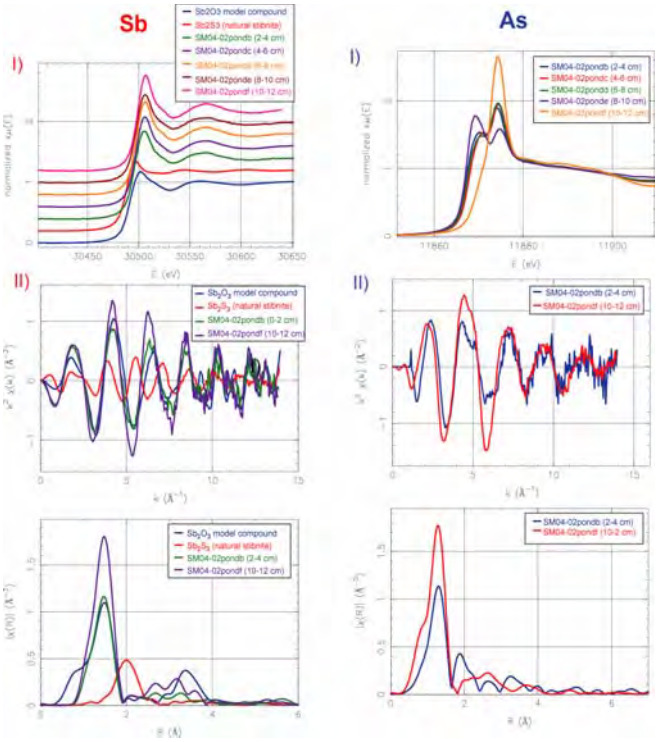


Figure 12. Antimony and Arsenic x-ray absorption of Scrafford Mine sediments. (I) Near edge spectra (XANES) of the reduced Sb_2S_3 arise are shifted to ~10 eV lower energy than the oxidized Sb(V) associated with sediments. As XANES show distinct signatures of As(III) at 11867 eV and As(V) at 11873 eV. (II) The extended x-ray absorption spectra and Fourier transforms (below) show distinct spectral features between sulfide (Sb_2S_3) and oxide coordination.

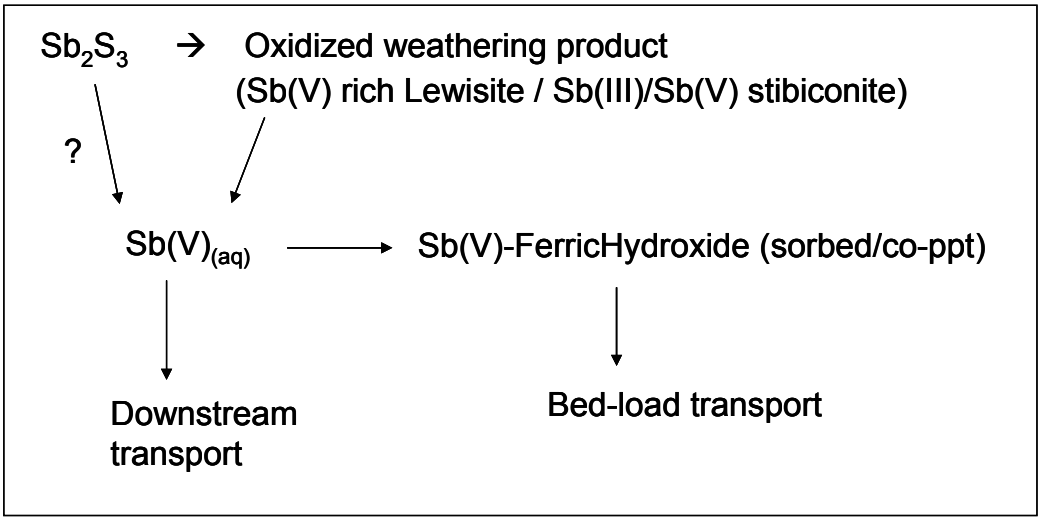


Figure 13. Simple pathway model consistent with observations for Sb speciation within TGP. Oxidation of the primary sulfide materials results in oxidized weathering products such as Lewisite. Dissolution of Lewisite introduced soluble Sb(V), which may be adsorbed to ferric (hydr)oxides. An unknown component within this model is the extent of direct dissolution of the primary sulfides, and homogenous or heterogeneous transformation between Sb(III)/Sb(V).