

HEMATITE AND SULFATE MINERALS IN LAVA TUBES, CRATERS
OF THE MOON, IDAHO: AN ANALOG FOR DIAGENESIS AT
MERIDIANI PLANUM, MARS

by

Joseph J. Ruffini

A Thesis Submitted in

Partial Fulfillment of the

Requirements for the Degree of

Masters of Science

in Geosciences

at

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ABSTRACT

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Joseph J. Ruffini

University of Wisconsin-Milwaukee, 2011
Under the Supervision of Dr. Lindsay McHenry

The Mars Exploration Rover Opportunity detected and analyzed sulfate, silica, and Fe-bearing minerals including hematite and jarosite at Meridiani Planum, inferred to be products of alteration of high-iron Martian basalt. The secondary mineral assemblages seen on Mars also occur in basaltic lava tubes on Earth. The Holocene basalt flows of

Craters of the Moon National Monument and Preserve (CRMO) have high $\text{Fe}_2\text{O}_3\text{T}$ contents (~18%) that closely resemble Martian basaltic compositions. Studying the alteration and precipitation products present in lava tubes in these flows can provide context for sedimentary processes and minerals formed through alteration of basalt and precipitation of leached ions on Earth and Mars.

Mineral samples were collected from lava tubes at CRMO and included floor mounds, ceiling and wall coatings (white, yellow, and orange encrustations, and alteration surfaces with metallic luster), the basaltic substrate beneath each deposit, and unaltered basalt. These samples were analyzed using X-Ray Diffraction, X-Ray Fluorescence, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, and Electron Probe Microanalysis. The white and orange ceiling coatings are calcite, silica, and/or gypsum, products of precipitation. The constituents of the metallic coatings are hematite, at times with calcite and silica as a subsequent layer. Olivine is absent in the metallic luster alteration surface, likely because of hydrothermal alteration as the lava tube cooled. The floor mounds are composed of sulfate, carbonate, and bicarbonate minerals including thenardite, mirabilite, and trona, and are possibly the products of microbiological activity or aqueous precipitation. One location had jarosite, inferred to be the product of limited water:rock interaction and local acidification of percolating water resulting from iron oxidation.

Hematite and jarosite occurrences are similar to assemblages seen at Meridiani Planum, though the Martian deposits are interpreted as products of non-thermal or hydrothermal groundwater alteration of pre-existing sulfates, and reworked and wind transported acidic playa deposits, respectively. Some sulfate minerals from CRMO are

similar to those on Mars (Ca and Fe sulfates), while others are not (Na-rich). Carbonate minerals are not found at Meridiani Planum, but have been identified elsewhere on Mars. Results from CRMO indicate that local acidification may precipitate jarosite while the aqueous system is mainly neutral pH, and hematite may have implications for fluctuating hydrothermal conditions on Mars.

Major Professor

Date

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Introduction

The Mars Exploration Rover (MER) Opportunity's exploration of Meridiani Planum starting January 25th, 2004 has produced a wealth of geochemical and mineralogical data that can be used to help reconstruct the geological history of Mars (e.g. Squyres et al., 2004a; Soderblom et al., 2004; Klingelhöfer et al., 2004; Carr and Head, 2010), and provides strong evidence for past aqueous processes (e.g. Squyres et al., 2004b; Herkenhoff et al., 2004). The rover observed a secondary mineral assemblage in the Burns Formation that includes silicate minerals, sulfate salts, and oxidized iron-bearing phases, especially hematite (Squyres et al., 2004a; Chevrier et al., 2007). The specific altered basaltic rocks and associated secondary mineral assemblages observed have led many investigators to search for terrestrial analogs with similar compositions (e.g. Fernández-Remolar et al., 2004; Morris et al., 2005). Specifically, the high iron basalts (approximately 18 wt. % $\text{Fe}_2\text{O}_3\text{T}$) observed on Mars have driven the search for an effective terrestrial basaltic analog with similar compositions (McSween et al., 2003, 2009; Minitti et al., 2007).

This study attempts to address these observations by studying the diagenetic minerals present in lava tubes in a high-iron basaltic flow field in south-central Idaho, at Craters of the Moon National Monument & Preserve (CRMO) (Kuntz et al., 1986a). CRMO lavas have $\text{Fe}_2\text{O}_3\text{T}$ concentrations approaching Martian values, and associated lava tubes preserve secondary minerals including hematite, silica, and a variety of sulfates (McHenry, 2009b), making them an exceptional analog for comparison to

Meridiani Planum. Lava tubes are relevant analogs because they have been observed on the Moon and Mars, and provide sheltered environments for the preservation of otherwise soluble mineral formations and easily destroyed biosignatures (Boston et al., 2001; Wyrick et al., 2004; Cushing et al., 2007; Haruyama et al., 2009; Léveillé and Datta, 2010). Lava tubes have also been suggested as human shelters for pioneering astronauts as protection against micrometeoroids, solar flares, UV radiation, and dust storms (Horz, 1985; Boston et al., 2003; Cushing et al., 2007). If these features occur on Mars, they may also have intercepted groundwater and created secondary minerals analogous to those in CRMO lava tubes.

Objectives

The main objectives of the proposed research are 1) to quantify the mineral assemblages, chemical compositions, and order of deposition of the CRMO secondary minerals and their substrates, 2) to use this data to determine the mechanisms that produced these mineral assemblages and the conditions under which they formed, and 3) to compare these terrestrial assemblages to those observed and proposed for Meridiani Planum.

To accomplish these objectives, I studied the mineral assemblages and geochemical compositions of the associated primary, alteration, and precipitate deposits using X-ray Diffraction (XRD), X-ray Fluorescence (XRF) Spectrometry, Scanning Electron Microscopy (SEM), Electron Probe Microanalysis (EPMA) and Fourier Transform Infrared (FTIR) Spectroscopy. Dissolved ion compositions of modern water

in the caves and at the surface were analyzed by Ion Chromatography (IC) and Atomic Absorption (AA). The main objective is to develop a model for the formation of the minerals observed in the lava tubes investigated. Based on the similarity of the minerals seen at CRMO on Earth and Meridiani Planum on Mars, this model can be extrapolated to the Burns Formation as a possible explanation for the diagenetic history of the outcrops.

The geochemical composition of the Blue Dragon lava flow from Kuntz (1985) (Table 1) and the Martian precursor basalt from Meridiani Planum are similar in many key elements. This study focuses primarily upon the iron content of these basalts and the role that this plays in alteration and precipitation processes. Another focus of this study is the mobility of sulfur, silica, calcium, sodium, and other elements that are concentrated in alteration rinds and sulfate minerals similar to those observed on Mars.

	<i>BD1</i>	<i>BD2</i>	OCBP1
SiO ₂	49.01	49.61	48.19
TiO ₂	2.87	2.75	1.01
Al ₂ O ₃	13.41	13.82	8.06
Fe ₂ O ₃ T	15.27	15.29	20.23
MnO	0.24	0.25	0.43
MgO	3.34	3.25	10.40
CaO	6.93	6.56	6.46
Na ₂ O	3.61	3.47	2.19
K ₂ O	2.03	2.05	0.75
P ₂ O ₅	1.77	1.88	1.37
Total	98.48	98.93	99.09

Table 1. Bulk composition of the Blue Dragon flow, BD1 and BD2, (Kuntz, 1985), compared to Meridiani Planum, Mars. OCBP1 is a calculated precursor basalt for Meridiani Planum (Morris et al., 2006)

I expect to find that aqueous processes were involved at CRMO, as inferred for Meridiani Planum. Some of the secondary minerals at both sites include structural water, and I hypothesize that hematite at CRMO was likely formed under hydrothermal conditions. I also hypothesize that the sulfate and carbonate minerals observed at CRMO formed at ambient temperatures through meteoric water interacting with basalt, leaching ions, and precipitating them on the cave ceilings, walls, and floors. Jarosite specifically was likely formed under at least locally acidic conditions (Glotch et al., 2006). These processes require available water, and if the mineral assemblages at CRMO and Meridiani Planum are similar enough, this could support the hypothesis that water was involved in the formation of the secondary minerals observed at Meridiani Planum. This could help constrain the nature of fluid interactions on Mars, perhaps indicating both hydrothermal and non-thermal conditions at different times.

Craters of the Moon Background

CRMO is a lava field produced by a volcanic rift zone (known as the Great Rift) within the eastern Snake River Plain province (Figure 1). The Snake River Plain is a 600-kilometer long depression in southern Idaho, which lies within the Yellowstone hotspot track (Pierce and Morgan, 2009). This basaltic lava field comprises more than 60 lava flows and flow units, 25 cinder cones, and 8 separate eruptive periods, with a total volume of over 30 km³ of flows (Kuntz et al., 1986a). Radiocarbon dating of charred sediment layers underlying the flows, along with paleomagnetic data, help define episodes of eruptions for the lava field (Kuntz et al., 1986a). The earliest basaltic

eruptive period is dated to roughly 15,100 years ago, and the most recent to 2,100 years ago.

Understanding the petrology of these high-iron basalts can help us determine the igneous conditions and processes of their formation. Petrologic studies of the proposed parent, the Snake River Plain olivine tholeiites, show a small compositional range with little influence from contamination or differentiation, making them a plausible primary magma (Kuntz et al., 1986a; Putirka et al., 2009). The Craters of the Moon basalts differ from this parent in their more variable compositions, likely the result of assimilation and fractional crystallization (AFC) during ascent of the parent Snake River Plain olivine tholeiite.

Craters of the Moon lavas are enriched in Fe_2O_3 , P_2O_5 , TiO_2 , and alkalis compared to the Snake River Plain tholeiites (Leeman 1976). The earliest Craters of the Moon basalts are compositionally unique relative to the majority of basalts around the world in that they are lower in silica and enriched in total alkalis and iron (Stout 1975, 1994). Subsequent eruptive periods show increasing silica content and more evolved lavas caused by increasing contamination and fractionation over time (Kuntz et al., 1986a). Magma mixing and fractionation likely play the largest roles, while crustal contamination may not be as important in shaping the basaltic composition since the K/Ba and K/Rb ratios are constant, whereas they would typically decrease with an increasing influence from crustal contamination.

A low inferred water content of 1-2 wt. % (based in part on the absence of hornblende) could have contributed to iron enrichment in the residual magma (Putirka et al., 2009). An experimental study (Whitaker, 2007) showed that differences in water

pressure during fractional crystallization can produce residual melts of variable composition, even when starting from a common parent. Residual melts from 0.5 wt % H₂O and 9.3 kbar experiments were depleted in silica, MgO and CaO and enriched in total alkalis, FeO_T, TiO₂, and P₂O₅ because of the crystallization and removal of plagioclase, pyroxene, and olivine under these conditions. The composition of these liquids is consistent with the low water content and high iron content of the CRMO basalt analyzed in this study.

From the many previous field and experimental studies on the variable CRMO basalts, we can deduce that a significant but small degree of fractional crystallization of plagioclase, pyroxene and olivine under relatively dry conditions must have occurred to reach the unique melt compositions necessary to create the high-iron CRMO basalts. Assimilation and magma mixing may play significant roles in a few of the CRMO basalts, influencing isotopic ratios and trace element and silica contents, however this interpretation is still a matter of debate (e.g. Leeman, 1976; Kuntz, 1986a; Putirka et al., 2009).

Blue Dragon Lava Flow

This study focuses on the Blue Dragon lava flow at CRMO because it has specific compositional characteristics that make it a good analog for Martian basalts and their diagenetic products. The Blue Dragon flow is a composite pahoehoe and a'a basalt-hawaiite flow erupted in the Holocene (Kuntz et al., 1986b).

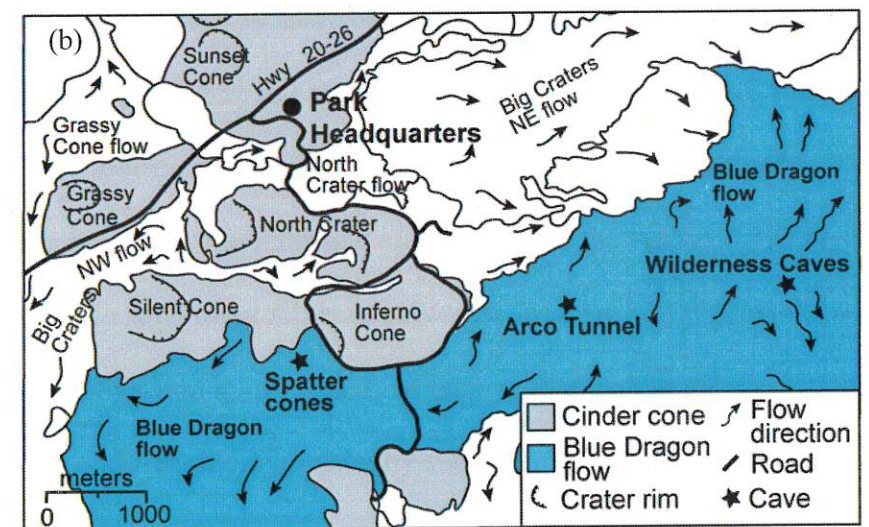
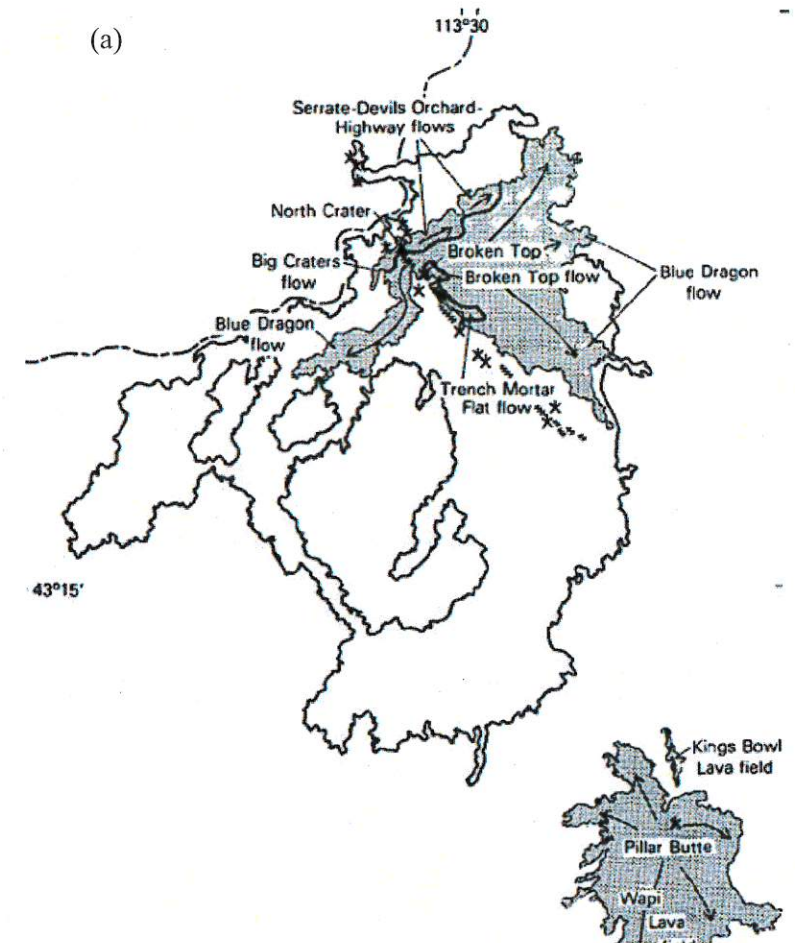


Figure 1. a) Eruptive Period A, which includes the Blue Dragon flow (upper shaded portion) (Kuntz, 1986a). b) Detailed map of the Blue Dragon Flow, with locations of sample cave areas (Wilderness, Arco Tunnel, Spatter Cones) labeled. Modified from Richardson et al., in review.

