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UNIVERSITY OF SAN DIEGO

San Diego

Geochemical Investigation of Anomalous Arsenic Enrichment in the Santiago Peak
Volcanics of Southern California

A thesis submitted in partial satisfaction of the
requirements for the degree of

Master of Science in Marine Science

by

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TABLE OF CONTENTS

List of Figures	vii
List of Tables	viii
Chapter 1: Introduction	2
1.1 Background	2
1.2 Arsenic in the natural environment: literature review	3
1.2.1 Geogenic arsenic enrichment	3
1.2.2 Arsenic host minerals	4
1.2.3 Provenance of arsenic	5
1.2.4 Arsenic in volcanic arcs	5
1.2.5 The Santiago Peak Volcanics	6
1.3 Aims of this study	8
1.4 Structure of thesis	9
1.5 Work cited	10
Chapter 2: Arsenic enrichment in the Santiago Peak Volcanics of Southern California: implications for As geochemical cycling in volcanic arc systems	12
2.1 Abstract	12
2.2 Introduction	13
2.3 Study area	15
2.4 Methods	17
2.4.1 Sample collection	17
2.4.2 Sample preparation	17
2.4.3 Lithology	17
2.4.4 Bulk rock geochemistry	17
2.3.5 Trace metals	18
2.5 Results	19
2.5.1 Lithology	19
2.5.2 Bulk geochemistry	21
2.5.3 Trace metal enrichment	26
2.6 Discussion	28
2.6.1 Volcanic arc provenance of rocks outcropping at Black Mountain	28
2.6.2 Arsenic enrichment in relation to volcanic arc processes	29
2.6.2.1 Partial melt evolution	29
2.6.2.2 Arsenic mobility in subduction zone fluids	32
2.6.3 Model for arsenic occurrence in Black Mountain SPV	34
2.6.4 Potential for groundwater As enrichment	36
2.7 Summary	37
2.8 Conclusion	38
2.9 Work cited	39
Chapter 3: Arsenic Mineral Associations in the Black Mountain SPV Ore Deposit	43

3.1 Introduction.....	43
3.2 Study area.....	44
3.3 Methods.....	46
3.3.1 Sample collection.....	46
3.3.2 Bulk rock preparation	46
3.3.3 Sub-sample preparation	46
3.3.4 Arsenic concentration	46
3.3.5 Mineralogical analysis	47
3.4 Results.....	50
3.4.1 Arsenic enrichment	50
3.4.2 Arsenic mineral associations.....	52
3.4.2.1 Field observations.....	52
3.4.2.2 Powder X-ray diffraction.....	52
3.5 Discussion	56
3.5.1 Arsenic enrichment in Black Mountain SPV	56
3.5.2 Arsenic in fresh versus weathered rock	56
3.5.3 Arsenic host minerals.....	56
3.5.4 Arsenopyrite weathering.....	57
3.5.5 Sulfate replacement by arsenate.....	58
3.5 Summary and conclusion.....	61
3.6 Work cited.....	62
Chapter 4: Summary and conclusion	63
4.1 Summary	63
4.2 Conclusion	66
4.3 Work cited.....	67
Appendix A: Sample locations	68
Appendix B: Trace metals in rhyolites and dacites (n = 20)	70
Appendix C: Trace metals in all samples and subsamples (n = 168)	71
Appendix D: Arsenic correlation with lead, antimony, copper, and zinc (n = 168).....	76
Appendix E: Trace metal content in fresh versus weathered subsamples of Black Mountain SPV (n = 44).....	77
Appendix F: XRD results for all samples and subsamples (n = 168).....	78
Appendix G: Sample photos	93
Appendix H: Analytical laboratory (EMA) results.....	128
Appendix I: Scanning electron microscope	132

LIST OF FIGURES

Figure 2.1. 1:30,000 geologic map of Black Mountain Open Space Park....	16
Figure 2.2. Photomicrographs taken in cross-polarizing light	20
Figure 2.3. Jensen Cation and TAS diagrams	22
Figure 2.4. Bivariate plots showing concentration of SiO ₂ relative to K ₂ O, Na ₂ O, Fe ₂ O ₃ , Al ₂ O ₃ , MnO, MgO, CaO, and TiO ₂	23
Figure 2.5. AFM diagram	24
Figure 2.6. Bivariate plots comparing As content to K ₂ O, Na ₂ O, Fe ₂ O ₃ , Al ₂ O ₃ , MnO, MgO, CaO, TiO ₂ , and SiO ₂	31
Figure 2.7. Model explaining provenance of As in Black Mountain SPV ...	35
Figure 3.1. Location of Black Mountain Open Space Park	45
Figure 3.2. Distribution of arsenic in rocks and soil	49
Figure 3.3. Photographs of arsenic host minerals	53
Figure 3.4. XRD spectra for arsenic host minerals	54
Figure 3.5. Arsenic in fresh versus weathered rocks	54
Figure 3.6. Schematic of arsenopyrite weathering.....	60

LIST OF TABLES

Table 2.1. QA/QC for Innov-X-5000	18
Table 2.2. Major element composition of bulk rock samples	25
Table 2.3. Summary of trace element enrichment in bulk rocks.....	27
Table 3.1. QA/QC for samples with anomalous arsenic concentrations.....	48
Table 3.2. Summary of trace element enrichment in all samples	51
Table 3.3. Trace metal content of samples containing goethite	55

CHAPTER 1: Introduction

1.1 Background

Black Mountain Open Space Park is located in the Rancho Peñasquitos neighborhood of northern San Diego, and is owned and managed by the City of San Diego. Though artisanal arsenic (As) mining occurred on-site during the 1920's (Stewart 1963), the park remains a popular destination for local hikers and bikers, and is surrounded by a relatively dense suburban population. Our initial investigation of soils and rocks throughout the park by field portable X-ray fluorescence (FP-XRF, Haffert and Craw 2009) revealed As concentrations up to 400,000 ppm. Such concentrations are nearly 100,000 times greater than average for the upper-crust (4.8 ppm, Rudnick and Gao 2003) and, thus, indicate the need to investigate As enrichment throughout the park and the potential for As to be mobilized off-site. This thesis investigates As distribution among rocks cropping out at Black Mountain Open Space Park.

1.2 Arsenic in the natural environment: literature review

Arsenic (As) occurs naturally as the 20th most abundant trace element in the Earth's crust and is widely distributed in the environment. Arsenic exists in organic and inorganic forms and in several valence states (e.g. -3, 0, +3, +5) that reflect the redox conditions of its geochemical environment. Toxicologists are primarily concerned with As³⁺ and As⁵⁺, since both are toxic and present in natural waters (Duker et al. 2005).

Of the various sources of As in the environment, ingestion of As-enriched groundwater poses the greatest threat to human health. However, inhalation of airborne As is an additional exposure pathway, along with consuming food grown in As-rich soil (Smedley and Kinniburgh 2001). Long-term exposure can cause chronic As poisoning, impairment of cognitive development, neurotoxicity, diabetes, cardiovascular disease, and bladder, lung, and kidney cancer, as demonstrated in India and Bangladesh, where an estimated 36 to 75 million people in the Bengal Delta were at risk from drinking As-contaminated groundwater at the end of the 20th century (Mukherjee and Bhattacharya 2001, Nordstrom 2002). Such findings have prompted further investigation of the factors controlling As distribution in the natural environment.

1.2.1 Geogenic arsenic enrichment

In the natural environment, As can be anthropogenic or geogenic. Geogenic As is a product of natural geological processes and is, therefore, not a result of human activities. Geogenic As is present in both terrestrial and marine environments, and its concentration varies greatly as a result of mobilization by natural and/or anthropogenic processes (Smedley and Kinniburgh 2001). The average As concentration in the upper continental crust is 4.8 mg/kg (Rudnick and Gao 2003), and average enrichment differs among rock types. In igneous rocks, the average As concentration is approximately 1.5 mg/kg. In metamorphic rocks, As is typically

less than 5 mg/kg (Smedley and Kinniburgh 2001), while As in sedimentary rocks ranges from 5 to 10 mg/kg (Webster 1999). Weathering, erosion, and sedimentation, in addition to As contribution from source magmas, lavas, and metamorphic fluids, are important natural processes in controlling As enrichment in the upper crust (Henke 2009). Therefore, As enrichment in individual rock units may deviate significantly from the averages presented above.

1.2.2 Arsenic host minerals

In As-rich rocks, As most commonly forms sulfide minerals, as well as associations with oxides and, less commonly, phosphates (Drahota and Filippi 2009, Majzlan et al. 2014). Arsenic-bearing sulfide minerals are especially common in hydrothermal deposits, causing As to be associated with metal ore minerals and their alteration products (Henke 2009). With exposure to the atmosphere and surface or groundwater, these primary minerals undergo alteration reactions to form secondary minerals, like As oxides or more complicated phases with As, oxygen, and metals (e.g. Fe, Mn, Ni, Drahota and Filippi 2009).

Modern water-rock interactions often cause As to be leached from primary and/or secondary host minerals, making As one of the most problematic trace metals in the environment (Smedley and Kinniburgh 2001). Human activities can greatly influence the stability of As host minerals by altering redox conditions. For example, mining As-bearing ore deposits exposes greater surface area of As-enriched minerals to air and aerated water, leading to increased As leaching and, thus, greater mobilization off-site (Henke 2009). Consequently, concentrations of natural As in drinking water above standards (10 µg/L) are not uncommon. Countries/regions with groundwater elevated in As include: Bangladesh (<1 to 2,500 µg/L), West Bengal, India (<10 to 3,200 µg/L), Thailand (1 to >5,000 µg/L), Argentina (<1 to 9,900 µg/L), Chile (100 to

1,000 µg/L), and the southwestern United States (0.38 – 1000 µg/L) (Smedley and Kinniburgh 2001, Nordstrom 2002).

1.2.3 Provenance of arsenic

Recent documentation of the acute and chronic effects of exposure to As in drinking water has emphasized the importance of better-understanding the sources, pathways, and controls on high As in various environmental systems (Smedley and Kinniburgh 2001). Source materials currently considered to be significant contributors of As in global drinking water supplies include: organic-rich black shales, Holocene alluvial sediments with slow flushing rates, mineralized and mined areas (most often gold deposits), volcanogenic sources, and thermal springs (Nordstrom 2002, Mukherjee et al. 2014). However, because aquifers in sediments and sedimentary rocks typically yield more water for drinking supplies (Smedley and Kinniburgh 2001), attention to other source materials, like volcanic host rocks, remains in deficit.

1.2.4 Arsenic in volcanic arcs

Mukherjee et al. (2014) suggest that the global distribution of geogenic As in groundwater is largely controlled by As mobilization in subduction zone fluids, since As enrichment tends to occur in orogenic belts, like the Himalayan, Andean, Western Cordilleran, and Appalachian mountain chains (Mukherjee et al. 2014). Their hypothesis is largely based on the work of Hattori and Guillot (2003), who provide a mechanism for As enrichment in such environments.

Specifically, Hattori and Guillot (2003) propose that the dehydration of subduction zone serpentinites accounts for the observed enrichment of soluble elements in volcanic arc magmas, which are later exhumed to form As-rich volcanic rocks that are eventually incorporated into mountain chains. During subduction, hydrous minerals in subducting slabs and overlying sediments release water and soluble elements (e.g. As, Pb, Sb) because of increased pressure and

temperature. After release, such elements and water migrate upward, hydrating the mantle peridotite and forming a serpentinite layer along the plate boundary. The dissolved elements become concentrated as water is consumed by dehydration and eventually become fixed in the serpentinites. Because serpentinites act as a sink for water, serpentinite layers prevent the mantle wedge from partially melting. Thus, the serpentinite layer will continue to subduct with the plate until depths exceed ~100km. Temperatures of about 650°C completely dehydrate the serpentinite to eclogite, releasing hydrothermal fluid and fluid-soluble elements, which hydrate and enrich the overlying mantle wedge and cause partial melting. When the angle of subduction is steep, fluids released from serpentinite dehydration may be focused on a relatively narrow zone more directly beneath the volcanic front, resulting in greater enrichments of fluid soluble elements (Noll et al. 1996). Partial melts eventually rise via buoyancy and hydrostatic pressure and are exhumed by volcanic arcs (Hattori and Guillot 2003). Due to its high solubility, Hattori and Guillot (2003) suggest that As is among the first elements released from the serpentinites and incorporated into the partial melt during serpentinite dehydration. (Breuer and Pichler 2013, Henke 2009, Ballantyne and Moore 1988). Consequently, As is often concentrated in rocks associated with ancient volcanic fronts (Hattori and Guillot 2003). However, Mukherjee et al. (2014) recommends targeted field studies to enhance understanding of this As cycling in these volcanic settings.