The rock is generally fine-grained ($<0.3\text{mm}$), dense, mostly hypocrystalline, and partly diktytaxitic (with microcrystalline structures protruding into vesicles). It also contains microphenocrysts of olivine (Fa_{35-45}), plagioclase (An_{50}), skeletal apatite, and some augite but is composed mostly of volcanic glass. Kuntz et al. (1986b) detail these flows as both tube and surface-fed and characterized by their fresh, iridescent, dark-to-light blue surfaces. The interiors of the flows are more massive and medium dark gray.

This flow erupted from fissure-controlled vents, specifically the spatter cones Crystal Pit, Snow Cone, and others to the south of Big Craters cinder cone. The lava tubes in this flow fed the eastern and western lobes of this unit. These flows are of main interest for this study, and contain numerous skylights and rootless vent complexes. Pressure ridges, pressure plateaus, and collapse depressions are common morphologic features on the surface and indicate a high-volume, short-lived eruption. The mean age of four radiocarbon samples of charcoal from tree molds and carbon-bearing material from sediment buried by this flow is $2,076 \pm 45$ years (Kuntz et al., 1986b).

The Blue Dragon flow is one of the largest and youngest subaerially exposed lava flows at CRMO. Because of the delicate nature of the secondary minerals, most of them would weather quickly in the semi-arid environment at the surface. Extensive investigation has located these minerals protected from surface processes under overhangs, in blisters, and in lava tubes, which are abundant in this flow since it is young, relatively fresh, and remains uncovered by subsequent flows that would destroy the lava tubes and various features.

An early study (Peck, 1974) of secondary minerals in the now empty magma chamber of the spatter cone Crystal Pit at CRMO identified secondary minerals similar to

those discovered later at Meridiani Planum, Mars. The magma chamber contains the sulfate minerals gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and jarosite ($\text{KFe}^{3+}_3[(\text{OH})_3(\text{SO}_4)]_2$). Peck's model states that these minerals were deposited by seeping groundwater, and he notes that the overlying basaltic substrate is depleted in calcium, sodium, and sulfur-bearing primary minerals.

Secondary Mineralization in Lava Tubes

Secondary mineralization in lava tubes has not been as extensively researched as that in limestone caves (e.g. Moore and Sullivan, 1978). A general overview of lava tube speleogenesis (Forti, 2005) describes the main processes at work (Figure 2). Some processes in lava tubes are vastly different from those at work in limestone caves because of the compositional difference and the great fluctuations in temperature that take place between the formation of the cave to its equilibration with ambient conditions.

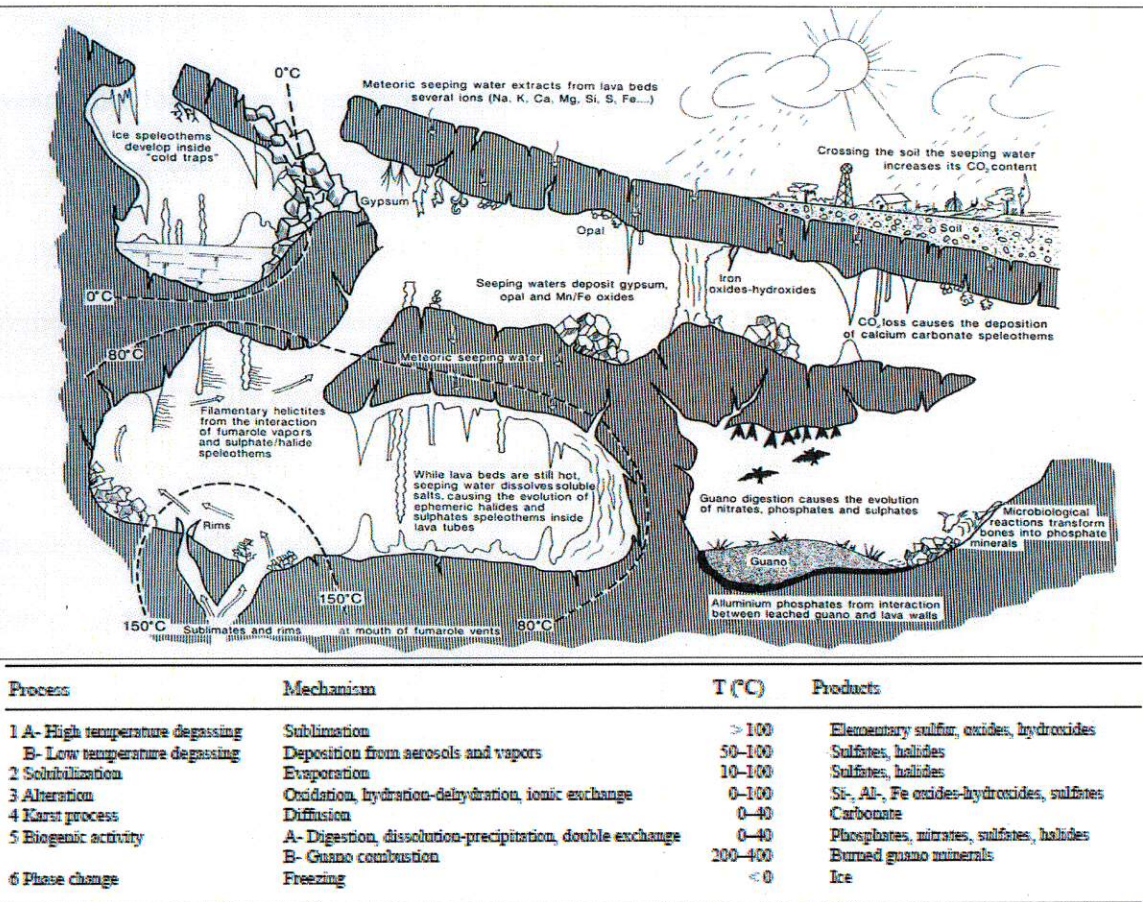


Figure 2. Graphical representation of secondary mineralization processes in lava tubes and table detailing each process, from Forti (2005).

According to Forti (2005), the first process that creates secondary minerals in a lava tube after formation is degassing. This process occurs only at temperatures above 100° C. Fumarolic gasses still residing in the lava tube cool and expand in the cave atmosphere. When this occurs, sublimation takes place and commonly deposits sulfur and some oxides, hydroxides, and rarely sulfates. The minerals created at this time are metastable because of their high temperature of formation and delicate nature and break down at lower temperatures. Low-temperature degassing is the next process as temperatures decrease. It occurs between 50 and 100° C as aerosols and vapors deposit

sulfates and halides (Forti, 2005). These minerals will break down within the first two years after formation, depending on the rate of precipitation (Bunnell, 2008).

According to Forti (2005), below 100° C and above 10° C, meteoric water begins to percolate into the contraction cracks and through the pores of the basalt. The water removes soluble material from the newly formed basalt. The high-temperature gases in the lava tube rapidly evaporate the fluid and precipitate the material in solution, producing sulfates and halides. This process halts once ambient temperatures are reached and a normal hydrogeologic system takes over, dissolving the original metastable high-temperature minerals. The dissolution rate is directly related to the amount of rainfall that percolates into the cave (Forti, 2005). White (2010) confirms these processes through observations in Hawaii, and investigations of newly formed lava tubes by Porter (2000) and Palmer and Palmer (2006) found minerals unstable at ambient conditions including bassanite, which had been replaced by stable assemblages such as calcite and gypsum after the cave was at ambient conditions for a significant period.

Alteration is the next process to occur in lava tubes, and can happen at any ambient temperature up to 100° C (Forti, 2005). Meteoric water seeps through and dissolves soluble components in the basalt, redepositing them as new minerals stable at ambient temperatures. This results in the oxidation of sulfide minerals, the weathering of silicate minerals, and the dissolution of silica glass. All of these weathering processes produce ions that can be transported in solution to the cave walls. Ions released include silica, calcium, magnesium, and other elements that are mobile in this temperature range and abundant in basalt. As the solution drips off the cave wall, these are deposited as oxy-hydroxides, opal, calcite, gypsum and other sulfates. This process usually creates

thin encrustations instead of large speleothems because of the limited availability of ions. This process may also end after a short period of time, on the scale of decades, but these mineral crusts will not easily redissolve once deposited (Forti, 2005).

Karst processes are the main mechanism of speleothem generation in limestone caves, but may play a role in lava tube speleogenesis as well. This process involves the diffusion of carbon dioxide into the cave leading to supersaturation of a solution in calcium carbonate (Forti, 2005). This process will not occur if two necessary conditions for carbonate deposition are not met. The first is that there must be an adequate supply of CO_2 , most often supplied by microbial processes in a somewhat mature soil layer above the cave, which may take thousands of years to develop. The other requirement is that sufficient amounts of calcium and magnesium ions are present to move into solution. These elements are present in moderate concentrations in mafic minerals. These factors keep karst mineral production to a minimum in young lava tubes and this is therefore not one of the major formation mechanisms for lava tube secondary minerals (Forti, 2005).

Unlike in limestone caves, calcium carbonate deposits are usually formed through deposition by simple evaporation rather than off-gassing of carbon dioxide (Bunnell, 2008). The source of carbonate may be eolian dust from other areas in the region, transporting and depositing carbonates in cracks and providing a carbonate source for percolating water.

Biological processes can also contribute to cave mineralization at low temperatures, and can include microbial alteration of basalt leaving an amorphous silica-rich "moon milk," or bat guano, which can produce phosphates, sulfates, nitrates, halides, oxides, and hydroxides (Boston et al., 2001; Forti, 2005).

Relevant Martian Geology

Recently obtained orbital and rover data show that the surface of Mars is largely basaltic, with some phyllosilicate and sulfate deposits which may be indicative of earlier, wetter environments. These potentially wet environments could have been habitable, and have thus been the focus of extensive research (e.g. Ezell and Ezell, 1984; Squyres et al., 2005; Bibring et al., 2007). Understanding the formation mechanisms behind the minerals on the surface of Mars can help produce models for the ancient environment.

A Brief History of Mars

The geologic history of Mars is divided into three periods: The Noachian (4.4 -3.8 Gya), Hesperian (3.8-2.0 Gya), and Amazonian (2.0 Gya – present) (Scott and Carr 1978; Bibring et al., 2005) (Figure 3). These periods have been further refined based on stratigraphy, crater density, and morphology (Tanaka, 1986).

Geomorphic evidence suggests the activity of liquid water at the surface during the Noachian. Networks of tributaries attributed to sapping groundwater or precipitation runoff carved the highlands and are largely Noachian in age (Carr, 1995; Solomon et al., 2005). Deposition occurred at high rates, implying long-standing bodies of water, and clay minerals are abundant (Bishop et al., 2008; Loizeau et al., 2007). This inferred wet period was short-lived, as Mars' atmosphere was slowly stripped (Pepin, 1994).