1.2.5 The Santiago Peak Volcanics

The Santiago Peak Volcanics (SPV) of Southern California and Northern Baja California, Mexico are remnants and a subaerial volcanic arc, located in the southern portion of the Western Cordilleran orogenic belt. Though its petrogenesis has been disputed (Fife et al. 1996), Herzig and Kimbrough (2014) suggest that the SPV evolved along the western coast of North America

during the Cretaceous and, thus, belong to the magmatic plumbing system of the western zone of the Peninsular Ranges Batholith (PRB). In the 1920's, the SPV outcropping at Black Mountain Open Space Park was mined for white As. Mining efforts were small-scale and short-lived, with just 700 pounds of material containing 31.4% As shipped from the property (Stewart 1963).

1.3 Aims of this study

Our findings of anomalous As enrichment ($>1,000$ ppm) in volcanic rocks exposed at Black Mountain Open Space Park provide an excellent opportunity to investigate As cycling in volcanic arcs, while examining the extent of As enrichment throughout the park and the potential for As to be mobilized from primary and/or secondary host minerals. Thus, this thesis poses the following research questions:

1. What is the geology of rocks cropping out at Black Mountain Open Space Park, and over what spatial scale does rock type vary?
2. What is the distribution of As among SPV rock types, and how can we use this knowledge to propose a model for As cycling in the ancient volcanic arc system?
3. What are the primary and secondary As host minerals in Black Mountain SPV, and how does knowledge of host minerals inform future research investigating As mobility?

1.4 Thesis structure

Research Questions 1 and 2 are presented in Chapter 2, while Chapter 3 addresses Research Question 3. Chapter 2 is written as a manuscript for publication, while Chapter 3 intends to inform future research at Black Mountain Open Space Park. Supplementary data, figures, and analyses are collated in the appendices of this thesis.

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CHAPTER 2: Arsenic enrichment in the Santiago Peak Volcanics of Southern California: implications for geogenic arsenic distribution in ancient and modern volcanic arc systems

2.1 Abstract

Arsenic (As) is enriched in the Santiago Peak Volcanics (SPV) that crop out at Black Mountain Open Space Park in San Diego, CA. Thus, the Black Mountain SPV present an excellent opportunity to investigate As enrichment in ancient volcanic arc systems as a result of deep earth subduction zone processes. Through targeted field study of this unit, we aim to (1) confirm the volcanic arc provenance of rocks cropping out at Black Mountain, (2) investigate As enrichment in relation to volcanic arc processes, and (3) propose a model for As occurrence in the SPV. Our findings indicate Black Mountain SPV evolved from the same magma system as Northern Santa Ana Mountain SPV during the Cretaceous, and that As content varied between the two dominant SPV rock types, with rhyolites containing more As ($n = 10$, mean = 586 ± 10 ppm As) than dacites ($n = 10$, mean = 14 ± 9 ppm As). Our proposed model for As enrichment in SPV suggests that As is among the first elements released during serpentinite dehydration (along with Pb), while less soluble elements (e.g. Cu) are released during later stages of subduction. Once As and Pb are released from serpentinites and incorporated into partial melts, we hypothesize that such elements behave like typical incompatible elements and remain dissolved in melts until they are eventually exhumed in rhyolitic lavas. Since As may dissolve out of volcanic host rocks in groundwater aquifers, this enhanced understanding of As distribution among ancient volcanic arc rocks may aid in identifying alternative drinking water sources in regions with known groundwater As enrichment.

2.2 Introduction

Modern volcanic arc systems provide conditions where fluid soluble elements like arsenic (As) can be enriched in subduction zone magmas (Ballantyne and Moore 1988, Hattori and Guillot 2003, Breuer and Pichler 2013). Thus, ancient volcanic arcs are plausible host provinces of As-enriched volcanic rocks (Mukherjee et al. 2014). However, this type of geologic province is not frequently targeted in studies of groundwater As exposure, since aquifers of sediments and sedimentary rocks typically yield more water for drinking supplies (Smedley and Kinniburgh 2002). Recent studies (e.g. O'Shea et al. 2015, Ryan et al. 2015) draw awareness to metamorphic aquifers as potential As hosts, but attention to volcanic rocks remains in deficit.

Mukherjee et al. (2014) hypothesize that geogenic As in groundwater may ultimately be sourced to deep earth processes. A key component of their proposed global As system is As mobilization by subduction zone magmas (Ballantyne and Moore 1988, Breuer and Pichler 2013, Mukherjee et al. 2014). During this process, subducted slabs and overlying sediments release water and soluble elements (e.g. As, Pb, Sb), which hydrate and enrich overlying serpentinites (Hattori and Guillot 2003). With further downward movement of the subducting slab the serpentinite layer transports these fluid-soluble elements to depth. Eventually dehydration of serpentinites occurs, releasing the slab-transported soluble elements and water, leading to partial melting of the mantle wedge and enrichment of such elements in volcanic arc fronts (Hattori and Guillot 2003). However, as recommended by Mukherjee et al. (2014), targeted field studies are required to enhance understanding of As cycling in these volcanic arc settings.

The Santiago Peak Volcanics (SPV) of Southern California (CA), USA and Northern Baja CA, Mexico are remnants of a subaerial volcanic arc that evolved along the west coast of North America during the Cretaceous. In studies by Herzig and Kimbrough (2014) of SPV

outcropping in the Northern Santa Ana mountains, parental magmas were likely derived from a shallow, hydrous source magma followed by up to 10% assimilation of continental crust. Rocks range in composition from basalt to rhyolite and likely underwent syn-volcanic greenschist facies metamorphism (Herzig and Kimbrough 2014).

Historical records indicate that the portion of the SPV cropping out 100 km south of the Northern Santa Ana SPV, at Black Mountain Open Space Park (San Diego, CA) was once mined for As (Stewart 1963), providing a unique opportunity to present an integrated view of the interactions between observed As anomalies and volcanic arc processes through targeted field study. The goals of this work are threefold: (1) confirm the volcanic arc provenance of rocks cropping out at Black Mountain, (2) investigate As enrichment in relation to volcanic arc processes, and (3) propose a model for As occurrence in the SPV. Such analysis may enhance understanding of As transport by subduction zone magmas and provide insight into the preferential concentration of As in volcanic arc rocks, which may aid in identifying areas that are susceptible to groundwater elevated in As (Mukherjee et al. 2014).

2.3 Study area

We examined SPV exposed at the surface of Black Mountain Open Space Park. The 950-hectare park is located in the Rancho Peñasquitos Community of northern San Diego (population density = $\sim 1,500$ people/mi²). The park encompasses most of Black Mountain, the highest peak (460 m) in the community, and surface water within the park drains into channels that eventually empty into the San Dieguito River. However, rainfall can be limited (< 30 cm/yr) in this semi-arid region of the Southwestern coast of the USA (Fig 2.1b). Field mapping produced a 1:30,000 geologic map (Fig 2.1a) for Black Mountain. Portions of the park surrounding abandoned mines were mapped with greater resolution and indicate that the lithology of Black Mountain SPV varies over a spatial scale of tens of meters.

Fig 2.1: a) 1:30,000 geologic map of Black Mountain Open Space Park. Dotted line shows study area, b) Location of study area in San Diego County, California, USA.

2.4 Methods

2.4.1 Sample collection

Following geological mapping and preliminary elemental analysis by field portable X-ray fluorescence (XRF, Haffert and Craw 2009), we collected 20 rock samples from in-situ outcrops at Black Mountain Open Space Park. Sampling was primarily focused around a 1 km² area surrounding abandoned mines (Fig 2.1). Though outcrops were limited and sometimes inaccessible, we sampled multiple lithologies so that the extent of heterogeneity is represented in the sample population.

2.4.2 Sample preparation

Bulk rock samples (n = 20) were pulverized into a fine powder using a Bico Pulverizer fitted with ceramic plates at the University of San Diego (USD). Though samples had undergone various extents of weathering, we targeted fresh portions of coherent samples by removing weathering rinds using a diamond-tipped Dremel tool. Powdered rocks were sieved to <53 microns before fusion. A representative subset of samples (n = 10) were cut into thin section for analysis by petrographic microscope. All equipment was routinely cleaned with acetone and compressed air to avoid cross contamination between samples.

2.4.3 Lithology

We analyzed thin sections following Perkins and Henke (2004) using a standard polarizing petrographic microscope at USD.

2.4.4 Bulk rock geochemistry

We examined major element composition using an XRF (Rigaku ZSX Primus II) at the College of Wooster following methods of Pollock et al. (2014). The resulting major element concentrations were used to characterize rock type by total alkali versus silica (TAS, Le Bas et

al. 1985) and Jensen Cation (Le Maitre et al. 1989) plots, since samples could have undergone metasomatic loss of alkalis during greenschist facies alteration (Rollinson 1993).

2.4.5 Trace metals

Bulk rock samples were analyzed for trace metals by an Innov-X-5000 X-ray Fluorescence (XRF) at USD. Before each analysis, the XRF passed calibration by reference to a factory provided calibration disc. The Certified Reference Material (CRM) NIST 2710a Montana I Soil was analyzed for data quality assurance before, after, and during analysis of rock powders. Accuracy was assessed by calculating relative percent difference (RPD) from the certified concentration. Duplicates were assessed by calculating relative standard deviation (RSD), and only elements with RSD at or below 5% precision are included in this report (Table 1).

Table 2.1: QA/QC for Innov-X-5000

Sample ID	As (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)	Sb (ppm)
NIST 2710a (1)	1,520	3,210	4,136	5,271	50
NIST 2710a (2)	1,517	3,228	4,151	5,276	49
NIST 2710a (3)	1,544	3,244	4,170	5,283	53
NIST 2710a (4)	1,559	3,283	4,192	5,325	50
NIST 2710a (5)	1,558	3,255	4,207	5,310	51
NIST 2710a (6)	1,563	3,340	4,260	5,389	50
NIST 2710a certified value	1,540	3,420	4,180	5,520	52.5
% RSD*	1%	1%	1%	1%	3%
% RPD**	0%	-5%	0%	-4%	-4%

*: Precision measured by %RSD = 100 * (standard deviation/average)

**: Accuracy measured by %RPD = 100 * [(ave. reported value for CRM - CRM certified value)/ CRM certified value]

2.5 Results

2.5.1 Lithology

Volcanic outcrops in the study area consist of crystallized lava flows (Fig 2.2a), welded tuff (Fig 2.2b), and volcanoclastic (epiclastic) rocks (Fig 2.2c). Subaerial eruptive features include vesicles, flow banding (Fig 2.2a), pumice fragments (Fig 2.2c), and accretionary lapilli (Fig 2.2d). We did not observe features indicative of subaqueous volcanic eruption. All coherent samples were porphyritic, containing relatively fresh crystals of quartz (Qtz, Fig 2.2e), plagioclase (Plag, Fig 2.2b), and pyrite (Py, Fig 2.2b), with plagioclase being the most abundant phenocryst type. However, many phases were pseudomorphs composed of greenschist minerals chlorite (Cl), epidote (Ep), and zoisite (Zo) (Fig 2.2f, Fig 2.2g). We also observed sericite (Ser) in some rhyolitic samples ($n = 3$, Fig 2.2i).

Fig 2.2: Photomicrographs taken in cross-polarizing light showing: a) Minimally altered rhyolite (R021i) exhibiting flow banding, b) Altered dacitic welded tuff (R065i) containing relatively fresh phenocrysts of plagioclase (Plag) and pyrite (Py), c) Altered volcaniclastic dacite (R055i), d) Accretionary lapilli, e) Moderately altered dacite (R049i) containing quartz (Qtz) phenocryst, with zoisite (Zo) and epidote (Ep) bordering phenocryst, f) Altered phenocryst containing quartz (Qtz), epidote (Ep), zoisite (Zo), and minor iron oxide in a moderately altered dacite (R049i), g) Twinned plagioclase phenocrysts in an altered rhyolite (Mr002) that have been almost completely replaced by chlorite (Cl) and epidote (Ep), h) Moderately altered dacitic welded tuff (R065i) containing hematite and pyrite (Py), and i) Highly altered rhyolite (Mr002) containing sericite (Ser), chlorite (Cl), and pyrite (Py).

2.5.2 Bulk geochemistry

Jensen Cation (Fig 2.3a, Le Maitre et al. 1989) and TAS (Fig 2.3b, Le Bas et al. 1985) plots of bulk rock samples identify sub-alkaline rhyolites, dacites, and minor andesites as the most abundant rock types in Black Mountain SPV, with lithology varying over a spatial scale of tens of meters (Fig. 2.1). We will hereafter use the Jensen Cation Plot (Fig 2.3a, Le Maitre et al. 1989) to classify Black Mountain SPV, thus our samples consist of volcanic rhyolites (n = 10) and dacites (n = 10).

Rhyolites typically contained greater SiO₂ (mean = 74.09 ± 2.13¹ wt%), Na₂O (mean = 4.81 ± 0.27 wt%), and K₂O (mean = 2.35 ± 0.25 wt%), while dacites were enriched in Al₂O₃ (mean = 16.84 ± 0.52 wt%), Fe₂O₃ (mean = 9.07 ± 0.35 wt%), CaO (mean = 5.56 ± 1.03 wt%), MgO (mean = 1.7 ± 0.20 wt%), and MnO (mean = 0.15 ± 0.01 wt%) (Table 2). We observed overall trends of decreasing Al₂O₃ (R² = 0.86), Fe₂O₃ (R² = 0.87), MgO (R² = 0.53), CaO (R² = 0.66), and TiO₂ (R² = 0.82) relative to SiO₂, while K₂O (R² = 0.34) and Na₂O (R² = 0.24) are positively correlated with SiO₂ (Fig 2.4). Black Mountain SPV lavas show Fe enrichment consistent with the tholeiitic magma series (Fig 2.5, Rollinson 1993).

¹ Standard error = $\frac{\text{Standard deviation } (\sigma)}{\sqrt{\text{Sample size } (n)}}$

* : Certified Reference Material (CRM). Basalt, Hawaii Volcanic observatory, BHVO-2 (Wilson, S.A. 1998).

Fig 2.3: a) Jensen Cation (Le Maitre et al. 1989) and b) TAS (Le Bas et al. 1985) plotting of cations measured in rock samples presented in Table 2. Samples are differentiated by As concentration. For comparison, blue hexagons show geochemistry of SPV in the northern Santa Ana Mountains (Herzig and Kimbrough 2014). CRM provided for reference.

Fig 2.4: Bivariate plots showing concentration of SiO_2 relative to a) K_2O , b) Na_2O , c) Fe_2O_3 tot, d) Al_2O_3 , e) MnO , f) MgO , g) CaO , and f) TiO_2 . Colors indicate relative As enrichment.

* Northern Santa Ana Mountain SPV whole rock geochemical data from Herzig & Kimbrough (2014), Table 5.

Fig 2.5: AFM (A – alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), F – total iron (Fe_2O_3), M – MgO) Diagram for lavas of the Santiago Peak Volcanics. BT = tholeiitic basalt, FB = ferro-basalt, ABT = tholeiitic basaltic andesite, AT = tholeiitic andesite, D = dacite, R = rhyolite, B = basalt, AB = basaltic andesite. Colors indicate relative As enrichment.

Table 2.2: Major element composition of bulk rock samples (n = 20).

Sample ID	Rock Type	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃ tot	BaO	Total
		mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
Mr001	Rhyolite	5.01	0.06	12.00	79.28	0.00	1.43	0.40	0.23	0.01	1.49	0.09	100
Mr002	Rhyolite	5.23	0.17	13.63	75.32	0.03	1.69	1.36	0.28	0.06	2.16	0.08	100
R004i	Rhyolite	4.15	0.24	14.52	71.66	0.03	2.81	0.44	0.31	0.03	5.67	0.14	100
R020i	Rhyolite	5.45	0.21	13.53	75.07	0.03	1.76	0.89	0.30	0.07	2.60	0.09	100
R021i	Rhyolite	3.65	0.17	14.15	74.36	0.06	3.33	1.41	0.19	0.07	2.56	0.07	100
R024wp	Rhyolite	5.54	0.20	13.30	72.62	0.03	1.65	0.40	0.36	0.03	5.77	0.09	100
R037i	Rhyolite	6.53	0.06	15.86	72.48	0.04	2.18	1.14	0.35	0.02	1.14	0.19	100
R044i	Rhyolite	4.62	0.21	14.41	71.83	0.01	1.65	2.79	0.31	0.11	3.98	0.07	100
R046i	Rhyolite	3.95	0.21	13.83	74.22	0.03	3.59	1.15	0.20	0.07	2.70	0.07	100
R060i	Rhyolite	3.94	0.11	14.17	74.10	0.01	3.43	1.58	0.18	0.04	2.37	0.07	100
Average	Rhyolite	4.81	0.16	13.94	74.09	0.03	2.35	1.16	0.27	0.05	3.04	0.10	100
Standard error	Rhyolite	± 2.7	± 0.02	± 0.30	± 0.67	± 0.00	± 0.26	± 0.22	± 0.02	± 0.01	± 0.48	± 0.01	
R038i	Dacite	0.90	0.35	19.66	52.43	0.07	0.19	14.98	1.06	0.21	10.14	0.01	100
R039i	Dacite	4.03	1.83	16.74	63.34	0.14	0.43	5.54	0.67	0.11	7.15	0.03	100
R049i	Dacite	3.58	1.06	14.82	64.32	0.38	0.49	5.93	1.03	0.19	8.19	0.02	100
R051i	Dacite	3.44	2.55	16.54	63.15	0.14	0.57	3.69	0.91	0.13	8.87	0.03	100
R053i	Dacite	3.64	1.25	15.52	62.74	0.20	1.39	4.63	0.87	0.16	9.56	0.05	100
R054i	Dacite	4.19	2.30	18.26	57.29	0.25	1.86	4.03	1.23	0.18	10.36	0.07	100
R055i	Dacite	2.92	2.31	16.35	62.02	0.13	1.87	3.44	0.97	0.13	9.82	0.05	100
R058i	Dacite	4.59	1.44	14.95	65.60	0.26	0.60	3.52	0.78	0.10	8.14	0.02	100
R065i	Dacite	4.27	2.12	19.45	56.40	0.18	1.44	4.66	0.74	0.14	10.54	0.06	100
R066i	Dacite	3.84	1.79	16.12	62.79	0.19	1.00	5.16	0.97	0.15	7.97	0.04	100
Average	Dacite	3.54	1.7	16.84	61.01	0.19	0.98	5.56	0.92	0.15	9.07	0.04	100
Standard error	Dacite	± 0.31	± 0.20	± 0.52	± 1.26	± 0.03	± 0.19	± 1.03	± 0.05	± 0.01	± 0.35	± 0.01	
BHVO-2 ⁺	Basalt CRM	2.20	7.11	13.55	49.99	0.26	0.51	11.29	2.70	0.17	12.20	0.01	100
Average in upper-crust*		3.27	2.43	15.40	66.62	0.15	3.27	3.59	0.64	0.10	5.04	0.07	

⁺ : Certified Reference Material (CRM). Basalt, Hawaii Volcanic observatory, BHVO-2 (Wilson, S.A. 1998).

*: Rudnick and Gao (2003)

2.5.3 Trace metal enrichment

Total As in Black Mountain SPV ($n = 20$) ranged from 5.2 ppm to 3,155 ppm. In addition to As, all samples contained copper (Cu), lead (Pb), and zinc (Zn). We detected antimony (Sb) in only a few ($n = 2$) samples. Rhyolites were typically more enriched in As ($n = 10$, mean = 586 ± 10 ppm As) than dacites ($n = 10$, mean = 14 ± 9 ppm As). Rhyolites also contained greater concentrations of Pb (mean = 28 ± 4 ppm As), while dacites were more enriched in Zn (mean = 114 ± 13 ppm). Rhyolites and dacites had similar average Cu concentrations (~ 30 ppm) (Table 3).

Table 2.3: Summary of trace element enrichment in Black Mountain SPV. Mean +/- standard error.

	As (ppm)	Cu (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
Bulk rhyolites (n = 10)	586 +/- 10	30 +/- 6	28 +/- 4	4 +/- 3	46 +/- 8
Bulk dacites (n = 10)	14 +/- 9	30 +/- 3	12 +/- 2	ND	114 +/- 13
Average in upper-crust*	4.8	28	17	0.4	47

*: Rudnick and Gao (2003)

2.6 Discussion

2.6.1 Volcanic arc provenance of rocks outcropping at Black Mountain

Given the geochemical similarities between Black Mountain SPV and Northern Santa Ana Mountain SPV (Herzig and Kimbrough 2014), we suspect that the two units evolved within the same volcanic arc system during the Cretaceous. Our hypothesis is supported by several lines of evidence. First, we observed welded tuffs, volcanoclastic (epiclastic) rocks, and accretionary lapilli in Black Mountain SPV, which suggest that several distinct stages of subaerial volcanic eruption occurred (Abbott et al. 1993, Herzig and Kimbrough 2014).

Second, we found that lavas were often porphyritic and ranged in composition from dacite to rhyolite (Fig 2.3), with rhyolites containing more SiO_2 , Na_2O , and K_2O than dacites (Fig. 2.4). Like Herzig and Kimbrough (2014), we also observed overall trends of decreasing Al_2O_3 , Fe_2O_3 , MgO , CaO , and TiO_2 relative to SiO_2 (Fig 2.4). Such trends are qualitatively consistent with low-pressure fractional crystallization of hydrous mafic magmas (Rollinson 1993) and, thus, suggest that rhyolites crystallized from more evolved melts than dacites.

Finally, all samples analyzed in thin section contain evidence of varying extents of syn-volcanic alteration (Fig 2.1). Though greenschist facies minerals (e.g. chlorite, epidote, zoisite) often replaced primary igneous phases (e.g. plagioclase) in highly altered samples, we found no evidence of penetrative cleavage indicative of a regional metamorphic event (Fig 2.1). Therefore, our findings corroborate the hypothesis that greenschist facies alteration of SPV occurred contemporaneously with arc volcanism (Herzig and Kimbrough 2014).

2.6.2 Arsenic enrichment in relation to volcanic arc processes

We found that As content varied between the two dominant SPV rock types, with rhyolites typically containing more As ($n = 10$, mean = 586 ± 10 ppm As) than dacites ($n = 10$, mean = 14 ± 9 ppm As) (Table 2.2). This finding is particularly interesting because typically igneous rocks report low (close to crustal average; Table 2.3) concentrations of As. For example, Smedley and Kinniburgh (2001) report an average of 1.5 ppm As for igneous rocks. The mean arsenic in these SPV rhyolites is thus about 120 times greater than the averages reported for the upper crust, and nearly 400 times the average for igneous rocks as reported by Smedley and Kinniburgh (2001). Even dacites are enriched above crustal averages, further indicating that volcanic arcs are plausible host provinces of As-enriched volcanic rocks.

2.6.2.1 Partial melt evolution

The enrichment of As in rhyolites may explain the weak to moderate positive correlation we observed between As and SiO_2 ($R^2 = 0.32$) and/or Na_2O ($R^2 = 0.43$), as well as the negative correlation between As and Fe_2O_3 ($R^2 = 0.30$), Al_2O_3 ($R^2 = 0.24$), MnO ($R^2 = 0.33$), MgO ($R^2 = 0.33$), CaO ($R^2 = 0.17$), and/or TiO_2 ($R^2 = 0.28$) (Fig 2.6), given that rhyolites are typically enriched in SiO_2 and Na_2O , but depleted Fe_2O_3 , Al_2O_3 , MnO , MgO , CaO , and TiO_2 (Fig 2.4).

These trends (Fig 2.6) also demonstrate that As is negatively correlated with elements (Fe, Al, Mn, Mg, Ca, and Ti) that are incorporated into minerals during the early stages of fractional crystallization, while As is positively correlated with elements (Si and Na) that incorporate into later-stage minerals. These findings suggest that As enrichment may be controlled, in part, by the fractional crystallization of partial melts, with rocks that crystallized from relatively evolved partial melts like these SPV rhyolites, containing greater As. The AFM diagram (Fig. 2.5), which gives As content in relation to tholeiitic differentiation trends, further

supports this hypothesis. The diagram demonstrates that As enrichment in Black Mountain SPV increases as Mg and Fe content of magmas decrease. Thus, felsic rocks that crystallized from more evolved melts typically contain greater As.

Our interpretation is supported by the findings of Johnson et al. 2013 who analyzed rhyolites in the Taupo Volcanic Zone (TVZ) of New Zealand. This work suggests that, throughout the processes of fractional crystallization and extensive degassing, metals (e.g. As) do not partition into an exsolved vapor and instead partition into crystallizing minerals or remain dissolved in the melt until they are eventually exhumed in rhyolites (Johnson et al. 2013).

It is important to note that we observed a strong negative correlation between As and K₂O ($R^2 = 0.80$, Fig 2.6a) in rhyolites, though greater K₂O is typically associated with more evolved melts. The replacement of K-feldspar, albite, and/or sericite by Mg-Fe chlorite (Eq 1, Fig 2.2g) and/or pyrite (Fig 2.2b) during syn-volcanic hydrothermal alteration (Large et al. 2001) may explain this trend, since such reactions suggest that K₂O is re-mobilized by hydrothermal fluids and, thus, may not be associated with the fractional crystallization of source melts.

Further, O'Shea et al. (2015) observed As enrichment in greenschist facies rocks containing chlorite and pyrite. In their study, arsenic was detected in pyrites when the index mineral chlorite was present, suggesting that pyrites, and potentially silicates like chlorites, are likely hosts of As in rocks subjected to greenschist facies metamorphism, like the SPV rhyolites.