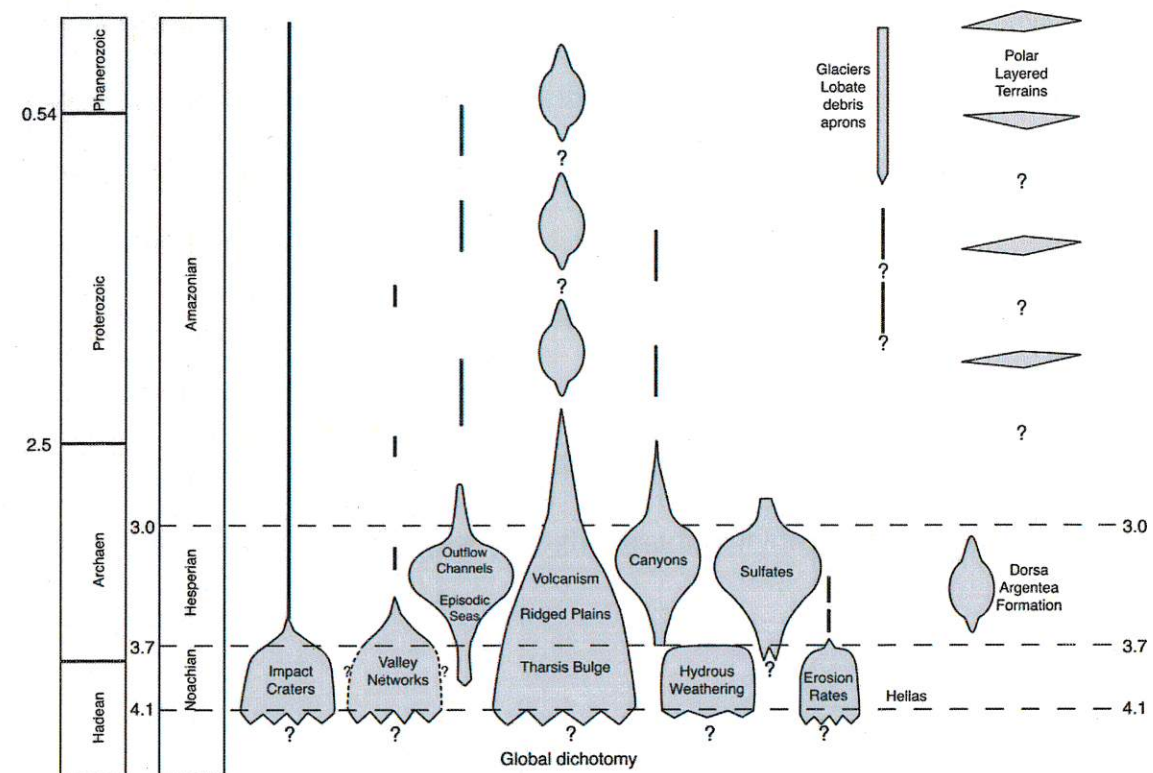


Figure 3. Approximate timing of geologic processes on Mars through time. Y-axis denotes billions of years (Carr and Head, 2010). Most active processes on the Martian surface occurred before 3.0 Gya.

The Hesperian starts with the end of the heavy bombardment at 3.7 Gya and continues until 3.0 Gya (Carr and Head, 2010). Characteristics of this period include episodic yet extensive volcanism forming lava plains, low erosion and impact rates, an end to clay mineral formation, and the beginning of sulfate deposition such as is observed at Meridiani Planum. Possible lakes, seas, and outflow channels also formed during this time, but this is debated. In general, Mars grew progressively drier over this period as the atmosphere continued to thin and temperatures dropped (Pepin, 1994).

The Amazonian extends from 3 Gya to present and covers two thirds of Martian history (Carr and Head, 2010). Low rates of impact, tectonism, volcanism, erosion and weathering distinguish this period. Ice is thought to have played a significant role in geomorphology during this period, and the ice at the poles is thought to have mostly accumulated during this period.

Bibring et al. (2005, 2006) break down the history of Mars differently, into three eras distinguished by their alteration mineral assemblages (Figure 4). The earliest phyllosian era produced clay minerals in Noachian terrain. These typically form through aqueous alteration at the surface, or through subsurface hydrothermal activity (Poulet et al., 2005; Mustard et al., 2008).

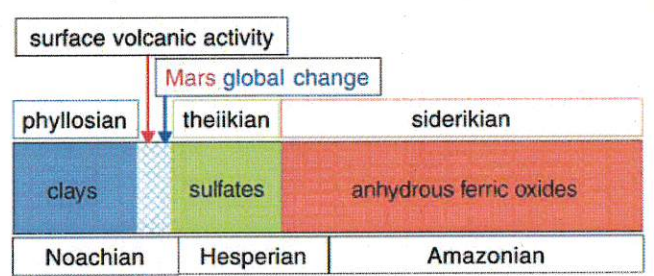


Figure 4. Bibring et al.’s (2006) breakdown of Martian history based on mineral formation processes.

Next, the theiikian era (late Noachian to early Hesperian) is characterized by extensive sulfate deposits. During this period, sulfates are believed to have formed as evaporites from substantial water bodies on the surface. The Meridiani Planum sulfate deposits observed by the MER Opportunity formed during this period. The sulfur and water source is believed to be the Tharsis Plateau volcanism and mare volcanism in the

northern plain and Hesperian ridged plains (Phillips et al., 2001). Oxidation and precipitation of sulfur and a rising water table created the conditions needed for the precipitation of sulfates. Active upwelling of deep fluids to the surface at Meridiani Planum in a drying environment formed evaporites. Increasing aridity led to the end of upwelling and left the sulfate deposits exposed to eolian processes (Andrews-Hanna et al., 2010; Andrews-Hanna and Lewis, 2011).

The final era, the siderikian, is distinguished by an absence of liquid water. Aqueous alteration ceases, and the main process was atmospheric weathering through peroxide reactivity or frost/rock interactions. These processes can only affect the very surface layer. This was directly observed by MER Spirit at Gusev crater as millimeter thick rinds on otherwise unaltered basalt (Squyres et al., 2004c; Ming et al., 2006).

Martian Petrology

The Mars Global Surveyor Thermal Emission Spectrometer (THEMIS) detected a basaltic signature on Mars, composed mostly of plagioclase (45%), clinopyroxene (26%), olivine (12%) and sheet silicates (15%) (Christensen et al., 2000b). McSween et al. (2009) compiled a database of Martian basalt compositions and hypothesized that early Noachian calc-alkaline magmatism depleted the mantle of certain elements, which led to later eruption of tholeiites in the Hesperian. The more differentiated "andesites" suggested by McSween et al. (2003) are now interpreted as basalts with thin surface alteration rinds (McSween et al., 2009).

The current hypothesis as to the formation of the tholeiites is that the magma source was relatively dry and shows iron enrichment during fractionation (McSween et al., 2009). Fractionation of pyroxenes, plagioclase and olivine in the magma chamber in conjunction with significant residence time and a low abundance of H₂O in the melt likely play a vital role in maintaining high iron and low silica, producing high-iron basalts similar to those observed at CRMO.

MER Opportunity Rover

The focus of this investigation is to compare the data obtained by the Mars Opportunity rover at Meridiani Planum to the CRMO terrestrial analog. The mission of the MER rovers was to analyze the geologic record of Mars, assess past environmental conditions, and determine if conditions were ever conducive to life by finding evidence for past aqueous processes (Squyres et al., 2005). The rovers were equipped with the ATHENA science payload, a suite of instruments used to analyze compositions and visually observe the surroundings. The instrumentation includes a panoramic camera (Pancam) and Mini-Thermal Emission Spectrometer (Mini-TES), which provide spectra to reveal the chemical compositions of outcrops and soils (Christensen et al., 2004). The tools also include a Rock Abrasion Tool (RAT) that can remove 5 mm of material from the surface and a Microscopic Imager (MI) that can produce high-resolution images similar to those seen through a geologist's hand lens. Other instruments include the Alpha Particle X-ray spectrometer (APXS), which measures elemental abundances in rocks and

soils, and the miniaturized Mössbauer spectrometer (MB) that determines mineralogy and oxidation state of Fe-bearing phases (Herkenhoff et al., 2004; Squyres et al., 2006a).

The Mars Opportunity rover landed in Eagle Crater at Meridiani Planum on January 25th, 2004. This site lies within the low-albedo region Sinus Meridiani, which lies on the Martian Prime Meridian between 10° W to 10° E, and 13° S to 7° N (Squyres et al., 2006b). This site was chosen for its flat terrain and an anomalous concentration of grey crystalline hematite detected from orbit using THEMIS (Christensen et al., 2000b; Bandfield, 2002).

Sedimentary Evidence for Aqueous Processes

The sedimentary rocks examined at Meridiani Planum have revealed information about the sedimentary history of Mars based on basic principles derived from terrestrial stratigraphy and sedimentary geology. The sedimentary units examined at Eagle Crater have certain characteristics that could indicate aqueous processes, including planar lamination, ripple cross-lamination, low angle cross-stratification, cross bed sets, embedded spherules, and vugs (Grotzinger et al., 2005).

The MI images reveal four main physical constituents in these outcrops (Figure 5). These include moderately rounded medium to coarse sand sized basaltic grains, embedded grey spherules with 4 to 6 mm diameters, fine-grained cement, and vugs with random orientations cutting across lamination, which are likely from earlier gypsum crystals (Squyres et al., 2004b). The MER team devised a stratigraphic section from

observations at Endurance crater (Figure 6) and combined with previous observations from Eagler crater, created a sedimentary history.

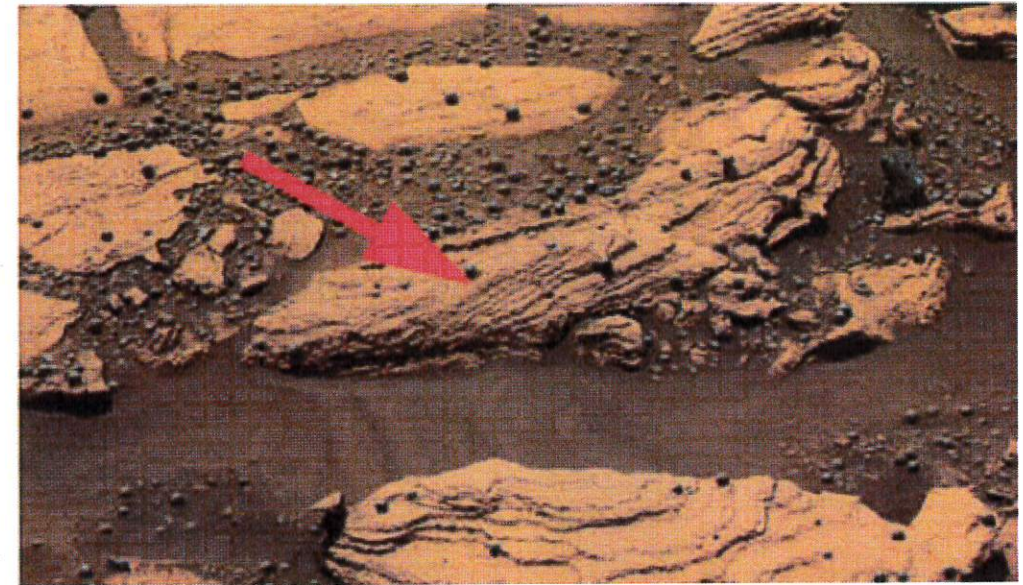


Figure 5. Shoemaker's Patio at Eagle Crater obtained by Pancam highlighting crossbeds and hematite spherules. Approximate true color rendering (Squyres et al., 2004b).

The bottom unit (Figure 6) has prominent cross bedding, interpreted to be sand dunes (Grotzinger et al., 2005). The upper contact is thought to be a deflation surface eroded by eolian processes. Above this is a unit with fine planar lamination and low-angle cross beds from eolian transport and deposition. The next contact is diagenetic, with increased porosity, recrystallization and a change in geochemistry above (Clark et al., 2005). The next unit displays wavy bedding and small-scale festoon cross lamination interpreted to be a result of ripple migration through surface flow of liquid water over sand, where the entire succession points to a 'wetting upward' process (Squyres et al., 2005). With respect to loose sediment at the surface, a bimodal distribution of fine sand

and spherules is inferred to be the product of wind transport and size sorting (Squyres et al., 2004b; Herkenhoff et al., 2004).

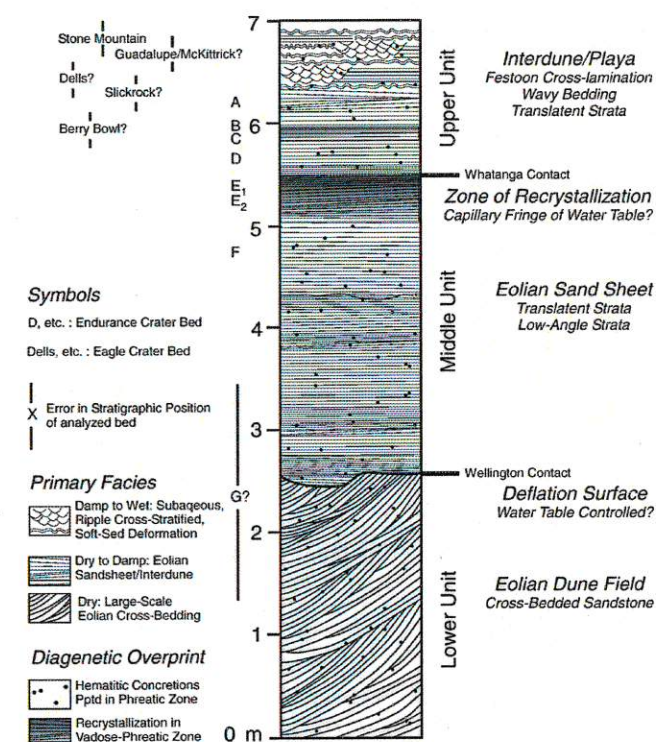


Figure 6. Stratigraphic column from Endurance crater wall with evidence for aqueous processes at Meridiani Planum. Grotzinger et al. (2005).

The Mineralogy and Geochemistry of Meridiani Outcrops

A probable precursor basaltic composition is calculated and presented in Table 1, from Morris et al. (2006). The substrate at Meridiani Planum has been identified as basalt, with a $\text{Fe}_2\text{O}_3\text{T}$ content of approximately 17 wt. % (Kligelhöfer et al., 2004). Cation abundances show that the outcrop composition can be best explained by chemical weathering of precursor olivine basalt (McLennan et al., 2005). Altered Meridiani

bedrock shows a distinct increase in sulfur with respect to Martian meteorites and unaltered Martian basalt with no corresponding increase in cations.

The sandstones exposed in outcrops are made up of altered siliciclastic debris (weathered basalt) along with sulfate minerals. The average results from APXS of six outcrop spectra at Meridiani (deconvoluted to remove the dust component) show mineral abundances of 25% sulfate, 20% hematite, 30% high-silica component (possibly as free silica), 20% igneous phases, and 5% oxides other than hematite (Rieder et al., 2004). Further deconvolution of Mini-TES data by Glotch and Banfield (2006) derived a modal mineralogy of Mg- and Ca-sulfates at 20% and 10%, 10% jarosite, 15% plagioclase feldspar, 5% hematite, possibly 10% nontronite, 5% quartz, and 25% Al-rich opaline silica and glass, some of which has been corroborated by CRISM orbital data (Milliken et al., 2008).