Fig 2.6: Bivariate plots comparing As content (ppm) to concentration of major ions (wt. %), a) K_2O , b) Na_2O , c) Fe_2O_3 tot, d) Al_2O_3 , e) MnO, f) MgO, g) CaO, f) TiO_2 , and g) SiO_2

2.6.2.2 Arsenic mobility in subduction zone fluids

Our findings of As enrichment in an ancient volcanic arc suggest that As in Black Mountain SPV may ultimately be sourced to deep earth subduction zone processes. Though neighboring intrusive igneous plutons of the western Peninsular Ranges Batholith (PRB) likely evolved from the same magma system as the SPV during the Late Cretaceous (Herzig and Kimbrough 2014), we are not aware of comparable degrees and/or extents of As enrichment elsewhere in the SPV or western PRB cropping out in Southern CA or Northern Baja CA, Mexico. Therefore, within the ancient subduction zone, As appears to be most enriched in rocks associated with ancient volcanic arc fronts (Noll et al. 1996).

Hattori and Guillot (2003) suggest that fluid-mobile elements, like As, Sb, and Pb, are enriched in volcanic arc fronts, because they are highly soluble in relatively low temperature aqueous fluids, allowing them to be easily volatilized from subduction zone serpentinites during dehydration and partial melting (Hattori and Guillot 2003). Other trace metals, like Cu, are less soluble and, thus, mobilized at higher temperatures (Hack et al. 2006). Therefore, these less soluble metals may not be as enriched as highly soluble metals in volcanic fronts overlying ancient subduction zones.

We observed higher concentrations of highly soluble metals, As and Pb, in rhyolites, but Cu was equally enriched in both rhyolites and dacites (Table 3). Zinc was much more enriched in dacites than rhyolites (Table 3), potentially resulting from its compatibility in ferromagnesian minerals (Stanton 1994, Johnson et al. 2013), like hornblende and biotite.

The high solubility of As and Pb initially caused these metals to be among the first released from subduction zone serpentinites during dehydration, leading to their initial enrichment in partial melts underlying volcanic arc fronts. Because of their incompatibility in

these melts (Hattori and Guillot 2005), As and Pb remained dissolved as melts evolved from mafic to felsic and, thus, were eventually exhumed in rhyolitic lavas. Since Cu is not as soluble as As and Pb (Hattori and Guillot 2003, Hack et al. 2006), Cu may have been released from serpentinites during later stages of subduction. The equivalent Cu content in dacites and rhyolites suggests that Cu enrichment was associated with a syn-volcanic hydrothermal intrusion that occurred during later-stage subduction (Nadeau et al. 2013).

2.6.3 Model for arsenic occurrence in Black Mountain SPV

Based on our results and incorporating the findings of others, we propose the following model to explain As enrichment in Black Mountain SPV (Fig 2.7):

1. During the Cretaceous, the oceanic Farallon Plate began to subduct beneath the continental North American Plate (Herzig and Kimbrough 2014), transporting oceanic sediment to depth.
2. At temperatures of around 650°C, serpentinite dehydration releases water and soluble elements, which migrate upwards and hydrate and enrich the overlying mantle wedge in As and Pb, in that order. Eventually, As and Pb are incorporated into the partial melt (Hattori and Guillot 2003).
3. Due to their high solubility and relative incompatibility (Hattori and Guillot 2003), As and Pb remain dissolved in the partial melt as it evolves from mafic to felsic and, thus, are eventually exhumed in rhyolitic magmas.
4. Because it is less soluble (Hack et al. 2006), Cu is released during later stages of serpentinite dehydration and, thus, likely has a different source melt than As and Pb.

Figure 2.7: Model explaining the provenance of As in Black Mountain SPV

2.6.4 Potential for groundwater arsenic enrichment in Black Mountain SPV

There are no domestic wells within a one mile radius of the study area, though groundwater is eligible for municipal use (CA EPA). Historic records report that, in wetter times, an As-rich spring existed (City of San Diego Cultural Report). Further, previous work in the Chaco-Pampean Plain of Argentina suggests that the dissolution of rhyolitic glass is the principle source for As in shallow groundwaters there (Raychowdhury et al. 2014; Bunduschuh et al. 2004). Raychowdhury et al. (2014) proposed that volcanic host rocks that formed via ancient volcanic arc processes may produce groundwater elevated in As (> 5 mg/L). Therefore, any groundwater flowing through the Black Mountain SPV arsenic-rhyolite is likely to be extremely elevated in dissolved arsenic and, thus, may pose a significant health threat if consumed.

2.7 Summary

- Black Mountain SPV evolved from the same magma system as Northern Santa Ana Mountain SPV (Herzig and Kimbrough 2014) during the Cretaceous.
- Arsenic enrichment in Black Mountain SPV is ultimately sourced to deep earth subduction zone processes as proposed globally by Mukherjee et al. (2014).
- Our proposed model for As enrichment in SPV (Fig 2.7) suggests that As is among the first elements released during serpentinite dehydration (along with Pb), while less soluble elements (e.g. Cu) are released during later stages of subduction.
- Once As and Pb are released from serpentinites and incorporated into partial melts (Hattori and Guillot 2003), we hypothesize that such elements behave like typical incompatible elements and remain dissolved in melts until they are eventually exhumed in rhyolitic lavas.

2.8 Conclusion

Our findings of As in an ancient volcanic arc system support the hypothesis that groundwater As may ultimately be sourced to deep earth processes (Mukherjee et al. 2014). Therefore, As tends to be enriched in volcanic arc rocks and, thus, other modern or ancient volcanic arc systems (e.g. Cascade Volcanic Arc, Aleutian Arc, Andean Volcanic Belt) may be prone to groundwater As enrichment (Mukherjee et al. 2014). Our work suggests that, within these ancient volcanic arc systems, As enrichment is associated with volcanic rocks that crystallized from relatively evolved partial melts underlying the volcanic front (e.g. rhyolite). Given that As may dissolve out of volcanic host rocks in groundwater aquifers (Bundschuh et al. 2004, Raychowdhury et al. 2014), this enhanced understanding of As distribution among ancient volcanic arc rocks may aid in identifying alternative drinking water sources in regions with known groundwater As enrichment.

2.9 Work cited

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CHAPTER 3: Arsenic Mineral Associations in the Black Mountain SPV Ore Deposit

3.1 Introduction

Minerals that host arsenic provide insight into arsenic (As) geochemical cycling, since As is present in over 560 chemically diverse minerals that form under a wide range of geochemical conditions (Majzlan et al. 2014). While As is not recognized as a significant component of major rock forming minerals (e.g. silicates and carbonates), it can easily take the place of sulfur in the abundant primary mineral, pyrite (FeS_2) (Smedley and Kinniburgh 2001, Drahota and Filippi 2009, Majzlan et al. 2014). When such primary As minerals are exposed to air and/or aerated water, alteration reactions form secondary minerals enriched in As, like scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Thus, As may be mobilized from both primary and secondary minerals during modern water-rock interactions, since it is soluble over a wide pH range and in both oxidizing and reducing conditions (Smedley and Kinniburgh 2001).

By examining primary and secondary As host minerals and their associated As concentrations, we aim to enhance our understanding of As geochemical cycling in Black Mountain SPV, especially during modern water-rock interactions. Such knowledge will inform future research on As transport from Black Mountain SPV, and provide insight into the potential for As to mobilize from host rocks into surrounding communities.

3.2 Study area

Black Mountain Open Space Park is located the Rancho Peñasquitos community of northern San Diego in Southern California (CA), USA (Fig 3.1a). The park contains >15 km of hiking and biking trails climbing to ~500 m and is composed of chaparral, chaparral-coastal sage scrub, and coastal sage scrub vegetation. Surface water within the park drains into channels that eventually empty into the San Dieguito River. However, rainfall is limited (<30 cm/yr) in this semi-arid region of the Southwestern USA.

Field mapping for this study produced a preliminary, 1: 30,000 geologic map (Fig 2.1b) for a portion of the Black Mountain SPV, where As may be enriched along a ~N15°W – N20°W striking fracture zone, since extrapolation of this fracture zone along strike beyond the study area led to the discovery of an artisanal strip mine approximately two miles north of the park (Fig 3.1b). Though portions of Black Mountain Open Space Park were mined for As in the 1920s (Stewart 1963), no previous work has attempted to characterize As host minerals in Black Mountain SPV. Because there are no reports of As enrichment elsewhere in the SPV, we will hereafter call As-enriched SPV cropping out at Black Mountain Open Space Park the Black Mountain SPV ore deposit.

Fig 3.1: A) Location of study area within State of California, USA. B) Location of Black Mountain Open Space Park, San Diego, CA. The park boundary is highlighted in green, and red triangles give locations of abandoned As mines.

3.3 Methods

3.3.1 Sample collection

Extent of As enrichment in Black Mountain SPV was initially evaluated by field-portable X-ray fluorescence (FP-XRF, Haffert & Craw 2009) (Fig 3.2), allowing us to collect in-situ and waste-rock samples ($n = 67$) with a wide range of As concentrations. The majority of samples ($n = 59$) were collected from the northern portion of Black Mountain Open Space Park surrounding abandoned As mines, and the remaining samples ($n = 8$) were collected from the artisanal strip mine to the north of the park (Fig 3.1b).

3.3.2 Bulk rock preparation

Bulk rock samples ($n = 67$) were pulverized into a fine powder using a Bico Pulverizer fitted with ceramic plates at the University of San Diego (USD). All equipment was routinely cleaned with acetone and compressed air to avoid cross contamination between samples.

3.3.3 Sub-sample preparation

Because many samples were highly heterogeneous, sometimes showing weathering rinds, metamorphic alteration assemblages, veins, and volcaniclastics on very small (mm) spatial scales, we used a diamond-tipped Dremel tool to target subareas of whole rock samples. The term “sub-sample” is hereafter used to define Dremel-targeted samples.

3.3.4 Arsenic concentration

Powdered rocks and sub-samples ($n = 168$) were analyzed for trace metals by an Innov-X-5000 X-ray Fluorescence (XRF) at USD. The quality assurance/quality control (QA/QC) procedures for samples with $<1,000$ ppm As are presented in Chapter 2 of this thesis under section 2.3.5. Because we detected anomalous As concentrations ($>1,000$ ppm) in 22% of samples and sub-samples ($n = 37$) of Black Mountain SPV, we conducted additional QA/QC

procedures to evaluate the accuracy of such anomalous concentrations. Three representative ultra-enriched samples were selected for analysis by EPA 6000/7000 series methods, and resulting As concentrations were compared to As content reported by the XRF. Compared to the EPA 6000/7000 series methods, the Innov-X-5000 XRF either reported anomalous As content accurately (<5% difference) or under-reported As by up to 24% (Table 3.1). While there are several possible reasons for this discrepancy in accuracy (e.g., analytical differences, sample heterogeneity) the purpose of analyzing these samples externally was to confirm the order of magnitude concentration of As being detected at Black Mountain since the As concentrations here are so anomalously enriched.

3.3.5 Mineralogical analysis

Powdered bulk rocks and sub-samples (n = 168) were analyzed by PANalytical X'Pert PRO X-ray diffraction (XRD) at San Diego State University (SDSU). The XRD used a copper K α X-ray source and operated at 45 kV and 40 mA. Mineral identification and pattern manipulation were conducted using X'Pert Data Software Suite and the Joint Committee on Powder Diffraction Standards (JCPDS) reference database. Identified minerals were assigned a score from 0 – 100 by HighScore PANalytical Software, where 100 is a perfect match with X-ray spectra from the JCPDS reference database.

Table 3.1: QA/QC for samples with anomalous As concentrations

Sample ID	As (ppm) USD ¹	As (ppm) EPA ²	% Difference ³
R022i	131,687	158,000	-17%
Mr002	167,070	165,000	1%
Mk004	297,156	390,000	-24%

¹: Arsenic concentration measured by Innov-X-5000 XRF at the University of San Diego (USD)

²: Arsenic content measured by EPA 6000/7000 series methods at EnviroMatrix Analytical, Inc.

³: % difference = $100 * ((As\ EPA - As\ USD) / As\ USD)$

Fig 3.2: Distribution of As in rocks and soil in a portion of Black Mountain Open Space Park. Preliminary As concentrations measured by FP-XRF (after Haffert & Craw 2009)

3.4 Results

3.4.1 Arsenic enrichment

The total As concentration of powdered bulk rock and sub-samples ($n = 168$) ranged from non-detectable (<2 ppm) to nearly 300,000 ppm (mean = $7,476 \pm 2,694^2$ ppm As). We found that As was most enriched in samples collected from abandoned As mines ($n = 27$, mean = $36,745 \pm 13,801$ ppm As), and samples and sub-samples of waste rocks were also highly enriched in As ($n = 12$, mean = $3,051 \pm 2,259$ ppm As). Subsamples of weathering rinds and veins typically contained greater As concentrations ($n = 44$, mean = $9,475 \pm 4,941$ ppm As) than subsamples of fresh rock ($n = 44$, mean = 538 ± 245 ppm As) (Table 3.2).