The outcrops have a high concentration of sulfur, up to 25 wt. % SO_3 , and up to 5 wt. % H_2O . The enrichment in sulfur has no corresponding enrichment in chlorine or any other cation, possibly the result of fractionation based on differential solubility. This type of local enrichment relative to chlorine is often indicative of evaporite deposits in terrestrial environments (Rieder et al., 2004). Modeling predicted that the removal of approximately half of the divalent cations from the precursor basalt simulates the current geochemistry effectively, which is reasonable for chemical weathering (Squyres et al., 2006b).

The Occurrence of Hematite at Meridiani Planum

Hematite was identified using Opportunity's Mössbauer Spectrometer and Mini-TES instruments (Klingerhöfer et al., 2004; Christensen et al., 2004). According to Mini-TES data, hematite spherules make up 2% of the rock by volume in all examined outcrops, and are not concentrated along bedding planes (Soderblom et al., 2004). They are also present as loose lag deposits, possibly deposited by erosion of an overlying hematite-rich layer and eolian transport of spherules across the plain and into craters. They have a range of sizes (0.6-6 mm in diameter) with an average diameter of 3mm (Christensen et al., 2004). Hematite in the soil is present as crystalline coarse-grain grey spherules and fragments. The total abundance for non-hematite components in the spherules from Mini-TES is less than 5-10% (Christensen et al., 2004). Mössbauer also detected hematite in spherule-free outcrops at approximately 36% (Christensen et al., 2004), and brick-red staining in RAT cuttings is consistent with the presence of fine-grained hematite (Squyres et al., 2004b).

At Victoria Crater, which is presumed to be up-section from earlier sites, the spherules are smaller. This could be related to a variation in the intensity of groundwater interaction with the sulfate-rich sand deposit, affecting the size of the diagenetic hematite spherules (Squyres et al., 2009; Metz et al., 2009).

Potential Meridiani Hematite Formation Mechanism

Multiple models for the formation of the Meridiani Planum hematite spherules have been suggested. Soderblom et al.'s (2004) initial hypotheses involved the formation of spherules within sediments during primary compaction under near-isotropic

permeability and near-static fluid conditions as seen in groundwater systems. This model involved the formation of hematite by replacement of sulfate minerals and precipitation in pore spaces from iron-rich fluids (Squyres et al., 2004b). Primary igneous minerals are not present in the spherule-bearing outcrop, indicating a significant degree of chemical alteration (Soderblom et al., 2004). The MER team invokes groundwater alteration of sulfate-rich sand deposits, concentrating fluids in iron and producing hematite spherules (Figure 7).

Squyres et al. (2005) refined this model, including episodic inundation by surface water to shallow depths, followed by evaporation, exposure, and desiccation as indicated by sedimentary features and geochemistry. Some of the spherules also have sulfate-rich coatings formed through interaction with the same environment that created the sulfate-rich outcrops from which they weathered. This process is believed to have occurred over an area of 500 by 250 km based on laser altimetry data (Hynek and Phillips, 2001; Bell et al., 2004; Wray et al., 2009). Groundwater upwelling at Meridiani Planum is supported by global groundwater modeling of ancient flow paths (Andrews-Hanna et al, 2007). Golden et al. (2008) also concluded that the spherules formed through aqueous processes. They were able to synthesize hematite spherules under hydrothermal conditions that were similar to those on Mars except for a great difference in size (Figure 8). It is likely that precipitation from a solute rich fluid is the mechanism based on these results.

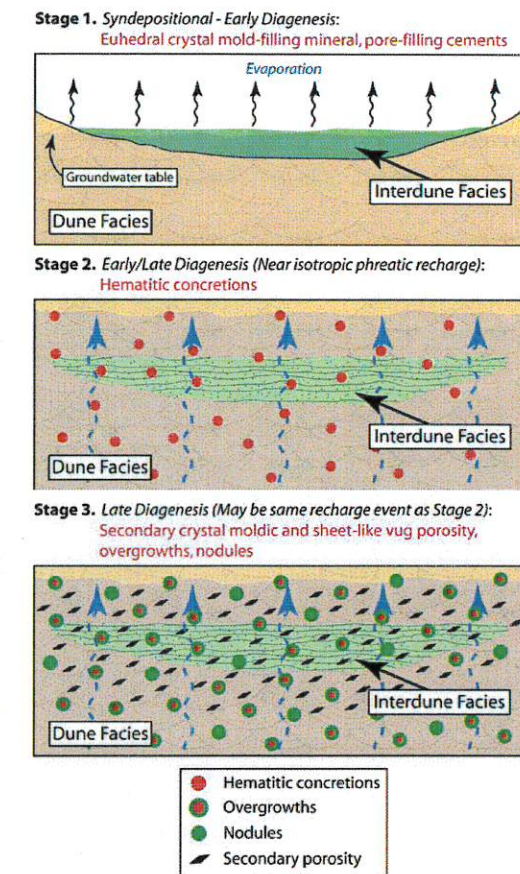


Figure 7. Diagenetic history proposed by McLennan et al. (2005). The figure shows early standing water evaporation to form sulfates in stage 1. Stage 2 shows groundwater interaction with sulfates to form hematite concretions. Stage 3 shows another less defined recharge event causing overgrowths of sulfate on hematite spherules and another vug forming phase.

The Occurrence of Sulfates and Jarosite at Meridiani Planum

Mössbauer spectrometry and Mini-TES detected the ferric sulfate mineral jarosite (general formula $[(K, Na, H_3O)(Fe_{3-x}Al_x)(SO_4)_2(OH)_6, x < 1]$) in many Meridiani Planum outcrop exposures, and Mini-TES detected 20 to 40% by weight Mg and Ca sulfates (Klingelhöfer et al., 2004). Hydrous and anhydrous sulfates could include kieserite ($MgSO_4 \cdot H_2O$), epsomite [$MgSO_4 \cdot 7(H_2O)$], and the Ca sulfate minerals anhydrite

(CaSO_4), glauberite [$\text{Na}_2\text{Ca}(\text{SO}_4)_2$], or gypsum [$\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$] (Christensen et al., 2004).

These findings of Mg- and Ca-sulfates are also supported by the high Mg, Ca, and S concentrations measured by APXS (Rieder et al., 2004).

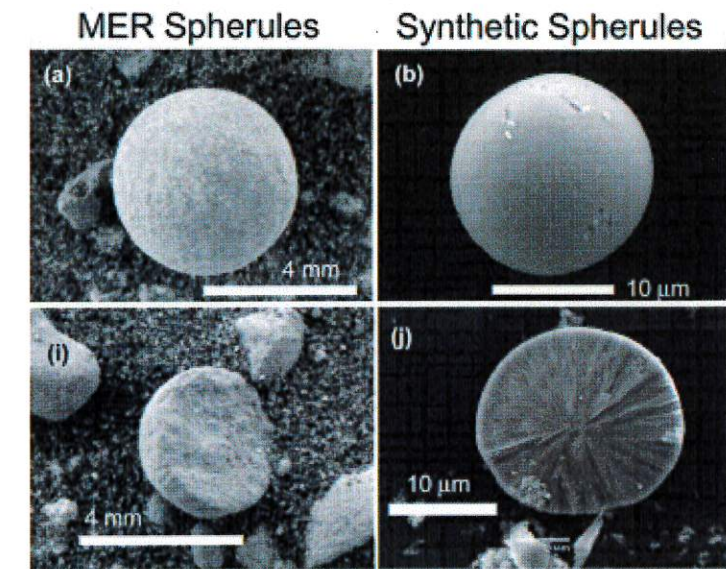


Figure 8. Comparison of Meridiani hematite spherules and synthetic spherules (Golden et al., 2008). Note the difference in scale. The synthetic spherules are products of hydrothermal precipitation.

Jarosite abundances greater than 5% were not detected by Mini-TES because it is difficult to detect in the presence of Mg- and Ca-sulfates (Christensen et al., 2004).

Mössbauer provided higher and more reliable values for jarosite abundance (Klingelhöfer et al., 2004). While the exact composition of the jarosite is unknown (Klingelhöfer et al., 2004), the APXS-determined elemental abundances (K, Na, Al, Fe, and S) for the outcrop are most consistent with Na-jarosite with possible minor Al for Fe substitution (Rieder et al., 2004) since there is insufficient K to account for all of the jarosite if it were the K-rich variety. The outcrop has 17 wt. % FeO, and 28% of this is in jarosite, indicating that

approximately 10 wt. % is jarosite, and the average outcrop density of 3.3 g/cm^3 from Mini-TES is also consistent with about 10 wt. % jarosite (Klingelhöfer et al., 2004).

Several hypotheses have been proposed to explain the formation of these mineral assemblages at Meridiani Planum. Rieder et al. (2004) proposed a model that involved water with sulfuric and hydrochloric acid from volcanic gases reacting with rock to form brines. Olivine would dissolve under these acidic and oxidizing conditions and Mg and Fe sulfates and silica would form (McLennan et al., 2003). Evaporation of this brine enriches the outcrop in sulfates, which were then eroded, transported, and then deposited and mixed with airborne siliciclastics, producing the multi-layer Meridiani outcrop (Rieder et al., 2004, Tosca et al., 2005).

Other studies conclude that the sulfate-rich deposits are the products of precipitation from brines at low temperatures (Elwood Madden et al., 2004), fluctuating water tables (McLennan et al., 2005), or extremely acidic aqueous conditions (Fernández-Remolar et al., 2004). Chevrier et al. (2006) proposed that these minerals are alteration products of Fe^{2+} -sulfates and ferric (oxy)hydroxides, which form stably in a $\text{CO}_2\text{-H}_2\text{O}$ atmosphere, under more oxidizing conditions. Dickinson and Rosen (2003) proposed that the water-based evaporites formed when atmospheric water vapor and brine films formed on the surface. Golden et al.'s (2008) experiments demonstrate that hematite spherules and jarosite can also form under hydrothermal conditions, suggesting that the alteration fluids involved could have been thermal (Figure 8). A similar mechanism has also been proposed based on examination of hematite and jarosite in a Martian meteorite (McCubbin et al., 2009).

Methods

Field Methods

Samples were collected between May and August 2010 from lava tubes and various basaltic flow features at the Craters of the Moon National Monument (CRMO) in south central Idaho. Figures 9 through 14 include photographs of example sample locations to show various relationships between samples and substrate. We focused on collecting basalt and secondary minerals from lava tubes, blisters, hornitos, and other features formed in the Blue Dragon flow.

Our main focus was on Arco tunnel, a more than 1 km long lava tube with known secondary mineral deposits (Sampling Map in Appendix C). This tunnel provided us with a reliable source of samples to expand upon the samples that Dr. McHenry obtained there in 2008. Samples were collected from the lava tube walls using rock hammer and chisel. Others were 'cave powder' samples, or loose mounds on the floor, which were scooped up and collected. For some samples, a piece of substrate basalt was also sampled to determine its composition relative to the deposits.

Meticulous field notes recording GPS location and surrounding features were taken. We sampled all encrustations with different appearance (including variation in color, hardness, location, and taste) in an attempt to obtain a sample representative of all minerals in the lava tube. During her previous visits, McHenry determined that many secondary deposits consisted of calcite. Since calcite is not a key mineral for this study,

these deposits were not sampled. Samples were preserved in sealable plastic sample bags and brought back to UWM for analysis.

Moonshine, Tom Thumb, Lava River, and unnamed caves (in the Wilderness Caves area, Figure 1b), along with protected exposures in lava blisters, shelly pahoehoe, and hornitos were also sampled to obtain a wider variety of sample locations and mineral occurrences. We also collected samples from a spatter cone and near-vent area with pits and very small caves in the Spatter Cone area (Figure 1b). Samples of fresh basalt were collected in previous years by Dr. McHenry to use as a control for our hypotheses of basalt alteration. In total, twenty-one samples were collected, including substrate samples, pure coatings, and some samples including both coating and substrate. Sample details are provided in table 2.

The second part of the study involved sampling standing water throughout the National Monument. As part of a Geo Corps project for the summer of 2010, Stewart Edie and I collected large amounts of data on all standing water, or water holes, throughout the Monument for a GIS file and future studies. The methods followed for this testing are documented in a Geo Corps project protocol (Version 4-14-2010, Appendix D). This protocol describes the task of collecting primary data on the waterholes spread across the National Monument and lava field. Waterholes are variably-sized bodies of standing surface water in the basalt field.