² Standard error = $\frac{\text{Standard deviation } (\sigma)}{\sqrt{\text{Sample size } (n)}}$

Table 3.2: Trace metal concentrations in Black Mountain SPV. Average +/- standard error. Geochemical techniques presented in Chapter 2 allowed lithologic confirmation of rocks described here as ‘bulk rhyolites’ and ‘bulk dacites’, which permitted them to be confidently presented separately from other sub-samples analyzed as part of this chapter.

	As (ppm)	Cu (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
All samples & sub-samples (n = 168)	7,476 +/- 2,694	105 +/- 17	79 +/- 12	58 +/- 4	139 +/- 16
Bulk rhyolites (n = 10)	586 +/- 10	30 +/- 6	28 +/- 4	4 +/- 3	46 +/- 8
Bulk dacites (n = 10)	14 +/- 9	30 +/- 3	12 +/- 2	ND	114 +/- 13
Mine samples & sub-samples (n = 27)	36,745 +/- 13,801	335 +/- 76	95 +/- 22	66 +/- 12	121 +/- 29
Waste rock samples & sub-samples (n = 12)	3,051 +/- 2,259	56 +/- 19	125 +/- 44	48 +/- 15	191 +/- 57
Fresh sub-samples (n = 44)	538 +/- 245	57 +/- 9	38 +/- 5	75 +/- 7	128 +/- 22
Weathered sub-samples (n = 44)	9,475 +/- 4,941	112 +/- 22	110 +/- 25	68 +/- 8	140 +/- 15
Average in upper-crust*	4.8	28	17	0.4	47

*: Rudnick and Gao (2003)

3.4.2 Arsenic mineral associations

3.4.2.1 Field observations

We observed evidence for several phases of primary and secondary As host minerals in Black Mountain SPV. First, field observation of areas where FP - XRF detected anomalous As ($>1,000$ ppm) revealed that As-rich outcrops characteristically exhibited bright colors of purple-red, maroon, orange, yellow, and grey veins varying in thickness from cm to massive, meter-sized areas of alteration. These outcrops had typically been disturbed into meter-scale pits and cave-like mines.

3.4.2.2 Mineral Identification by Powder X-ray diffraction

Targeted Dremel sampling (Fig 3.3d) and XRF analysis of each distinctively colored vein or crystal mass revealed As concentrations ranging from 923 ppm to 297,156 ppm. We then identified potential As host minerals using XRD. We found evidence of arsenopyrite (FeAsS , Fig 3.4a) in a powder containing 297,156 ppm As (Fig 3.3a). We identified natrojarosite (Fig 3.4b) in a powder containing 49,660 ppm As (Fig 3.3b), and pyrite (FeS_2) and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) (Fig 3.4c) were detected in a powder containing 110,100 ppm As (Fig 3.3c). In a powder with 167,070 ppm As, we identified natropharmacosiderite $[(\text{Na,K})\text{Fe}_4^{3+}(\text{AsO}_4)_3(\text{OH})_4 \cdot 6-7\text{H}_2\text{O}]$, arsenosiderite ($\text{Ca}_2\text{Fe}^{3+}\text{O}_2(\text{AsO}_4)_3 \cdot 3\text{H}_2\text{O}$), and yukonite ($\text{Ca}_7\text{Fe}^{3+}(\text{AsO}_4)_{10}(\text{OH})_{20} \cdot 15\text{H}_2\text{O}$) (Fig 3.4d). We detected schauertite ($\text{Ca}_3\text{Ge}(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$) in a powder containing 8,507 ppm As. Finally, we identified gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Fig 3.4f) in a powder containing 923 ppm As (Fig 3.3f). The XRD detected goethite in 17 powders. Analysis by XRF indicates that such powders contain $4,402 \pm 2,516$ ppm As (Table 3.3).

Fig 3.3: Photographs showing: a) Field observations of an arsenopyrite vein, b) Field observations of natrojarosite, c) Sample of scorodite and pyrite in laboratory, d) Method for Dremel-targeted sampling, e) Field observations of schaurteite, and f) Field observations of gypsum.

Fig 3.4: XRD spectra for samples: a) Mk004, b) Mk001, c) R022i, d) Mr002, e) Mk005, and f) Mk003. Values to right of identified mineral names represents a score assigned by X'Pert Data Software Suite. The score ranges from 0 – 100, with 100 being a perfect match with X-ray spectra from JCPDS Reference Database.

Table 3.3: Trace metal content of powered bulk rock samples and subsamples containing goethite

Sample ID	As (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Minerals detected by XRD	Score*
R002wp_w	663	367	<LOD	156	Quartz	61
					Goethite	43
R003wp	267	123	17	62	Quartz	66
					Albite low	47
					Magnetite	36
					Goethite	22
R003wp_w	958	484	565	304	Quartz	70
					Goethite	30
R004i_w	598	510	644	100	Quartz	52
					Goethite	45
R005wp_w	1523	320	<LOD	163	Quartz	64
					Goethite	45
R008f	2787	66	50	197	Quartz	48
					Goethite	36
					Rutile	29
					Hematite	20
R008f_w	6658	<LOD	<LOD	377	Quartz	62
					Hematite	40
					Goethite	15
R010f	806	42	508	37	Hematite	67
					Quartz	43
					Goethite	34
R010f_w	659	<LOD	629	26	Hematite	76
					Quartz	38
					Goethite	21
R015f	<LOD	62	1007	276	Goethite	77
R015f_w	85	35	<LOD	135	Goethite	69
R017f_w2	575	84	<LOD	146	Quartz	69
					Hematite	30
					Goethite	25
R017f_w3	327	120	348	126	Goethite	50
					Baumite	30
R018f_w	113	84	40	120	Goethite	69
					Hematite	53
					Quartz	41
R018f_w2	185	98	203	163	Quartz	71
					Goethite	49
					Hematite	44
R024wp_w	5274	199	304	124	Hematite	61
					Quartz	50
					Albite low	28
					Goethite	22
R043wp_w	43147	163	437	168	Quartz	65
					Kusachiite	21
					Goethite	20
R044i_w	10205	323	<LOD	336	Goethite	38
					Quartz	27
					Albite, Ca-rich, ordered	16
Average	4,402 ± 2,516	193 ± 38	396 ± 72	168 ± 24		
Min	85	35	17	26		
Max	43,147	510	1,007	377		

*Values represent a score from 0 – 100, with 100 being a perfect match with X-ray spectra from JCPDS Reference Database

3.5 Discussion

3.5.1 Arsenic enrichment in Black Mountain SPV Ore Deposit

Unlike other trace metals detected by XRF (e.g. Pb, Cu, Sb, Zn), we found that As was consistently anomalously enriched (>1000 ppm) in the Black Mountain SPV ore deposit (Table 3.2). We detected As concentrations up to almost 300,000 ppm in samples and subsamples ($n = 168$) of Black Mountain SPV. Approximately 93% of samples ($n = 168$) exceed the average As concentration for the upper crust (4.8 ppm As, Rudnick and Gao 2003), and 94% exceed the average As concentration for igneous rocks (1.5 ppm As, Smedley and Kinniburgh 2001). Within the Black Mountain SPV ore deposit, As was often present in weathering rinds, veins, and/or along fractures.

3.5.2 Arsenic in fresh versus weathered rock

Subsampling of rocks with coherent weathering rinds and/or veins ($n = 44$) allowed us to compare As content in the weathered components to the As content of the fresh component of the same rock. We found that for 95.5% of such samples, the weathered portion contained more As (Fig 3.5). Further, subsamples of weathering rinds and veins typically contained greater As concentrations on average ($n = 44$, mean = $9,475 \pm 4,941$ ppm As) than subsamples of fresh rock ($n = 44$, mean = 538 ± 245 ppm As) (Table 3.2). This finding indicates that As in Black Mountain SPV is re-dispersed into secondary host minerals during modern water-rock interactions.

3.5.3 Arsenic host minerals

We observed evidence for several phases of primary and secondary As host minerals, including primary minerals arsenopyrite (FeAsS) and pyrite (FeS_2), which can incorporate up to 46% and 10% As (Kolker and Nordstrom 2001), respectively. Primary minerals in Black

Mountain SPV were likely altered to form several phases of secondary host minerals. In in-situ Black Mountain SPV disturbed by mining, we observed evidence for As in known secondary host minerals, like scorodite ($\text{FeAsO}_4 \cdot \text{H}_2\text{O}$), natropharmacosiderite $[(\text{Na},\text{K})\text{Fe}_4^{3+}(\text{AsO}_4)_3(\text{OH})_4 \cdot 6\text{-}7\text{H}_2\text{O}]$, arseniosiderite $(\text{Ca}_2\text{Fe}^{3+}\text{O}_2(\text{AsO}_4)_3 \cdot 3\text{H}_2\text{O})$, and yukonite $(\text{Ca}_7\text{Fe}^{3+}(\text{AsO}_4)_{10}(\text{OH})_{20} \cdot 15\text{H}_2\text{O})$.

3.5.4 Arsenopyrite weathering

Though scorodite is one common weathering product of arsenopyrite (Eq. 3.1, Foster et al. 1998, Savage et al. 2000, Asta et al. 2009), arsenopyrite may also weather to hydrous ferric oxides (HFO) (Eq 3.2, Majzlan et al. 2014). Subsequently, HFOs age, remobilize, and crystallize to eventually form minerals of the pharmacosiderite supergroup (Eq 3.3, Haffert et al. 2010), like natropharmacosiderite and arseniosiderite. Yukonite is relatively rare, but is often found in association with minerals of the pharmacosiderite supergroup (Majzlan et al. 2014). Minerals of this group eventually weather to become goethite (Eq 3.4, Eq 3.5, Majzlan et al. 2014). Thus, As-rich goethite is a likely end-product of the Black Mountain SPVAs mineral weathering system.

In Black Mountain SPV, we found that As content was highest in a powder containing arsenopyrite (297,156 ppm As), while a powder containing natropharmacosiderite, arsenosiderite, and yukonite contained 167,070 ppm As. Powders containing goethite and no other known As host minerals (other than hematite) contained As concentrations ranging from 85 ppm As to 43,147 ppm As ($n = 17$, mean = $4,402 \pm 2,516$ ppm As). Thus, we found evidence for several stages of alteration and As remobilization, and that As content is lower in later-stage minerals (Fig 3.6).

3.5.5 Sulfate replacement by arsenate

We detected 49,660 ppm As in a powder containing natrojarosite. (Natro)jarosite $[(Na)Fe_3(SO_4)_2(OH)_6]$ is an important constituent of mine wastes derived from arsenian pyrite. Previous studies (e.g. Savage et al. 2000, Asta et al. 2009) have demonstrated that arsenate (AsO_4) may replace sulfate (SO_4) within the crystalline matrix of jarosite. Other studies (e.g. Foster et al. 1998, Myneni et al. 1997) demonstrate that AsO_4 can also take the place of SO_4 in other common secondary minerals, such as gypsum ($CaSO_4 \cdot 2H_2O$). Our findings of 923 ppm As in a powder containing gypsum support this hypothesis. We also detected 8,507 ppm As in a powder containing the rare mineral schauertite ($Ca_3Ge(SO_4)_2(OH)_6 \cdot 3H_2O$), further supporting our hypothesis of SO_4 replacement by AsO_4 .

Fig 3.5: Arsenic in fresh versus weathered SPV subsamples.

Fig 3.6: Schematic showing arsenopyrite weathering and associated As content of primary and secondary mineral phases.

3.6 Summary and conclusion

We discovered As enrichment in Black Mountain SPV ($n = 168$) ranging from non-detect (<2 ppm As) to nearly 300,000 ppm As (mean = $7,476 \pm 2,694$ ppm As). This wide range in As content indicates that As is present in several primary and secondary host mineral phases, including those we've identified as arsenopyrite, scorodite, jarosite, iron oxides, and gypsum, among other host minerals presented in this paper. Our work also demonstrates that As content is likely highest in primary host minerals and decreases with each phase of primary mineral weathering (Fig 3.7). However, As content, even in late-stage secondary host minerals, is anomalous ($>1,000$ ppm As). We detected greater As in weathering rinds and veins (mean = $9,475 \pm 4,941$ ppm) than the fresh components (mean = 538 ± 245) of the same rock ($n = 44$, Fig 3.6), further indicating that As is mobilized during modern water-rock interactions. Our findings suggest the potential for As to be mobilized off-site during storm events, or via groundwater flow (assuming the ore deposit extends below the water table), and indicates a need for future research investigating As transport from host rocks.

3.7 Work cited

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CHAPTER 4: Summary and Conclusion

4.1 Summary

1. *What is the geology of rocks cropping out at Black Mountain Open Space Park, and over what spatial scale does rock type vary?*

- The Santiago Peak Volcanics (SPV) outcropping at Black Mountain Open Space Park (i.e. Black Mountain SPV) are remnants of a subaerial volcanic arc that underwent syn-volcanic greenschist facies alteration
- Given the geochemical similarities between Black Mountain SPV and Northern Santa Ana Mountain SPV (Herzig and Kimbrough 2014), the two units likely evolved within the same volcanic arc system during the Cretaceous
- We observed welded tuffs, volcanoclastic (epiclastic) rocks, and accretionary lapilli in Black Mountain SPV, suggesting that several distinct stages of subaerial volcanic eruption occurred (Fig 2.2)
- Lavas ranged in composition from dacite to rhyolite (Fig 2.3)
- In areas of Black Mountain Open Space Park, rock type varies over the spatial scale of tens of meters (Fig 2.1)

2. *What is the distribution of As among SPV rock types, and how can we use this knowledge to propose a model for As cycling in the ancient volcanic arc system?*

- We found that As content varied between the two dominant SPV rock types, with rhyolites typically containing more As ($n = 10$, mean = 586 ± 10 ppm As) than dacites ($n = 10$, mean = 14 ± 9 ppm As) (Table 2.2)

- Our findings of As enrichment in rhyolites, indicate that such enrichment may be controlled by the fractional crystallization of mafic magmas, with rocks crystallizing from more evolved melts containing greater As
 - While highly soluble metals, As and Pb, were more enriched in rhyolites, Cu was equally enriched in both rhyolites and dacites (Table 2.2).
 - The high solubility of As and Pb likely caused these metals to be among the first released from subduction zone serpentinites during dehydration (Hattori and Guillot 2003), leading to their initial enrichment in partial melts underlying volcanic arc fronts
 - Because of their incompatibility in these melts, As and Pb remained dissolved as melts evolved from mafic to felsic and, thus, were eventually exhumed in rhyolitic lavas
 - Since Cu is not as soluble as As and Pb (Hack et al. 2006), Cu may have been released from serpentinites during later stages of subduction
 - Based on our results and incorporating the findings of others, we propose a model to explain As enrichment in Black Mountain SPV (Fig 2.7)
3. *What are the primary and secondary As host minerals in Black Mountain SPV, and how does knowledge of host minerals inform future research investigating As mobility?*
- Primary host minerals likely include: pyrite and arsenopyrite (Fig 3.3, Fig 3.4)
 - Secondary host minerals likely include: scorodite, jarosite, natropharmacosiderite, arseniosiderite, yukonite, iron oxides, and gypsum (Fig 3.3, Fig 3.4)

- We found that As content is highest in primary host minerals and decreases with each phase of primary mineral weathering (Fig 3.6). However, As content, even in late-stage secondary host minerals, is anomalous ($>1,000$ ppm As)
- We detected greater As in weathering rinds and veins (mean = $9,475 \pm 4,941$ ppm) than the fresh components (mean = 538 ± 245) of the same rock ($n = 44$, Fig 3.5), indicating that As is mobilized during modern water-rock interactions
- Our findings of As enrichment in primary and secondary host minerals suggest the potential for As to be mobilized off-site during storm events, or via groundwater interaction, and indicate a need for future research investigating As transport from host rocks

4.2 *Conclusion*

While the first two questions above contribute to growing knowledge of Black Mountain SPV and provenance of As in volcanic arc systems, the third question attempts to inform future research on As mobility at Black Mountain Open Space Park, given that As host minerals may exert an important and predictable control on As mobility in the natural environment (Smedley and Kinniburgh 2001). Based on the findings of this thesis, I recommend that future research conducted at Black Mountain Open Space Park address the following broad questions:

1. What is the spatial extent of geogenic As enrichment at Black Mountain Open Space Park, and what is the potential for human exposure to such As?
2. Is As being mobilized from host rocks, sediments, and soils during rain events, and does storm water transport As into communities surrounding Black Mountain Open Space Park?
3. How does geogenic As enrichment at Black Mountain Open Space Park affect plant and wildlife?

4.3 Work cited

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- Smedley, P.L., D.G. Kinniburgh, 2001. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* 17: 517-668.

APPENDIX A: Sample locations

Sample ID	Latitude	Longitude
R001i	32.99292	-117.11329
R002wp	32.99331	-117.11061
R003wp	32.99331	-117.11061
R004i	32.99329	-117.11086
R005wp	32.99331	-117.11061
R006i	32.99327	-117.11083
R007wp	32.99325	-117.11084
R008f	33.03348	-117.12427
R009f	32.98861	-117.11211
R010f	33.03352	-117.12445
R011i	33.03349	-117.12428
R012f	32.992672	-117.11568
R013f	32.992672	-117.11568
R014f	33.033043	-117.12011
R015f	33.033043	-117.12011
R016f	33.03352	-117.12445
R017f	33.033043	-117.12011
R018f	33.033043	-117.12011
R019f	32.98861	-117.11211
R020i	32.98885	-117.11236
R021i	32.99295	-117.10976
R022i	32.98974	-117.11196
R023i	32.98974	-117.11196
R024wp	32.99024	-117.11132
R025i	32.993056	-117.113056
R026i	32.9925	-117.113056
R027wp	32.981389	-117.113056
R028f	32.973056	-117.120833
R029i	32.976389	-117.121111
R030f	32.976667	-117.120556
R031i	32.976111	-117.117222
R032wp	32.981389	-117.113056
R033f	32.99083333	-117.1119444
R034f	32.99111111	-117.1125
R035wp	32.99138889	-117.1130556
R036i	32.99055556	-117.1113889
R037i	32.98972222	-117.1119444
R038i	32.99000	-117.1111111

Sample ID	Latitude	Longitude
R039i	32.99	-117.1116667
R040i	32.98972222	-117.1119444
R041i	32.99	-117.1116667
R042i	32.99027778	-117.1113889
R043wp	32.99027778	-117.1113889
R044i	32.99138889	-117.1122222
R045f	32.99027778	-117.1113889
R046i	32.993611	-117.110833
R047f	32.9975	-117.115488
R048i	32.99111111	-117.1152778
R049i	32.99027778	-117.1116667
R050f	32.990421	-117.111697
R051i	32.99055556	-117.1108333
R052f	32.99055556	-117.1111111
R053i	32.99055556	-117.1111111
R054i	32.99055556	-117.1102778
R055i	32.99111111	-117.110556
R056f	32.990921	-117.11032
R057i	32.99111111	-117.11
R058i	32.99166667	-117.11
R059i	32.99166667	-117.11
R060i	32.99222222	-117.1094444
R061i	32.99277778	-117.1097222
R062i	32.99305556	-117.1097222
R063i	32.9888	-117.11278
R064i	32.991667	-117.11
R065i	32.989953	-117.11204
R066i	32.991434	-117.110306
R067i	32.989722	-117.113056
Mk001	32.98974	-117.11196
Mk002	32.98974	-117.11196
Mk003	32.98974	-117.11196
Mk004	32.98974	-117.11196
Mk005	32.98974	-117.11196
Mk006	32.98974	-117.11196
Mr001	32.98868	-117.11211
Mr002	32.98868	-117.11211
Mr003	32.98868	-117.11211
Mr004	32.98868	-117.11211
Mr005	32.98868	-117.11211
Mr006	32.98868	-117.11211

APPENDIX B: Trace metals in rhyolites and dacites (n = 20)

		As (ppm)	Cu (ppm)	Pb (ppm)	S (ppm)	Sb (ppm)	Zn (ppm)
Mr001	Rhyolite	347	17	12	483	0	14
Mr002	Rhyolite	1,024	53	33	0	0	65
R004i	Rhyolite	109	67	57	0	23	23.7
R020i	Rhyolite	3155	11	33.4	0	0	72
R021i	Rhyolite	12.6	12	19	0	0	43.7
R024wp	Rhyolite	734	42	29.5	0	0	32.4
R037i	Rhyolite	305	27	26	497	0	14
R044i	Rhyolite	158	18	15.1	0	13	57
R046i	Rhyolite	7.2	38	27	0	0	84
R060i	Rhyolite	5.5	18	28.2	0	0	52
R038i	Dacite	24.8	19	27	0	0	31
R039i	Dacite	10.8	23	11.8	0	0	89
R049i	Dacite	5.2	17	15.2	0	0	125
R051i	Dacite	11	37	14	0	0	161
R053i	Dacite	16.6	47	0	0	0	178
R054i	Dacite	9	22	6	0	0	126
R055i	Dacite	6.3	33	13.1	0	0	113
R058i	Dacite	31.6	41	10.3	0	0	121
R065i	Dacite	15	38	8	0	0	114
R066i	Dacite	9	20	14.2	0	0	85

APPENDIX C: Trace metals in all samples and subsamples (n = 168)

Sample ID	As (ppm)	Cu (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
R001i_Bulk	4	7	16	0	34
R002wp_Bulk*	50	27	17	0	14
R002wp_f*	113	279	32	80	56
R002wp_w*	663	367	0	143	156
R003wp_Bulk*	267	123	17	18	62
R003wp_f*	121	130	45	81	96
R003wp_w*	958	484	565	117	304
R004i_Bulk	109	67	57	23	23.7
R004i_f	50	71	44	98	41
R004i_w	598	510	644	118	100
R005wp_f	64	232	72	65	52
R005wp_w	2,007	461	523	85	170
R006i_Bulk	17	20	12	0	29
R006i_f	59	97	91	62	72
R006i_w	185	38	0	26	46
R007wp_Bulk*	5	12	23	0	49
R007wp_f*	11	50	76	35	97
R007wp_w*	39	62	48	0	166
R008f_Bulk	2,787	66	50	20	197
R008f_w	6,658	0	0	79	377
R009f_Bulk	244	22	10	0	34
R009f_f	494	200	49	46	86
R009f_w	2,167	46	26	22	31
R010f_Bulk	806	42	508	19	37
R010f_w	659	0	629	33	26
R011i_Bulk	35	0	0	0	10
R012f_Bulk	14	45	66	0	35
R014f_f	8	102	37	68	39
R014f_w	359	47	213	60	83
R015f_Bulk	0	62	1,007	42	276
R015f_f	28	18	44	41	110
R015f_w	85	35	0	0	135
R016f_Bulk	24	28	8	0	41
R016f_f	114	53	15	51	52
R016f_w	550	26	364	26	43
R016f_w2	29	34	6	0	34
R016f_w3	396	0	0	88	0

Sample ID	As (ppm)	Cu (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
R017f_Bulk	53	19	8	10	12
R017f_f	88	0	40	166	64
R017f_w	296	50	18	98	68
R017f_w2	575	84	0	111	146
R017f_w3	327	120	348	27	126
R018f_f	172	33	38	41	149
R018f_w	113	84	40	0	120
R018f_w2	185	98	203	107	163
R019wp_f*	274	0	37	177	0
R019wp_w*	1,321	0	31	195	31
R019wp_w2*	5,460	0	42	212	0
R020i_Bulk	3155	11	33.4	0	72
R020i_f	6,211	31	42	93	91
R020i_w	142,291	0	119	98	81
R021i_Bulk	12.6	12	19	0	43.7
R021i_f	0	32	48	0	69
R021i_w	48	163	57	0	157
R022i_Bulk*	175,294	1,075	227	190	0
R022i_2*	131,687	937	152	124	0
R022i_pyrite*	7,518	678	260	30	36
R023i_Bulk*	28,795	891	0	110	0
R023i_2*	32,822	1,154	183	85	0
R023i_pyrite*	19,777	1,153	261	22	0
R024wp_Bulk*	734	42	29.5	0	32.4
R024wp_f*	562	50	29	151	39
R024wp_w*	5,274	199	304	45	124
R026i_Bulk	3	9	10	0	46
R027wp_f*	116	0	44	105	132
R027wp_w*	1,038	24	291	24	474
R027wp_w2*	860	0	0	65	516
R028f_Bulk	9	25	9	0	82
R029i_Bulk	18	26	18	0	78
R029i_f	36	27	0	43	133
R029i_w	240	37	122	0	92
R030f_Bulk	13	13	23	0	100
R031i_Bulk	183	25	8	10	45
R032wp_Bulk*	21	15	14	0	28
R032wp_w*	365	37	241	24	525
R033f_f	42	46	125	87	403