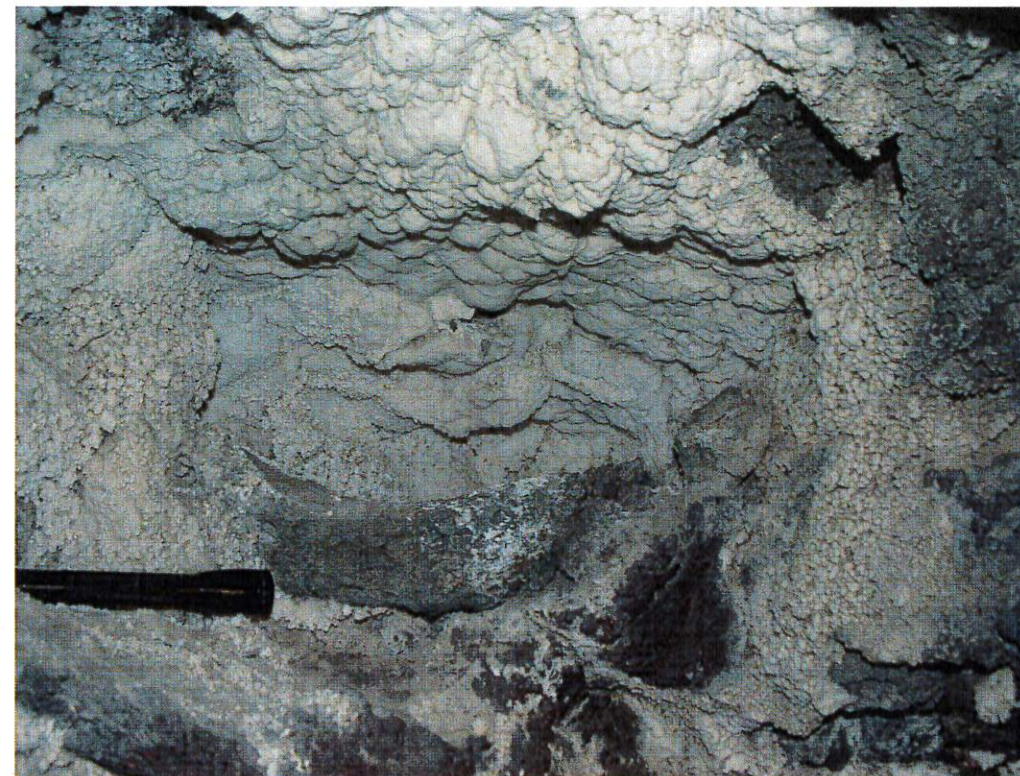


Figure 9. Sample 01: gypsum. Mini-mag light for scale (10 cm)



Figure 10. Sample 03: snow-like Na-sulfates. GPS for scale (7cm wide)



Figure 11. Sample 06: jarosite. Rock hammer for scale (neck 2cm wide)



Figure 12. Sample 15: powdery Na-sulfates. Field book for scale (15 cm long)

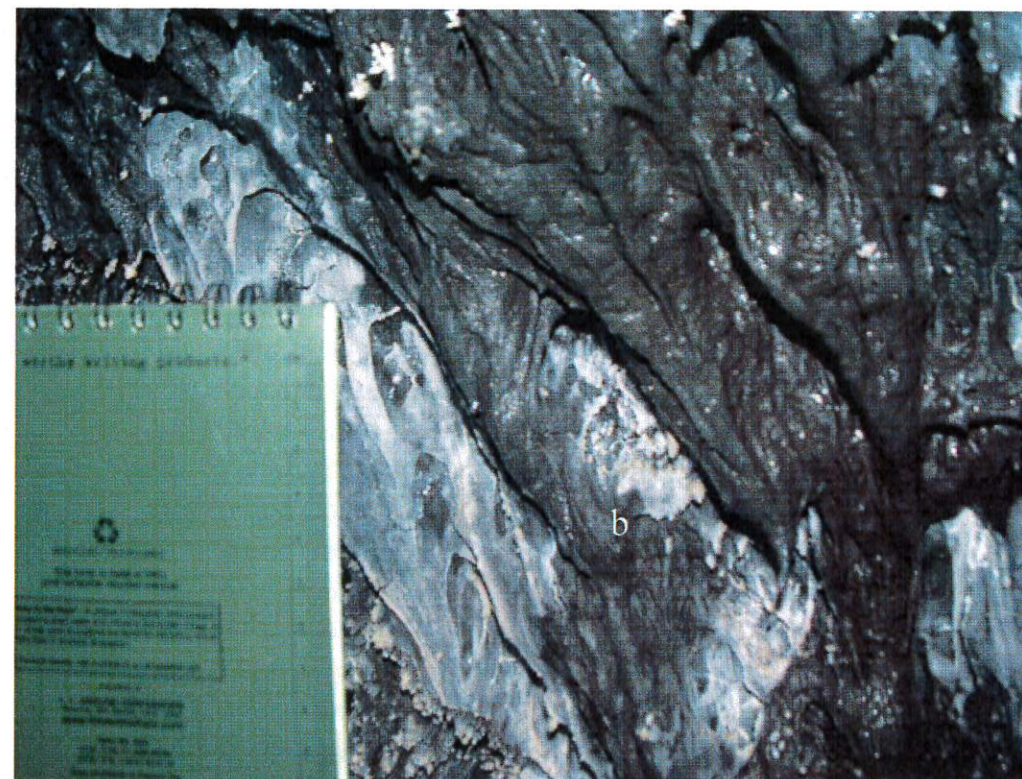


Figure 13. Sample 20: hematite with amorphous silica. Field book with cm ruler



Figure 14. Sample 05: calcite. Chisel for scale (20 cm)

Table 2. Sample number, type, and location.

	Sample Type	Sample Location
L-05	Unaltered Basalt	Lava River Cave
02(01)	Altered Basaltic Substrate	Spatter Cone
03S	Altered Basaltic Substrate	Moonshine Cave
08(07)	Altered Basaltic Substrate	Arco Tunnel
04	Specular Coating	Moonshine Cave
09	Specular Coating	Arco Tunnel
19	Specular Coating	Collapse Cave, Near Tree Molds
20	Specular Coating	Arco Tunnel
18	Yellow Rind	Collapse Cave, Near Tree Molds
06	Yellow Coating	Arco Tunnel
01	White Coating	Spatter Cone
05	White Coating	Arco Tunnel
12	White Coating	Arco Tunnel
13	White Coating	Arco Tunnel
03	White Powder	Moonshine Cave
07	White Powder	Arco Tunnel
10	White Powder	Arco Tunnel
14	White Powder	Lava Blister, Wilderness Caves Trail
15	White Powder	Hornito, Wilderness Caves Trail
17	White Powder	Lava River Cave
16	Crystalline Mass	Tom Thumb Cave

Samples arranged by type. Samples with numbers in parenthesis are substrate samples, and the second number tells which sample the substrate was sampled from. Also, 03S is the substrate sample associated with sample 03.

Water from precipitation usually quickly percolates through the highly fractured basalt to the deep Snake River Plain Aquifer, but in rare cases snow accumulates in cave entrances and rubble piles where it is protected from the sun, and turns to ice. This ice then acts as an aquitard and supports small perched aquifers. The first step of the project was to note the water hole's proximity to vents or lava tubes. Next we measured its dimensions and sketched a profile and took pictures clearly showing its dimensions and depth, and recording the azimuth at which the picture was taken. We then measured and recorded its conductivity and pH.

Water samples were collected from surface waterholes and subterranean pools in caves on and within the Blue Dragon lava flow to help determine the role of precipitation with respect to diagenesis at ambient conditions. We observed and documented the pH, conductivity, and temperature of the water at the time of collection. This preliminary conductivity and pH data will help us constrain the aqueous geochemical environment, and provide insight into the interaction of this meteoric water with the basalt. Temperature and dissolved species are directly related, since higher temperature water has the potential to dissolve more material in solution.

Two water samples of 125 mL from each pool were collected and filtered through 0.2 micron filters to eliminate further alteration of chemistry by biological processes. 1 mL of nitric acid (HNO_3) was added to one of the samples to preserve the cations in solution so that soluble materials would not precipitate. The other 125 mL sample was used for anion analysis and not preserved by acidification. We then executed a field titration to determine the amount of bicarbonate in the sample. This entailed collecting and filtering a 50 mL sample. The sample was titrated to a pH of 4.5 by dripping known amounts of 0.2 N hydrochloric acid (HCl) and the amount added was recorded to later determine the amount of dissolved bicarbonate. pH was monitored constantly during this process. Two samples were collected at each of the nine water hole locations visited. Sites were chosen based on the availability of water, and the proximity to collected mineral deposits.

The objective of the water sampling was to analyze pools sitting above the lava and pools in caves to determine if percolation through the lava has an effect on ion composition. This can help us determine the significance of ambient temperature water

interaction with the basalt. This interaction may play an important role in depleting the basalt in certain ions, and enriching the water in soluble ions that then precipitate onto cave walls as secondary minerals. A change in chemistry of the water after interaction with the basalt, will allow the determination of which ions are still being actively leached 2,100 years after the extrusion of the flow.

Analytical Methods

Analyses consist of data collection by means of X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscope (SEM), and electron probe microanalysis (EPMA) for mineral and rock composition and textural data, and aqueous geochemical analyses by Atomic Absorption and Ion Chromatography.

XRD analysis of twenty-two samples was performed at University of Wisconsin – Milwaukee in Dr. McHenry's X-ray laboratory. The purpose of this was to determine the minerals present in the samples (especially diagenetic phases) and determine the mineralogical differences between the coatings and the basaltic substrate. The samples were prepared by grinding the mineral encrustations from the surface of the rock with a dental drill, attempting to produce a pure sample of mineral powder. One gram of sample was necessary for analysis by both XRD and XRF. The powder was then ground in a mortar and pestle or shatterbox to reduce the grain size for optimal analysis. Acetone was at times used as a lubricant for grinding samples with the mortar and pestle to help further decrease the grain size. After the mineral coating was sufficiently separated, select samples of the immediately underlying substrate, from the exposed surface to

about 5 mm maximum depth, were also powdered. The substrates chosen for analysis were meant to be representative of substrates occurring under each different secondary mineral suite.

The resulting powders were mounted as random powders for XRD analysis. Sample JR-CM10-06 was a very thin layer and did not yield one gram of material, so it was instead mounted as a smear slide for XRD analysis. All samples were analyzed using a Bruker D8 Focus Powder XRD (Cu K α radiation), at 1 s per 0.02° 2 θ , 2°-60° range, with a Sol-X energy dispersive detector. The resulting diffraction patterns were smoothed and the background was removed to aid in the pattern matching process. The patterns were then compared to the ICDD database using Bruker's EVA pattern matching software, allowing us to determine the mineral assemblages and relative abundances.

When sample volume was limited, the powdered samples analyzed by XRD were reused for XRF analysis since no chemical change should occur during XRD analysis. XRF was used to quantify the elemental composition of the samples. Where sufficient material was available, Loss on ignition (LOI) values were determined by weighing samples, then heating specimens in porcelain crucibles to 1050°C in a muffle furnace and weighing again to determine loss of volatiles.

For XRF analysis, fused beads were prepared using the leftover powders. Approximately one gram of ammonium nitrate was added as an oxidizer, followed by 10.000 grams of Claisse 50:50 lithium metaborate: lithium tetraborate flux with an integrated LiBr non-wetting agent. Then 1.000 grams of sample was added and the materials were mixed thoroughly. The mixture was then poured into a platinum-gold alloy crucible and heated to approximately 1050 °C in a Claisse M4 fluxer using a ~20

minute pre-programmed routine. The resulting glass beads were then analyzed using a Bruker S4 Pioneer 4 kW WDS XRF spectrometer for major, minor, and some trace elements. Eleven USGS rock standards were used for calibration of major and minor elements. Statistical error was minimal for each element, and was nearly constant for each element between runs. Repeatability tests have been conducted on this instrument to determine instrument accuracy (McHenry, 2009a). The elements measured were silicon, titanium, aluminum, iron, manganese, magnesium, calcium, sodium, potassium, phosphorous, and zirconium.

Sixteen small chips from samples, consisting of alteration rind/diagenetic product and substrate, were selected and prepared for SEM analysis. This was done to determine compositional and textural differences between primary igneous minerals, glass, and diagenetic minerals. Chips were mounted in epoxy, exposed, and then polished using 6 μ m and 1 μ m diamond grits. The polished samples were then photographed under reflected light using a microscope and then carbon coated. Samples were analyzed using a Hitachi S-4800 Scanning Electron Microscope with a tungsten filament in backscatter mode (BSE) under vacuum using the Photo-diode backscatter electron detector at 15 kV accelerating voltage, 10 μ A emission current, and high probe current. A Bruker energy dispersive X-ray spectrometer (EDS) was used to qualitatively determine elemental compositions. Element maps created using EDS, along with line traverses and point composition, show the spatial distribution of elements. Targeted areas included the contacts between rinds and substrates, mineral concentrations around vesicles, and baseline substrates to determine the starting compositions.

Forty spots on the same mounts were also analyzed for quantitative elemental composition using a Cameca SX-50 electron microprobe at UW Madison using 15 kV accelerating voltage and 20 nA and a focused beam (for augite, titanomagnetite, and olivine), or 10 nA with a 5 μm spot size (for plagioclase).

Eight samples were sent to the University of Arkansas for analysis by near infrared (NIR) and Fourier transform infrared reflectance (FTIR) spectroscopy to help determine their water content and temperature of formation. FTIR spectra were recorded using a Nicolet 6700 Smart Diffuse spectrometer. A N_2 purge gas was used to reduce the interference of atmospheric gases such as H_2O and CO_2 . NIR spectra were collected in the range of 2850 - 10,000 cm^{-1} (1.0-3.5 μm) with a resolution of 2 cm^{-1} . This range optimizes the equipment ranges, such as source, beamsplitter and detector, and optimizes the signal to noise ratio. The configuration uses a quartz-halogen IR source, a CaF_2 beamsplitter, and a DTGS detector. Spectra were normalized to an Al_2O_3 (anhydrous) background spectrum. These samples were prepared as powdered samples and analyzed by Patricia Gavin at the Arkansas Center for Space and Planetary Science at the University of Arkansas.

The water samples from the eight sample locations were analyzed for the major cations calcium, magnesium, sodium, and potassium using a ThermoScientific iCE 3000 series atomic absorption spectrometer. The major anions analyzed were sulfate, chloride, phosphate, and nitrate, measured using a DIONEX ICS-100 ion chromatography spectrometer. The samples were diluted before analysis so ion concentrations would occur within the linear range of the instrument's maximum and minimum detection

limits. Parts per million (ppm) concentrations were measured and converted to molar concentrations and molar equivalence to help determine the total ion balance and percent of each species. An electrical balance was calculated, along with ionic strength, to determine the accuracy of analyses. Total dissolved solids (TDS) were calculated by placing 50 g of a water sample (it is assumed 50 g = 50 mL since the samples have little dissolved material) into an aluminum cup and drying them at 150° C for two days, then weighing the dried material. The TDS values were used to verify the quality of the ion analysis. Bicarbonate was measured in the field by titration with hydrochloric acid, which enables us to calculate the alkalinity. The alkalinity can be determined as follows:

$$\text{Alkalinity, meq/L} = \frac{(\text{mL acid})(\text{normality})(1000)}{\text{mL sample}} \quad (\text{Grundl 1993})$$

A Piper diagram of the aqueous geochemistry helps show trends in the water chemistry between the surface and the caves. The piper diagrams were created using a USGS program called GW_Chart

(http://water.usgs.gov/nrp/gwsoftware/GW_Chart/GW_Chart.html).

Results

XRD

Figures 15 and 16 show XRD plots, with representative patterns indicating sample mineralogy. Additional plots are provided in Appendix A. The results of the XRD analyses from mineral samples and select substrate samples are presented below (Table 3). The unaltered basalt sample (L-05) and the basaltic substrates (02, 03S, 08, 19S) reflect the original igneous mineral assemblage. The Blue Dragon basalt samples all contain plagioclase, and most contain pyroxene, hematite, and apatite ($(\text{Ca}_3(\text{PO}_4)_3 (\text{F}, \text{Cl}, \text{OH}))$). Olivine occurs only in the unaltered basalt sample.

Specular samples occur as thin, grey, partly metallic surface coatings with thicknesses usually less than 1 mm. These coatings occurred on the walls, ceilings, and floors in most sections of the lava tubes visited. The specular coatings collected (04, 09, 19, 20) are composed of predominantly hematite and plagioclase. All specular samples also have pyroxene in lower abundance than the fresh basalts, and all but one (09) have apatite.

The single yellow rind collected (18) occurred in a collapse feature in a ceiling collapse rock pile. This sample's mineral assemblage was dominated by plagioclase, hematite, and pyroxene, with lesser goethite. Yellow coatings were rare, and only a single sample (06) was collected from Arco tunnel, from a protected upper chamber about 6 meters above the floor. It was moist, thin, easily smeared and scraped, and

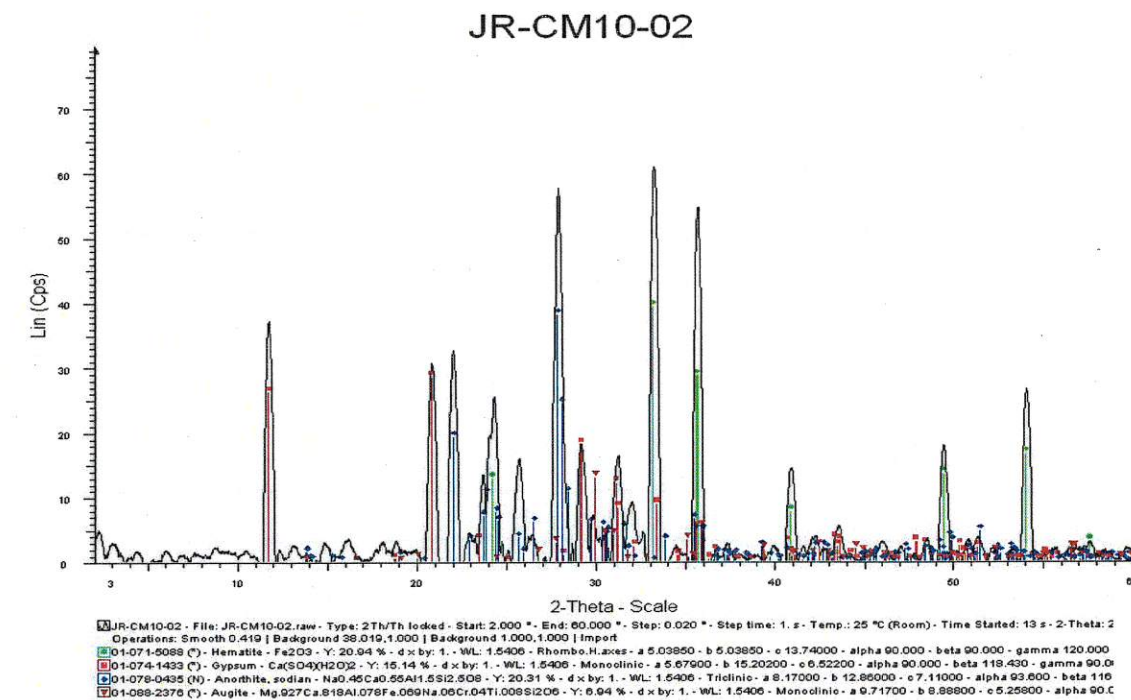


Figure 15. XRD plot generated using Bruker's EVA software, showing representative mineralogy. Sample 02 is an altered basaltic substrate beneath a gypsum-rich white coating (red), and contains hematite (green), plagioclase (blue), and pyroxene (brown). Y axis is in counts per second.

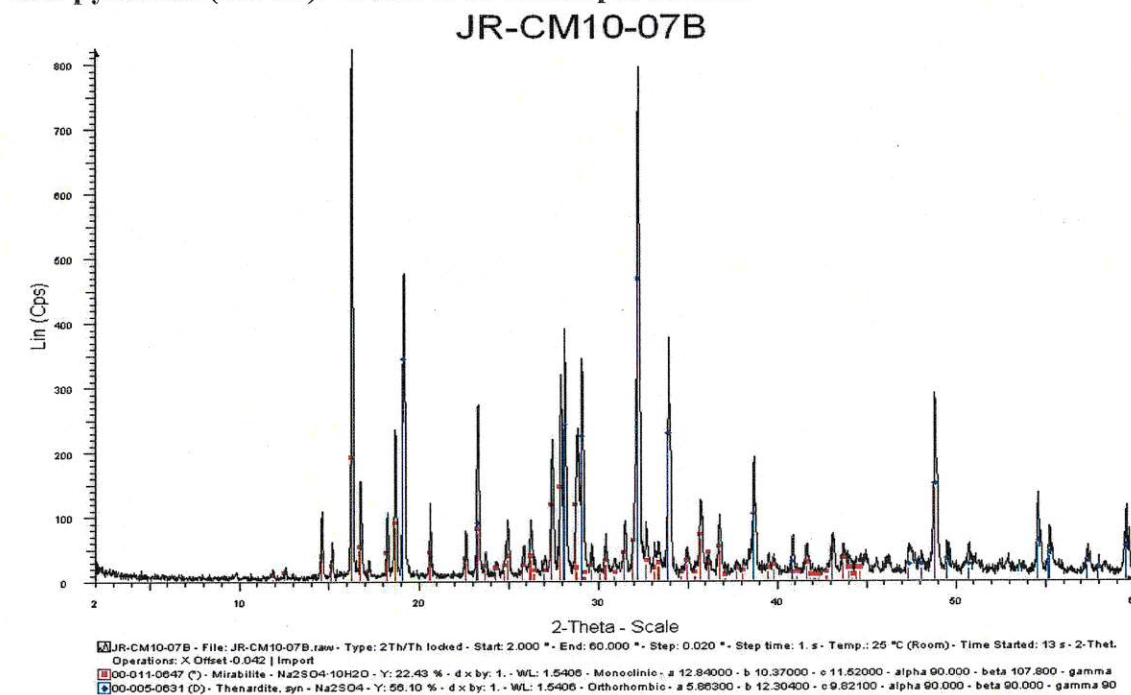


Figure 16. XRD pattern for sample 07, showing thenardite (blue) and mirabilite (red). Sample 07 is an example of Na-sulfate powder mounds.

Table 3. Sample Mineralogy

	Plagioclase	Pyroxene	Olivine	Apatite	Hematite	Goethite	Gypsum	Calcite	Thenardite	Mirabilite	Trona	Natron	Burkeite	Jarosite
Basalts														
L-05	XX	XX	XX	X	-	-	-	-	-	-	-	-	-	-
02(01)	XX	X	-	-	XX	-	+	-	-	-	-	-	-	-
3S	XX	-	-	X	XX	-	-	-	-	-	-	-	-	-
08(07)	XX	X	-	-	XX	+	+	-	-	-	-	-	-	-
19S	XX	+	-	+	XX	-	-	-	-	-	-	-	-	-
Specular Coatings														
4	XX	X	-	X	XX	-	-	-	-	-	-	-	-	-
9	XX	+	-	-	XX	-	-	-	-	-	-	-	-	-
19	X	+	-	+	XX	-	-	-	-	-	-	-	-	-
20	XX	X	-	+	XX	-	-	-	-	-	-	-	-	-
18	XX	XX	-	-	XX	+	-	-	-	-	-	-	-	-
Yellow Coating														
6	XX	+	-	+	XX	-	-	-	-	-	-	-	-	+
White Coatings														
1	-	-	-	-	-	-	XX	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	XX	-	-	-	-	-	-
12	-	-	-	-	-	-	-	XX	-	-	-	-	-	-
13	-	-	-	-	-	-	XX	-	-	-	-	-	-	-
White Powders														
3	-	-	-	-	-	-	-	-	XX	X	-	-	-	-
7	-	-	-	-	-	-	-	-	XX	XX	-	-	-	-
10	-	-	-	-	-	-	-	XX	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	XX	-	X	-	-	-
15	-	-	-	-	-	-	-	-	XX	+	-	-	-	-
17	-	-	-	-	-	-	-	-	-	-	+	X	XX	-
16	-	-	-	-	-	-	-	-	XX	XX	-	-	-	-

XX represents minerals in greatest abundance, X represents minerals that are present but in lower amounts, + means rare and - means absent. Sample 18 is grouped with specular coatings because it has the same general mineralogy as the specular samples.

contains a basaltic mineral assemblage with abundant plagioclase and hematite, some pyroxene and apatite, and jarosite, likely between 1-5% based on relative peak height.

White coatings (01, 12, 13) and off-white coatings (05) consisted of ceiling and wall coatings of variable thickness from approximately 7 cm to 0.5 cm. The nature of these coatings was highly variable, from soft crystalline crusts to hard, thin coatings on lava stalactites. Two samples (01, 13) are pure gypsum, and the other two (05, 12) are pure calcite.

White powder samples (03, 07, 10, 14, 15, 17) were collected from various sources. Sample 03 is mostly thenardite (Na_2SO_4) with some mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). There is a dehydration-hydration reaction that allows thenardite to rapidly convert into mirabilite and the reverse, based on temperature and relative humidity (Rodriguez-Navarro et al., 2000; Richardson et al., *in review*). Samples 07 and 15 are also a mixture of thenardite and mirabilite. Sample 10 is calcite sampled from a floor mound. Sample 14 is thenardite with a lesser amount of trona ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$). Sample 17 contains natron ($\text{Na}_2\text{CO}_2 \cdot 10\text{H}_2\text{O}$), burkeite ($\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$), and some trona. Finally, the crystalline mass (16) collected from Arco Tunnel from an area named 'mineral deposit' on the Arco Tunnel (Idaho Cave Survey, 1994) map had approximately equal amounts of thenardite and mirabilite. The proportions of mirabilite to thenardite likely do not reflect the original ratios since no precaution was taken to conserve the temperature and humidity of samples for transport and analysis.

XRF

The XRF results are presented in Table 4. OCBP1 is reported for comparison and represents the composition of a likely precursor basalt for the Burns Formation of Meridiani Planum from Morris et al. (2006), extrapolated from APXS data (Rieder et al., 2004). These samples also range from 14.1-17.1 weight % Fe_2O_3 , which is significantly higher than common terrestrial basalts, and higher than most high-iron basalts on Earth. TiO_2 and P_2O_5 are also high. CaO and Na_2O vary significantly between unaltered basalt and substrate samples. Sample 9B is a replicate analysis of sample 09 and the two analyses can be compared for accuracy. Specular samples, including 9B, show a slightly higher or equal concentration of SiO_2 compared to the basaltic samples. The yellow rind (18) sample is very similar in composition to the specular coating with its high Fe_2O_3 concentration.

White coating samples 01 and 13 have very low totals because they are predominantly sulfate and sulfur was not analyzed. Sample 12 is high in CaO and has a high LOI (consistent with its abundant calcite), but also has high SiO_2 and is depleted in all other oxides. The white powder samples have varying compositions and are thus difficult to describe as a group. Sample 10 is calcite, so it is enriched in CaO and has a high LOI. Samples 03, 07, 15, and 16 consist of the sulfate minerals mirabilite and thenardite, and have very low totals since sulfur was not analyzed. Sample 14 is similar, consisting of thenardite and trona but has a high LOI (attributable to the loss of CO_2 from the trona). Sample 17 consists of two hydrous Na-carbonate minerals and one Na-sulfate mineral containing carbonate, and has an unrealistically high LOI value that may need to be repeated.

Table 4. XRF results reported in weight percent

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Zr (ppm)	Sr (ppm)	Ba (ppm)	LOI	Total
Basalts															
L-05	47.97	2.93	12.50	17.06	-	3.34	7.05	3.18	1.89	1.96	-	299	1347	-	97.86
02	42.71	2.54	10.50	15.73	0.24	1.90	8.16	2.79	2.37	1.28	910	269	1433	8.70	96.95
03S	41.96	2.18	10.90	14.12	0.23	2.44	5.13	9.55	2.24	1.36	872	270	1337	1.20	91.38
08	45.44	2.50	11.80	15.69	0.25	2.79	6.07	5.17	2.45	1.57	938	265	1409	1.80	95.54
19S	49.00	2.57	12.50	16.94	0.27	2.89	6.25	3.27	2.17	1.60	1027	264	1604	1.20	99.66
OCBP1	48.19	1.01	8.06	20.23	0.43	10.40	6.46	2.19	0.75	1.37	-	-	-	-	99.09
Specular Coatings															
04	49.61	2.56	12.90	16.46	0.27	2.88	6.49	3.80	2.45	1.59	1068	272	1650	0.80	100.93
09	47.25	2.55	12.00	16.72	0.30	3.11	7.17	3.57	2.82	1.78	983	304	2508	2.00	99.32
09B	47.57	2.67	12.30	16.73	0.28	2.98	6.20	3.60	3.41	1.57	976	284	1529	1.50	98.96
19	48.26	2.53	12.30	16.40	0.27	2.80	5.75	3.93	2.43	1.52	1023	274	1506	1.20	98.45
20	46.99	2.48	11.50	16.73	0.27	2.84	6.84	4.04	2.41	1.51	938	312	1764	0.60	96.28
18	47.10	2.38	12.10	15.82	0.27	2.71	6.54	3.79	3.51	1.49	963	334	1837	-	95.84
White Coatings															
01	3.92	0.01	0.72	0.16	-	0.49	39.20	0.38	0.27	0.07	-	269	-	2.60	47.88
12	46.70	0.17	1.10	1.19	0.03	1.00	26.90	0.34	0.18	0.68	68	322	365	26.00	103.90
13	24.28	0.66	3.28	4.51	0.10	1.59	30.00	0.90	0.90	0.68	241	713	632	15.00	81.64

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Zr (ppm)	Sr (ppm)	Ba (ppm)	LOI	Total
	White Powders														
3	2.57	0.09	0.66	0.74	0.01	0.51	0.41	41.6	0.1	0.08	30	36	-	1.7	48.43
7	1.3	0.01	0.3	0.14	-	0.48	0.45	40.9	0.03	0.04	-	-	-	11	54.48
10	1.76	0.03	0.52	0.28	-	0.22	69.9	0.02	0.02	0.03	-	158	-	11	83.8
14	1.57	0.01	0.29	0.09	-	0.23	0.1	54.5	0.06	0.5	-	-	-	34	91.72
15	5.29	0.22	1.38	1.37	0.03	0.69	0.92	37	0.38	0.19	83	55	-	2	49.38
17	1.26	0.01	0.26	0.07	-	0.27	0.08	50.9	0.04	0.09	-	-	-	61.00	114.19
16	1.72	0.03	0.4	0.23	-	0.44	0.15	41.1	0.03	0.05	-	-	-	55	99.52

OCBP1 represents likely precursor basalt for Meridiani bedrock. Analytical errors were low (ppm range: McHenry, 2009) and thus not reported. Note that the calibration curve consisted of a variety of silicate igneous rocks, and is thus poorly suited for determining the compositions of sulfate and carbonate rocks. Sulfur was not measured, and sulfate does not volatilize during LOI analysis, so many totals are low.