Sample ID	As (ppm)	Cu (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
R033f_w	85	37	16	0	214
R034f_f	116	38	125	67	934
R034f_w	2,674	95	0	70	201
R035wp_f*	76	96	112	106	170
R035wp_w*	126	42	18	0	81
R036i_f	41	54	16	44	155
R036i_w	122	29	18	0	130
R037i_Bulk	305	27	26	0	14
R037i_2	4,259	148	502	47	85
R038i_Bulk	24.8	19	27	0	31
R038i_f	35	101	34	93	117
R038i_w	116	10	30	0	84
R039i_Bulk	10.8	23	11.8	0	89
R039i_f	13	28	0	0	86
R039i_w	598	120	109	96	180
R040i_Bulk	92	27	0	0	56
R040i_f	1,214	53	0	44	203
R040i_w	161	45	37	0	97
R041i_f	20	17	0	0	97
R041i_w	193	34	48	84	107
R042i_f	21	15	7	0	97
R042i_w	315	63	55	36	216
R043wp_f*	244	10	9	0	11
R043wp_w*	27,473	163	437	57	168
R044i_Bulk	158	18	15.1	13	57
R044i_f*	224	64	37	186	105
R044i_w*	10,205	323	0	129	336
R045f_f	31	61	19	50	184
R045f_w	452	45	0	47	275
R046i_Bulk	7.2	38	27	0	84
R046i_f	0	9	12	0	30
R046i_w	15	0	20	184	63
R047f_f	23	36	0	104	173
R047f_w	97	23	0	36	206
R048i_f	36	0	32	143	45
R048i_w	161	44	30	81	150
R049i_Bulk	5.2	17	15.2	0	125
R049i_porphyry	0	0	35	120	29
R049i_matrix	11	0	22	55	210

Sample ID	As (ppm)	Cu (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
R050f_porphry	71	87	79	52	84
R050f_matrix	41	0	0	57	243
R051i_Bulk	11	37	14	0	161
R051i_f	63	28	65	56	166
R051i_w	0	32	25	88	78
R052f_f	13	122	66	0	124
R053i_Bulk	16.6	47	0	0	178
R053i_f	19	133	30	45	205
R054i_Bulk	9	22	6	0	126
R055i_Bulk	6.3	33	13.1	0	113
R055i_f	13	29	52	68	136
R055i_w	37	68	17	73	94
R056f_f	335	27	59	68	60
R056f_w	31,235	440	103	118	149
R057i_f	0	0	23	154	89
R057i_w	0	0	29	114	30
R058i_Bulk	31.6	41	10.3	0	121
R058i_f	0	0	27	163	61
R058i_w	0	0	22	173	173
R059i_f	16	69	185	59	21
R060i_Bulk	5.5	18	28.2	0	52
R060i_f	11	13	17	0	27
R061i_f	0	0	36	94	0
R061i_w	40	139	29	101	404
R062i_f	20	66	110	37	175
R063i_f	87	30	0	0	191
R064i_f	25	71	57	36	476
R065i_Bulk	15	38	8	0	114
R065i_f	46	43	0	45	1,795
R066i_Bulk	9	20	14.2	0	85
R066i_f	37	0	31	40	149
R067i_f	69	50	21	82	375
Mr001_Bulk	347	17	12	0	14
Mr001_f*	1,397	46	21	47	33
Mr001_w*	6,048	132	64	38	43
Mr001_w2*	7,812	169	66	16	27
Mr002_Bulk	1,024	53	33	0	65
Mr002_f*	8,944	61	36	58	289
Mr002_w*	25,915	132	0	73	678

Sample ID	As (ppm)	Cu (ppm)	Pb (ppm)	Sb (ppm)	Zn (ppm)
Mr002_w2*	167,070	0	173	70	0
Mr003_f*	101	51	0	29	146
Mr003_w*	297	36	13	0	65
Mr004_f*	370	68	12	72	215
Mr004_w*	2,814	99	159	52	161
Mr005*	1,479	67	0	23	309
Mr006_f*	1,799	146	15	81	238
Mr006_w*	4,191	287	0	57	111
Mk001*	49,660	67	351	0	0
Mk002*	375	81	291	0	97
Mk003*	923	78	0	0	151
Mk004*	297,156	0	0	211	0
Mk005*	8,507	489	0	0	56
Mk006*	930	762	231	78	169

*: sample collected from abandoned mine or waste rock pile

APPENDIX D: Arsenic correlation with lead (Pb), antimony (Sb), copper (Cu), and zinc (Zn)
n = 168

* R^2 value was calculated for points where both metals were detected

APPENDIX E: Trace metal content in fresh versus weathered subsamples of Black Mountain SPV (n = 44)

APPENDIX F: XRD results for all samples and subsamples (n = 168)

Sample ID	Minerals present (XRD results)	Score*
R001i	Quartz	77
	Albite low	32
R002wp	Quartz	63
	Albite	49
	Orthoclase	36
R002wp_f	Quartz	74
	Albite low	35
R002wp_w	Quartz	61
	Goethite	43
R003wp	Quartz	66
	Albite low	47
	Magnetite	36
	Goethite	22
R003wp_f	Quartz	76
	Albite low	36
R003wp_w	Quartz	70
	Goethite	30
	Kusachiite	24
R004i	Quartz	54
	Albite low	42
	Magnetite	26
R004i_f	Quartz	70
	Albite	34
	Biotite	13
R004i_w	Quartz	52
	Goethite	45
R005wp_f	Quartz	72
	Albite low	35
	Biotite	21
R005wp_w	Quartz	64
	Goethite	40
	Albite low	26
R006i	Quartz	52
	Albite, ordered	49
	Roscoelite	29
R006i_f	Quartz	71
	Albite, Ca-rich, ordered	35

Sample ID	Minerals present (XRD results)	Score*
R006i_w	Quartz	66
	Volkonskoite	36
	Metaschoepite	28
R007wp	Quartz	58
	Albite, Ca-rich, ordered	37
	Rectorite	26
R007wp_f	Quartz	76
	Albite low	36
	Biotite	22
R007wp_w	Quartz	70
	Kusachiite	16
	Eastonite	16
R008f	Quartz	48
	Illite	35
	Goethite	36
	Rutile	29
	Muscovite	37
	Hematite	20
R008f_w	Quartz	62
	Hematite	40
	Goethite	15
R009f	Quartz	59
	Albite, ordered	55
	Ankerite	23
	Muscovite (NH ₄ -rich)	27
	Vermiculite	16
R009f_f	Quartz	71
	Albite, Ca-rich, ordered	39
	Biotite	30
R009f_w	Quartz	66
	Albite, ordered	36
	Kaolinite	42
	Illite	14
	Paranatisite	14
R010f	Hematite	67
	Quartz	43
	Goethite	34
	Goldfieldite	22
	Pseudorutile	26

Sample ID	Minerals present (XRD results)	Score*
R010f_w	Hematite	76
	Quartz	38
	Goethite	21
R011i	Quartz	61
R012f	Quartz	70
	Albite, Ca-rich, ordered	34
	Mica	36
	Calcite	34
	Birnessite	22
	Muscovite	19
R014f_f	Quartz	78
R014f_w	Baumite	46
	Kaolinite	40
	Quartz low	36
R015f	Goethite	77
R015f_f	Quartz	75
	Polyolithionite, Fe-rich	39
	Brucite	30
	Albite, Ca-rich, ordered	14
	Gobbinsite	13
R015f_w	Goethite	69
	Spangolite	10
R015f_w_SDSUduplicate	Goethite	41
R016f	Quartz	65
	Muscovite	42
	Gobbinsite	20
	Zemannite	12
R016f_f	Quartz	73
	Muscovite	27
	Zinnwaldite	17
R016f_w	Hematite	73
	Quartz	60
R016f_w2	Quartz	71
	Muscovite	53
	Hematite	40
	Illite	41
R016f_w3	Hematite	63
	Quartz	47
	Giniite, Fe-rich	26

Sample ID	Minerals present (XRD results)	Score*
R017f	Quartz Baumite Maricite Andalusite	52 32 29 23
R017f_f	Quartz Sodalite Mica Birnessite Zinnwaldite Claudetite Kroehnkite	75 38 44 35 20 20 9
R017f_w	Quartz Sodalite Birnessite Braunite Kroehnkite	78 28 23 15 7
R017f_w2	Quartz Hematite Goethite Moissanite Maucherite subcell Baumite	69 30 25 21 25 32
R017f_w3	Goethite Baumite Periclase Muscovite (Ba-rich) Quartz	50 30 23 31 31
R018f_f	Quartz Mica Zinnwaldite Mgriite	80 20 22 14
R018f_w	Goethite Quartz Hematite Goldfieldite Enstatite ferroan	69 41 53 8 14
R018f_w2	Quartz Goethite Hematite	71 49 44

Sample ID	Minerals present (XRD results)	Score*
R019f_f	Quartz	73
	Albite, Ca-rich, ordered	34
	Phlogopite	15
R019f_w	Quartz	60
	Fraipontite	39
	Anorthite, ordered	28
R019f_w2	Quartz	64
	Heulandite	31
	Fraipontite	23
	Magnetite	19
	Phlogopite	15
R020i_f	Quartz	68
	Albite low	39
	Moissanite	30
	Microcline intermediate	13
R020i_w	Quartz	54
	Scorodite	47
	Bariumpharmacosiderite	46
	Albite low	28
R021i_f	Quartz	75
	Albite low	31
R021i_w	Quartz	71
	Albite	25
	Eastonite	21
	Heterogenite deuterated	21
R022i	Scorodite	59
	Pyrite	57
R022i_2	Scorodite	68
	Pyrite	58
R022i_pyrite	Pyrite	67
R023i	Pyrite	70
	Melanterite	19
R023i_2	Pyrite	71
	Montomorillonite	33
	Scorodite	40
	Rozenite	40
R023i_pyrite	Pyrite	72
R023i_R022i_pyrite	Pyrite	74

Sample ID	Minerals present (XRD results)	Score*
R024wp	Quartz	57
	Albite low	53
	Microcline intermediate	22
	Enstatite ferroan	26
R024wp_f	Quartz	69
	Albite low	45
R024wp_w	Hematite	61
	Quartz	50
	Albite low	28
	Goethite	22
R026i	Quartz	66
	Albite, Ca-rich, ordered	44
	Phlogopite, Fe-rich	21
	Muscovite	17
R027wp_f	Quartz	68
	Albite low	39
	Dolomite, Ferroan	23
	Lindackerite	18
R027wp_w	Quartz	44
	Westerveldite	29
R027wp_w2	Quartz	49
	Birnessite (K-exchanged)	20
	Cryptohalite	21
	Copper arsenate hydrate	15
	Iowaite	18
R028f	Quartz	62
	Albite low	34
	Clinochlore, Mn-rich	45
	Rutile	22
	Dickite	17
R029i	Quartz	48
	Clinochlore	36
	Albite low	32
	Muscovite	33
R029i_f	Quartz	66
	Clinochlore ferroan	50
	Mgriite	53
	Albite low	26
	Muscovite	15

Sample ID	Minerals present (XRD results)	Score*
R029i_w	Quartz Volkonskoite Nimite Epidote	56 47 30 29
R030f	Quartz Albite, ordered Vermiculite Muscovite Saponite	69 41 27 25 21
R031i	Palygorskite Cuprite Quartz Pinakiolite	49 47 37 32
R032wp	Quartz Albite, Ca-rich, ordered Microcline intermediate	65 46 35
R032wp_w_ABA	Sodalite lithian Pharmacosiderite Cryptohalite Westerveldite	33 29 26 23
R033f_f	Quartz Albite, ordered Dolomite, ferroan Clinocllore, Fe- rich Epidote Phlogopite	59 37 29 30 26 25
R033f_w	Quartz Birnessite (K-exchanged) Ankerite Kusachiite Brucite Epidote	68 19 22 19 28 24
R034f_f	Quartz Albite low Microcline intermediate Ankerite	70 37 16 21
R034f_w	Quartz Albite low Mercury chloride	74 32 21

Sample ID	Minerals present (XRD results)	Score*
R035wp_f	Quartz Albite low Ankerite Biotite, Ti- rich	69 34 25 18
R035wp_w	Quartz Albite low Ankerite Jordanite Mica Eastonite (mica)	77 24 22 9 18 14
R036i_f	Quartz Albite low Fraipontite Ankerite	59 40 29 27
R036i_w	Quartz Albite low Ankerite Birnessite (K-exchanged)	67 26 23 10
R037i	Quartz Jarosite Hydrotalcite Cerianite Sylvite Albite, disordered Gypsum	35 49 25 32 24 14 25
R038i_f	Quartz Epidote	67 54
R038i_w	Quartz Albite low Bemenite Spessarite	66 41 24 18
R039i_f	Quartz Albite, Ca-rich, ordered Clinocllore, Fe-rich Biotite	66 38 40 28
R039i_w	Quartz Albite, Ca-rich, Ordered Fraipontite Annite	68 39 28 18