FTIR

Eight samples were analyzed by FTIR, and characteristic reflectance spectra were obtained. Samples included L-05 (unaltered basalt), 01 (gypsum), 03 (mirabilite, thenardite), 09G (grey hematite), 09R (red hematite), 10 (calcite), 14 (natron, trona), and 19 (hematite). All samples exhibited a large absorption band near $3.0\mu\text{m}$, which is indicative of molecular water (Figure 17). This water could be in the sample, in the mineralogical structure, or on the sample's surface. Sample L-05 of basalt showed very weak bands, indicative of a slightly altered basalt. The weak bands that do appear may be alteration products, but the specific minerals cannot be identified at such low abundances. Sample 01 is consistent with the spectra for gypsum, sample 3 with mirabilite and thenardite, and sample 14 with natron and trona.

Sample 10, which is calcite-rich according to its XRD pattern, showed no bands except for at $3.0\mu\text{m}$. The characteristic spectrum for calcite usually has major bands at 2.3 and $2.5\mu\text{m}$ and minor bands at 1.9 and $2.0\mu\text{m}$, but these do not appear in our sample. Analysts at University of Arkansas (where the samples were analyzed) explain this discrepancy as possibly the product of amorphous silica, which are common alteration products in basaltic flows (Crisp et al., 1990). Amorphous silica does not have a signal in this range and could likely be "cancelling out" the calcite signal. This agrees with our idea that many of the calcite coatings formed simultaneously with amorphous silica, as is apparent in the high concentration of SiO_2 in some samples where only calcite is identified using XRD. Samples 9G, 9R, and 19 also have few bands, which is consistent with altered basalt and hematite, since neither have signals in the NIR range.

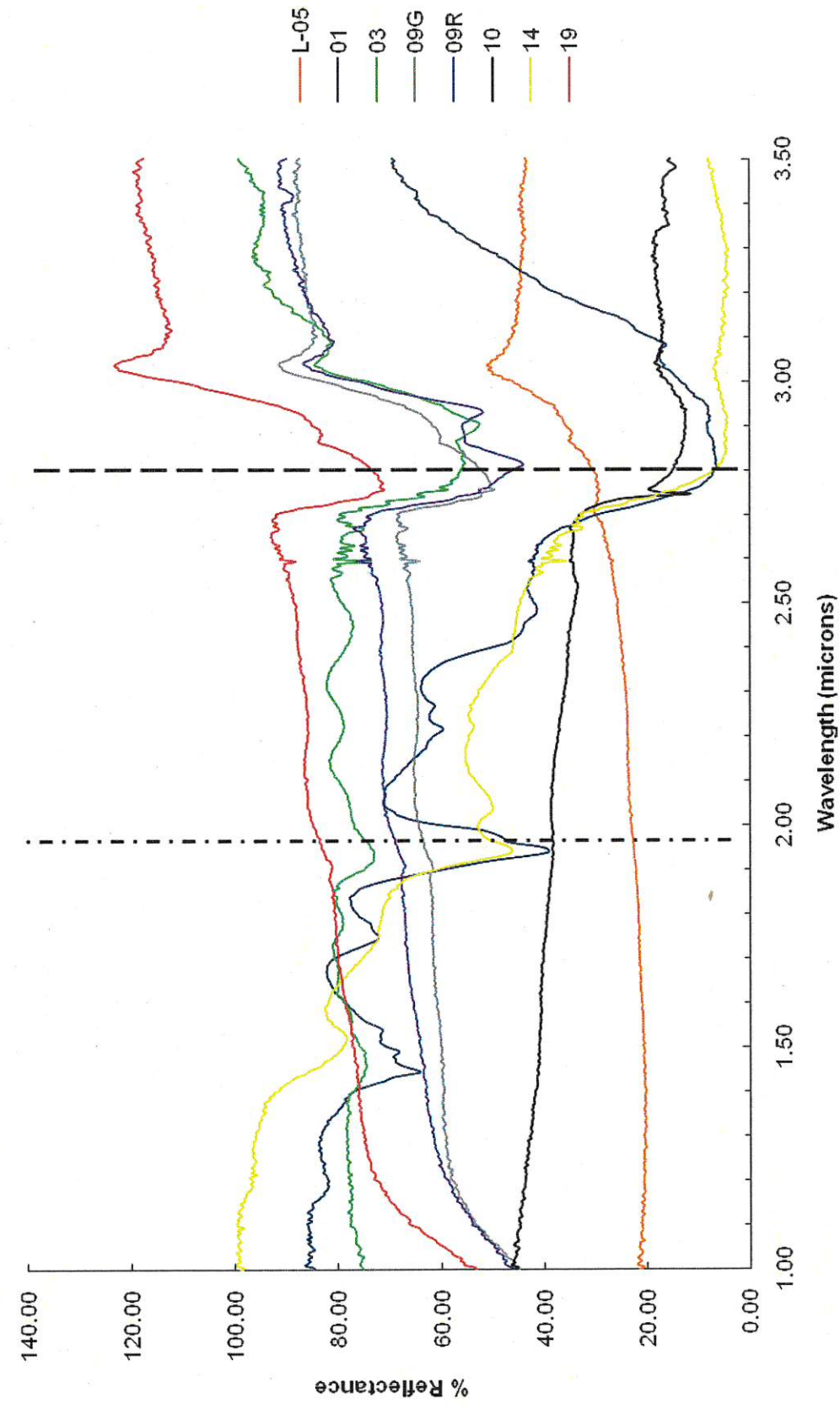


Figure 17. VNIR results. The dashed line just below 3.0 μm highlights the absorption band representative of water. The dash-dot line at 1.9 μm represents a characteristic absorption band for Na-sulfates in samples 01, 14, and 03.

SEM/EPMA

EPMA analysis and SEM using BSE and EDS provided a way to quantify the geochemical changes occurring on a micron scale. EPMA allowed for analysis of mineral grains, glass, and alteration rinds to determine the distribution of elements and quantitative abundance. The BSE images (Figure 18.a, 19.a) are labeled with X's showing the type of area sampled using EPMA. Exact locations of individual analyses cannot be replicated because the imaging and quantitative analysis occurred on two separate instruments. The trends presented by the EPMA data are clear and can be seen in Table 5. Appendix B provides supplementary SEM images depicting common basaltic substrate minerals and textures, gypsum coatings, and additional examples of hematite and silica coatings.

Table 5. EPMA results

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	BaO	Total
Augite											
04b-aug X ₂	35.3	2.8	8.62	17.0	0.7	10.5	20.3	0.56	0.0	-	95.7
04c-aug	33.7	1.96	5.77	13.4	0.4	8.61	26.2	0.75	0.1	-	90.8
15b-aug	35.2	1.84	6.18	21.9	0.6	8.76	15.0	1.81	0.3	-	91.6
16c-aug	41.1	3.33	7.76	17.0	0.4	8.47	20.6	1.60	0.3	-	101.0
19a-aug	42.7	2.47	6.20	15.3	0.4	10.3	21.4	1.00	0.1	-	99.7
Olivine											
12a-ol	48.9	0.33	0.95	11.8	1.3	24.8	1.53	0.50	0.2	-	90.3
12b-ol	36.8	2.46	0.47	21.4	0.9	22.8	0.78	0.02	0.0	-	85.6
16a-ol	33.8	2.22	1.94	31.7	0.8	24.6	3.36	0.85	0.4	-	99.7
Oxides											
2b-ox	0.76	18.9	2.64	64.1	0.4	3.39	0.05	-	-	-	90.3
4b-ox	0.73	2.18	0.69	82.1	1.1	1.43	0.45	-	-	-	88.7
4c-ox X ₃	0.50	0.92	1.61	72.9	2.9	9.41	0.44	-	-	-	88.7
05a-ox	0.09	24.0	1.88	65.2	0.8	1.72	0.15	-	-	-	93.7

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	BaO	Total
15a-ox	0.14	2.51	1.20	81.8	0.9	1.43	0.28	-	-	-	88.3
15b-ox	0.10	3.13	1.01	81.4	1.1	1.57	0.20	-	-	-	88.5
12a-ox	2.74	4.01	1.53	78.6	0.5	2.04	0.08	-	-	-	89.5
12b-ox	0.12	4.82	1.21	78.1	0.4	2.17	0.13	-	-	-	87.0
18b-ox	0.56	3.54	0.79	81.5	0.2	1.32	0.51	-	-	-	88.4
16c-ox	1.48	1.37	1.07	82.7	0.9	0.74	0.9	-	-	-	89.1
19a-ox	0.06	2.6	1.16	81.1	1.1	1.43	0.34	-	-	-	87.8
19aa-ox	0.31	2.19	1.26	81.2	1.2	1.44	0.58	-	-	-	88.1
Plagioclase											
03a-plag	56.6	-	26.8	0.64	-	-	8.98	5.07	0.9	0.2	99.2
04a-plag	56.0	-	27.4	0.85	-	-	8.87	5.62	0.6	0.2	99.5
X ₁	62.2	-	19.4	4.02	-	-	2.65	6.82	3.0	1.0	99.1
04c-plag	63.7	-	18.8	2.84	-	-	1.41	7.01	4.4	0.8	99.0
15b-plag	57.2	-	26.7	0.88	-	-	7.98	5.96	0.9	0.1	99.7
18a-plag	58.1	-	25.5	2.12	-	-	8.06	5.76	0.7	0.3	101.0
15a-plag	69.8	1.01	16.2	3.02	0.0	0.17	0.17	1.73	4.5	-	96.6
Other											
01c	46.5	0.28	35.7	4.79	0.4	2.01	3.8	2.66	0.5	-	96.6
15a-si-ca	44.8	0.0	0.02	0.12	0.0	0.3	29.0	0.02	0.0	-	74.3
15b-si-ca	61.9	0.17	22.0	2.24	0.0	0.05	4.12	7.2	1.9	-	99.6
12a-si-ca	47.9	1.76	2.8	18.3	0.5	10.1	17.5	0.58	0.1	-	99.6
18a-si-ca	34.0	3.61	0.63	26.1	0.6	0.41	32.1	0.23	0.1	-	97.8
18b-si-ca	30.3	5.72	1.91	24.9	1.7	0.46	30.4	0.73	0.1	-	96.3
18b-si-ca	33.6	3.14	4.18	21.8	0.9	0.61	28.8	0.41	0.1	-	93.5
19a-si-ca	38.8	0.86	13.2	16.3	0.5	6.85	22.3	0.65	0.0	-	99.5
19aa X ₄	91.4	0.06	0.28	0.28	0.1	0.3	0.67	0.04	0.1	-	93.2
19aa X ₅	5.73	0.0	0.06	0.32	0.0	0.58	53.4	0.2	0.1	-	60.4
01b	13.4	4.44	10.1	33.9	0.6	1.02	1.73	0.0	0.0	-	65.0
02a	57.8	0.0	26.5	1.09	0.0	0.0	9.04	4.9	0.7	0.1	100.0
16b-ox-si	59.6	2.52	12.4	9.82	0.2	1.79	3.19	0.0	0.0	-	89.4

Quantitative EPMA analyses in wt. %, X₁₋₅ denote approximate locations of analysis on BSE images below. Olivine compositions range from Fo₅₈-Fo₇₈, and plagioclase compositions range from An₄₇-An₅₅

Figure 18 shows a BSE plot and element maps for an area of sample 04. Na₂O, Al₂O₃, SiO₂, and K₂O decrease rapidly over this traverse of less than 30 μ m from the interior of the substrate to the exterior. FeO is more than 85 times more concentrated in the exterior layer than in the interior. Silica, aluminum, calcium, and sodium partition

into plagioclase, while iron is concentrated in iron-bearing minerals. The abundance of iron oxides in the substrate is significantly lower compared to the rim, where they concentrate in a layer that parallels the exterior of the basalt. Spot X₂ is augite, with higher MgO, lower SiO₂ and higher CaO, FeO, and TiO₂ compared to the substrate. X₃ is almost completely iron with some magnesium. This zone likely represents the specular samples run in XRD and is most compositionally compatible with hematite.