Sample ID	Minerals present (XRD results)	Score*
R040i	Quartz low Albite low Giniite	74 23 26
R040i_f	Quartz Anorthite sodian Dickite Fraipontite	64 40 21 28
R040i_w	Quartz Fraipontite Albite low	72 19 26
R041i_f	Albite, Ca-rich, ordered Quartz Vermiculite Dickite	64 50 30 15
R041i_w	Quartz Albite, Ca-rich, ordered Brucite Jordanite Gobbinsite	74 39 26 10 7
R042i_f	Quartz low Albite, Ca-rich, ordered Gismondine	69 44 33
R042i_w	Quartz Albite, Ca-rich, ordered Eastonite (mica)	76 34 22
R043wp_f	Quartz Albite low Microcline intermediate Zinnwaldite	62 58 22 19
R043wp_w	Quartz Kusachiite Goethite Arsenopyrite Chalcocite, high Iron sulfide	65 21 20 16 15 11
R044i_f	Quartz Albite low Lindackerite	70 35 13

Sample ID	Minerals present (XRD results)	Score*
R044i_w	Goethite Quartz Albite, Ca-rich, ordered	38 27 16
R045f_f	Quartz Albite, Ca-rich, ordered Ankerite Phlogopite, Fe-rich Fraipontite	65 43 27 28 24
R045f_w	Quartz Hematite Ankerite Albite, ca-rich, ordered Fraipontite Phlogopite, Fe-rich	70 36 30 29 17 11
R046i_f	Quartz Albite low Microcline, intermediate Tephorite, Ca-rich Albite Siderophyllite lithian	65 53 31 26 28 19
R046i_w	Quartz Albite low Microcline, intermediate Biotite	70 33 28 13
R047f_f	Quartz Fraipontite Anorthite sodian, intermediate	72 41 58
R047f_w	Quartz Hematite Kusachiite	60 37 16
R048i_f	Quartz Albite, Ca-rich, ordered	71 33
R048i_w	Quartz Albite, Ca-rich, ordered Montomorillonite	69 26 13
R049i_porphry	Quartz Mgriite	78 13

Sample ID	Minerals present (XRD results)	Score*
R049i_matrix	Quartz Albite low Ankerite Biotite Birnessite (K-exchanged) Epidote	67 34 28 28 21 37
R050f_porphry	Quartz Albite, Ca-rich, ordered Epidote Muscovite	72 28 31 11
R050f_matrix	Quartz Albite, Ca-rich, ordered Birnessite (K-exchanged) Phlogopite, Fe-rich	67 39 26 36
R051i_f	Quartz Albite, Ca-rich, ordered Birnessite (K-exchanged)	79 34 12
R051i_w	Quartz Albite, Ca-rich, ordered Faujasite (Ce-exchanged)	77 36 26
R052f_f	Quartz Albite low Phlogopite, Fe-rich Eastonite (mica)	70 32 26 22
R053i_f	Quartz Albite, Ca-rich, ordered Phlogopite, Fe-rich Birnessite (K-exchanged)	73 33 31 17
R054i_f	Quartz Phlogopite, Fe-rich Albite, Ca-rich, ordered	72 33 27
R055i_f	Quartz Biotite Albite, Ca-rich, ordered Bearsite	69 38 24 13
R055i_w	Quartz Birnessite Albite low Schoepite	66 25 22 19

Sample ID	Minerals present (XRD results)	Score*
R056f_f	Quartz Albite low Dolomite, ferroan Biotite	69 27 17 12
R056f_w	Quartz Kusachiite Colusite Goethite Krautite Asselbornite	53 19 13 10 6 12
R057i_f	Quartz Phlogopite, Fe-rich Albite, Ca-rich, ordered	62 15 16
R057i_w	Quartz Albite, Ca-rich, ordered Phlogopite, Fe-rich	77 21 19
R058i_f	Quartz Fraipontite Kusachiite	65 40 20
R058i_w	Quartz Clinocllore, Fe- rich Calcite magnesian	71 55 20
R059i_f	Quartz Albite low Biotite	75 24 15
R060i_f	Quartz Albite, Ca-rich, ordered Micropertthite	68 47 34
R061i_f	Quartz Albite low Phlogopite, Fe-rich	76 30 12
R061i_w	Quartz Phlogopite	39 7
R062i_f	Quartz Albite low Biotite	73 40 21
R063i_f	Quartz Albite calcian low Ferropargasite	64 50 29

Sample ID	Minerals present (XRD results)	Score*
R064i_f	Moissanite	65
	Quartz	61
	Albite, ordered	44
R065i_f	Quartz	49
	Anorthite, Na-rich, intermediate	35
	Moissanite	20
	Phlogopite, Fe-rich	40
	Birnessite (K-exchanged)	16
R066i_f	Quartz	67
	Albite, Ca-rich, ordered	38
	Dolomite, ferroan	31
	Phlogopite, Fe-rich	26
R067i_f	Quartz	72
	Albite calcian low	31
	Phlogopite, Fe-rich	34
Mr001_f	Quartz	67
	Albite low	34
Mr001_w	Quartz	65
	Albite low	28
	Illite	20
	Carphosiderite	26
	Eastonite (mica)	26
Mr001_recentweathering?	Quartz	70
	Kusachiite	26
	Goethite	19
	Pharmacosiderite	11
	Cristobalite	13
Mr002_hydrothermal?	Sodiumpharmacosiderite	47
	Arseniosiderite	38
	Yukonite	31
Mr002_f	Quartz	63
	Moissanite	42
	Albite, Ca-rich, ordered	35
	Meixnerite	32
	Phlogopite, Fe-rich	24
Mr002_w	Quartz	61
	Vanuralite	25
	Albite low	20
	Jachymovite	20

Sample ID	Minerals present (XRD results)	Score*
Mr003_f	Quartz Anorthite sodian Lindackerite Cordierite (dehydrated, Ar-bearing)	67 38 15 9
Mr003_w	Quartz Albite calcian low Faujasite (Ag-exchanged)	64 48 26
Mr004_f	Quartz Albite low Faujasite (Ag-exchanged)	66 44 16
Mr004_w	Quartz Albite low Eastonite (mica)	51 30 24
Mr005	Quartz Fraipontite Jachymovite Faujasite (Ag-exchanged)	44 37 19 22
Mr006_f	Quartz Albite low Birnessite (K-exchanged) Natrojarosite Faujasite-Na	64 34 23 32 16
Mr006_w	Quartz Natrojarosite Albite low Birnessite (K-exchanged)	64 42 31 30
Mk001	Natrojarosite	70
Mk002	Natrojarosite Plumbojarosite Tellurium Iron sulfide Birnessite (K-exchanged)	58 30 23 16 15
Mk003	Gypsum Quartz Albite low	61 50 18
Mk004	Arsenopyrite Quartz	64 23
Mk005	Schaurteite	70

Sample ID	Minerals present (XRD results)	Score*
Mk006	Gypsum	56
	Natroalunite	38
	Quartz	36
	Aluminite	29
	Uranopilite	16

* Identified minerals were assigned a score from 0 – 100 by HighScore PANalytical Software, where 100 is a perfect match with X-ray spectra from the JCPDS reference database.

APPENDIX G: Sample photos

R001i

R002wp

R003wp

R004i

R005wp

R006i

R007wp

R008f

R009f

R010f

R011i

R012f

R013f

R014f

R015f

R016f

R017f

R018f

R019f

R020i

R021i

R022i

R023i

R024wp

R025i

R026i

R027wp

R028f

R029i

R030f

R031i

R032wp

R033f

R034f

R035wp

R036i

R037i

R038i

R039i

R040i

R041i

R042i

R043wp

R044i

R045f

R046i

R047f

R048i

R049i

R050f

R051i

R052f

R053i

R054i

R055i

R056f

R057i

R058i

R059i

R060i

R061i

R062i

R063i

R064i

R065i

R066i

R067i

Mr001

Mr002

Mr003

Mr004

Mr005

Mr006

Mk001

Mk002

Mk003

Mk004

Mk005

Mk006

Client Name: University of San Diego
Project Name: Black Mountain Arsenic Verification

EMA Log #: 16G0820

ANALYTICAL REPORT FOR SAMPLES

Sample ID	Laboratory ID	Matrix	Date Sampled	Date Received
R022i >Microns	16G0820-01	Solid	12/15/15 12:00	07/26/16 15:05
Mr002	16G0820-02	Solid	12/15/15 12:00	07/26/16 15:05
Mk004	16G0820-03	Solid	12/15/15 12:00	07/26/16 15:05

The results in this report apply to the samples analyzed in accordance with the chain of custody document. This analytical report must be reproduced in its entirety.

EnviroMatrix Analytical, Inc.

Client Name: University of San Diego
Project Name: Black Mountain Arsenic Verification

EMA Log #: 16G0820

Total Metals by EPA 6000/7000 Series Methods

Analyte	Result	Reporting Limit	Units	Dilution	Batch	Prepared	Analyzed	Method	Notes
R022i >Microns (16G0820-01) Solid Sampled: 12/15/15 12:00 Received: 07/26/16 15:05									
Arsenic	158000	100	mg/kg	100	6073002	07/30/16	07/31/16	EPA 6010	HT-04
Mr002 (16G0820-02) Solid Sampled: 12/15/15 12:00 Received: 07/26/16 15:05									
Arsenic	165000	100	mg/kg	100	6073002	07/30/16	07/31/16	EPA 6010	HT-04
Mk004 (16G0820-03) Solid Sampled: 12/15/15 12:00 Received: 07/26/16 15:05									
Arsenic	390000	100	mg/kg	100	6073002	07/30/16	07/31/16	EPA 6010	HT-04

The results in this report apply to the samples analyzed in accordance with the chain of custody document. This analytical report must be reproduced in its entirety.

EnviroMatrix Analytical, Inc.

Client Name: University of San Diego
 Project Name: Black Mountain Arsenic Verification

EMA Log #: 16G0820

Total Metals by EPA 6000/7000 Series Methods - Quality Control

Analyte	Result	Reporting Limit	Units	Spike Level	Source Result	%REC	%REC Limits	RPD	RPD Limit	Notes
Batch 6073002										
Blank (6073002-BLK1)										
Arsenic	ND	1.00	mg/kg							Prepared: 07/30/16 Analyzed: 07/31/16
LCS (6073002-BS1)										
Arsenic	103	1.00	mg/kg	100		103	75-125			Prepared: 07/30/16 Analyzed: 07/31/16
LCS Dup (6073002-BSD1)										
Arsenic	101	1.00	mg/kg	100		101	75-125	2	20	Prepared: 07/30/16 Analyzed: 07/31/16
Duplicate (6073002-DUP1)										
Arsenic	5.45	1.00	mg/kg		6.06			11	20	Source: 16G0771-01 Prepared: 07/30/16 Analyzed: 07/31/16
Matrix Spike (6073002-MS1)										
Arsenic	91.6	1.00	mg/kg	92.6	6.06	92	75-125			Source: 16G0771-01 Prepared: 07/30/16 Analyzed: 07/31/16
Matrix Spike Dup (6073002-MSD1)										
Arsenic	94.0	1.00	mg/kg	96.2	6.06	91	75-125	3	20	Source: 16G0771-01 Prepared: 07/30/16 Analyzed: 07/31/16

The results in this report apply to the samples analyzed in accordance with the chain of custody document. This analytical report must be reproduced in its entirety.

EnviroMatrix Analytical, Inc.

Client Name: University of San Diego
Project Name: Black Mountain Arsenic Verification

EMA Log #: 16G0820

Notes and Definitions

HT-04 This sample was received outside of the EPA recommended holding time for this analysis.

ND Analyte NOT DETECTED at or above the reporting limit

NR Not Reported

dry Sample results reported on a dry weight basis

RPD Relative Percent Difference

The results in this report apply to the samples analyzed in accordance with the chain of custody document. This analytical report must be reproduced in its entirety.

EnviroMatrix

Analytical, Inc.

APPENDIX I: Scanning Electron Microscope (SEM)

1. Methods

A representative subset of whole rock samples ($n = 7$) were cut into billets for analysis by Scanning Electron Microscope (SEM) at the University of San Diego. Billets were first polished using 600, 800, and 1,200 grit polishing papers and gold coated for 30 seconds with a sputter coater. Energy dispersive spectrometry (EDS) at 15 keV was then used to perform surface imaging using backscattered electron (BSE) techniques, and elemental mapping was conducted using wavelength dispersive spectroscopy (WDS).

2. Results

Fig 1: BSE images of a) scorodite-bearing quartz vein in an altered rhyolite (R037i), b) ~1 mm arsenopyrite crystals in rock disturbed by mining (R019wp), c) highly weathered pyrite in an altered dacite (R058i), d) pyrite with scorodite halo in rock disturbed by mining (R019wp). Blue and red squares represent areas of the sample that were point analyzed by WDS, and resulting atomic percentages are given in tables of corresponding color.

Fig 2: SEM image and elemental mapping indicate presence of As-bearing iron oxides along fractures of an altered dacite (R058i).