Sample 19 (Figure 19) shows another iron-rich rind with an additional coating. This coating is a mixture of calcium and silica as is apparent from EDS element mapping. EPMA data provides quantitative results for these coatings (X₄, X₅). The calcium-rich coating has a low total because carbon and oxygen were not analyzed. Also, this calcium enrichment is not likely apatite, because the phosphorous element map shows no concentration in this layer (Fig 19.e), and it is not gypsum because gypsum shows a characteristic striated pattern when polished, as is apparent in BSE images of sample 01 (Appendix B Figure 37). Apatite also coats vesicle walls and forms exterior layers in some samples (Figure 20).

When viewing these two alteration patterns together, a progression of minerals layers can be seen. It appears that augite concentrates at the rim first, mixed with minor amounts of iron oxide. Then iron oxide forms a successive layer, but this layer seems to be discontinuous with the basalt, as gaps between it and the substrate are apparent in the BSE image. Sample 19 also contains a layer of mixed calcite and silica over the hematite layer. Also, nearly all calcite samples analyzed were present in a layer on top of the hematite layer. This was also observed in sample 15 (Figure 21), which also seems to repeat calcite and silica layers.

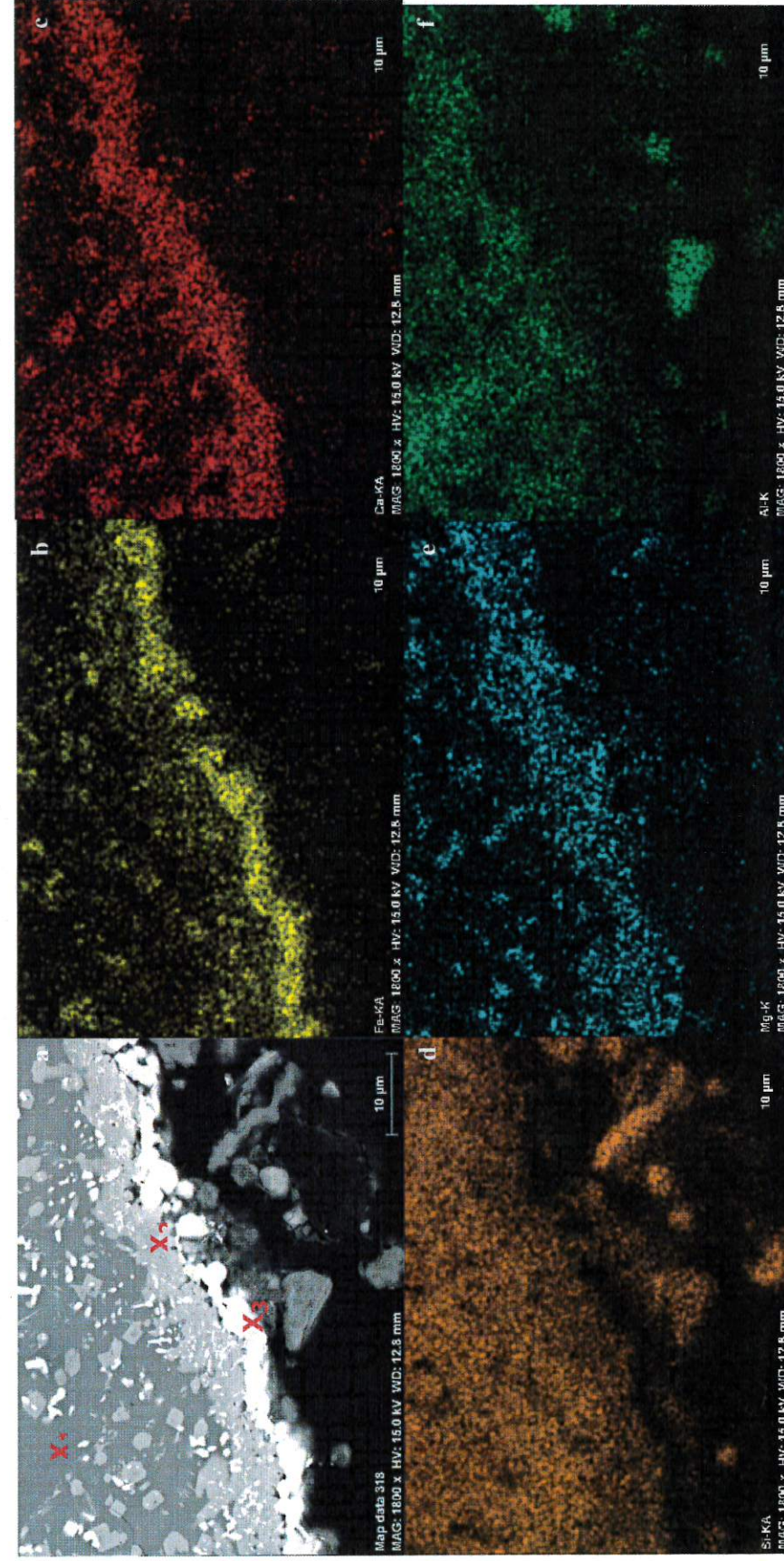


Figure 18 a) BSE image of specular coating of sample 15. X₁₋₃ represent EPMA analysis locations provided in table 6 b) EDS-generated Fe distribution of same image c) Ca distribution d) Si distribution e) Mg distribution f) Al distribution. Na₂O, Al₂O₃, SiO₂, and K₂O decrease from X₁ to X₃. The FeO concentration is 85 times higher in the rim than in the interior. Spot X₂ is augite. X₃ is almost completely iron with some magnesium, likely hematite.

19. a) BSE image of edge of sample 19. X_{4,5} represent EPMA analysis spots provided in table 6. EDS generated elemental distribution: Fe, Ca, Si, P, and Al, respectively. b) Slight Fe enrichment in a thin layer shows the hematite layer. c) Ca and d) Si enrichment is seen in the outermost layer. e) The absence of P suggests calcite, and the absence of XRD data for a Si-rich phase suggests that it is amorphous. f) Al distribution

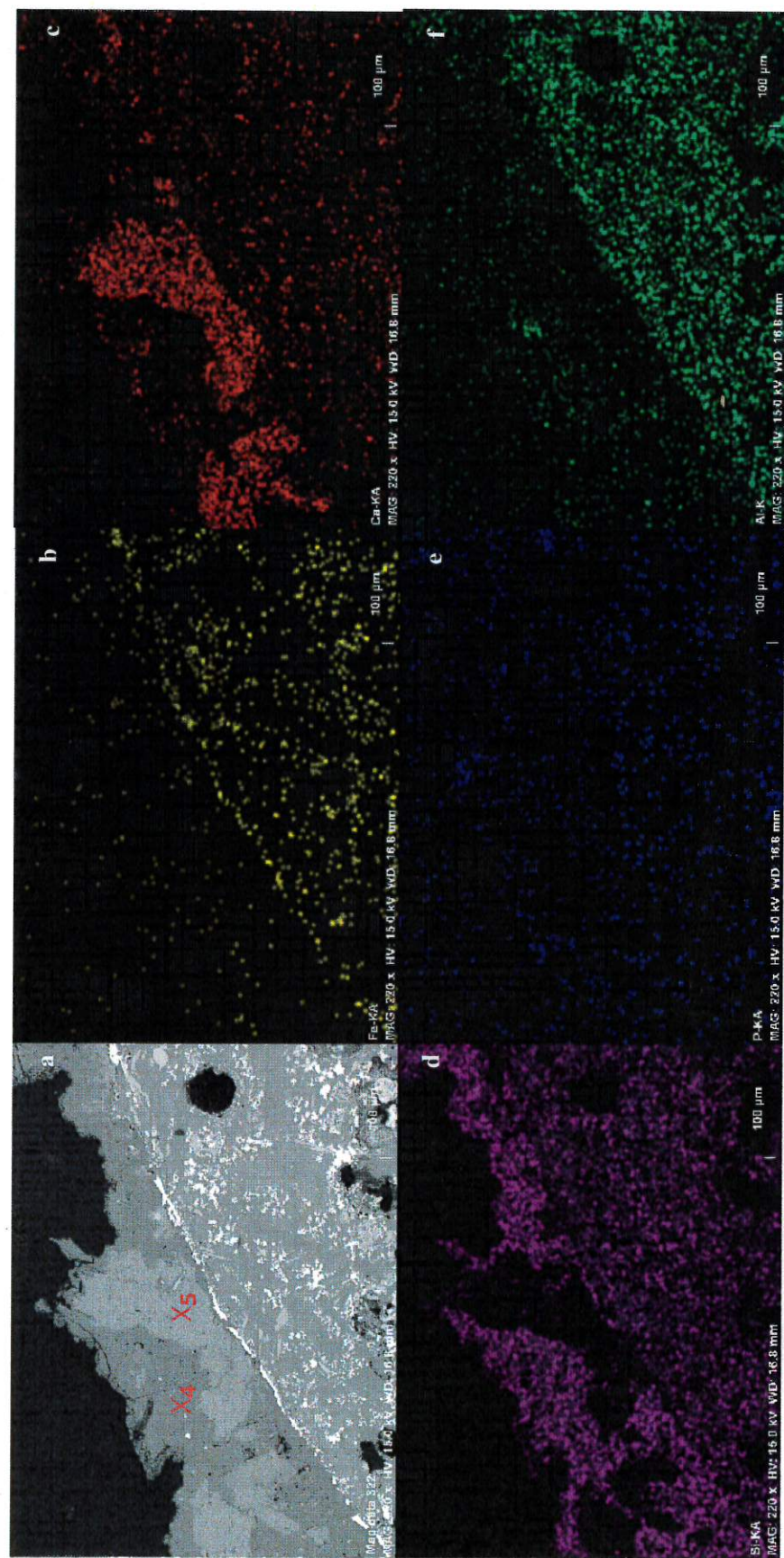


Figure 19. a) BSE image of edge of sample 19. X_{4,5} represent EPMA analysis spots provided in table 6. EDS generated elemental distribution: Fe, Ca, Si, P, and Al, respectively. b) Slight Fe enrichment in a thin layer shows the hematite layer. c) Ca and d) Si enrichment is seen in the outermost layer. e) The absence of P suggests calcite, and the absence of XRD data for a Si-rich phase suggests that it is amorphous. f) Al distribution

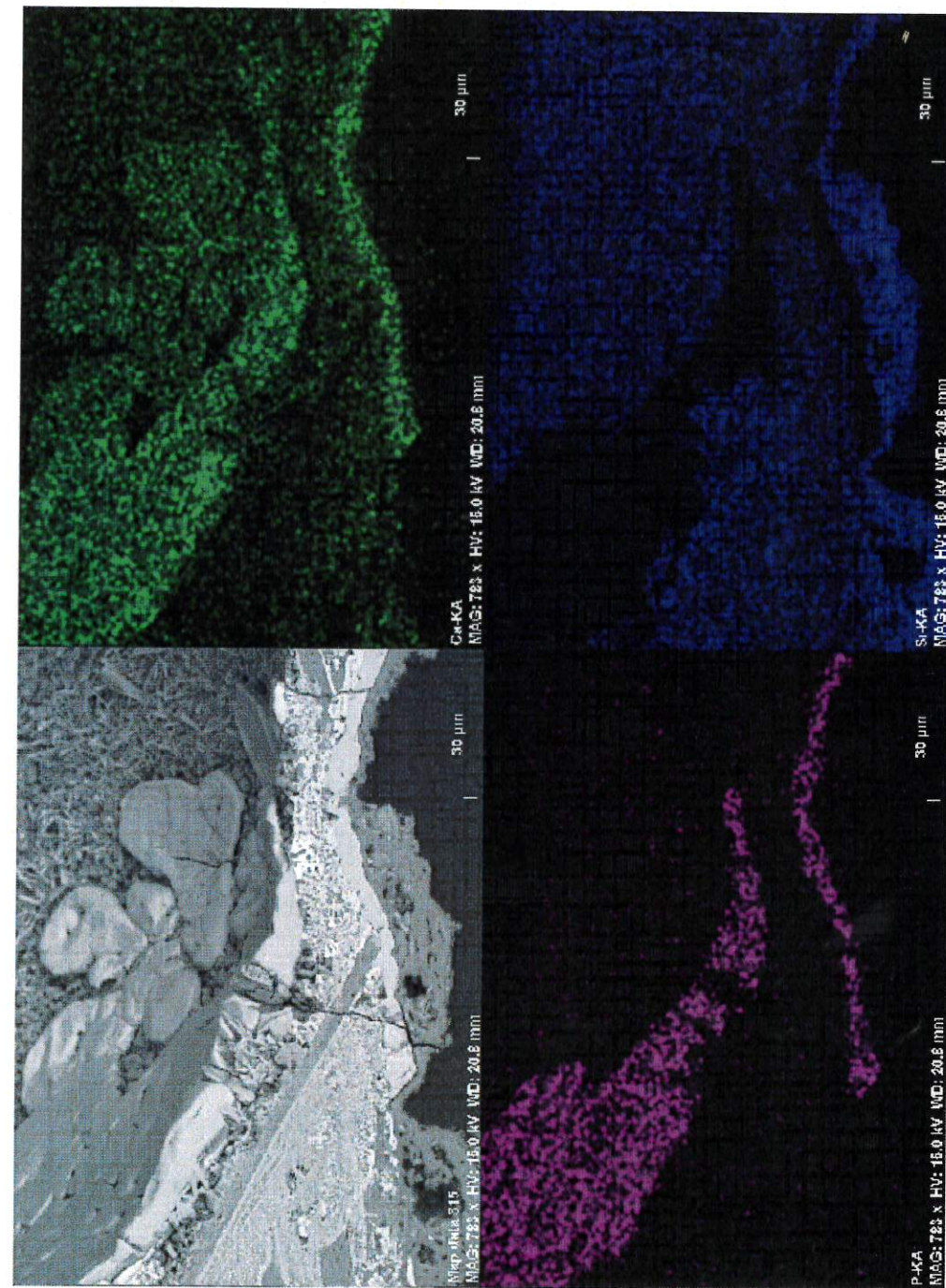


Figure 20. Sample 16 BSE image and element maps for Ca, P, and Si. The figure shows a vesicle in the upper right and the cave interior at the bottom. Apatite is clearly forming on both of these exposed surfaces, highlighted by enrichment in Ca and P

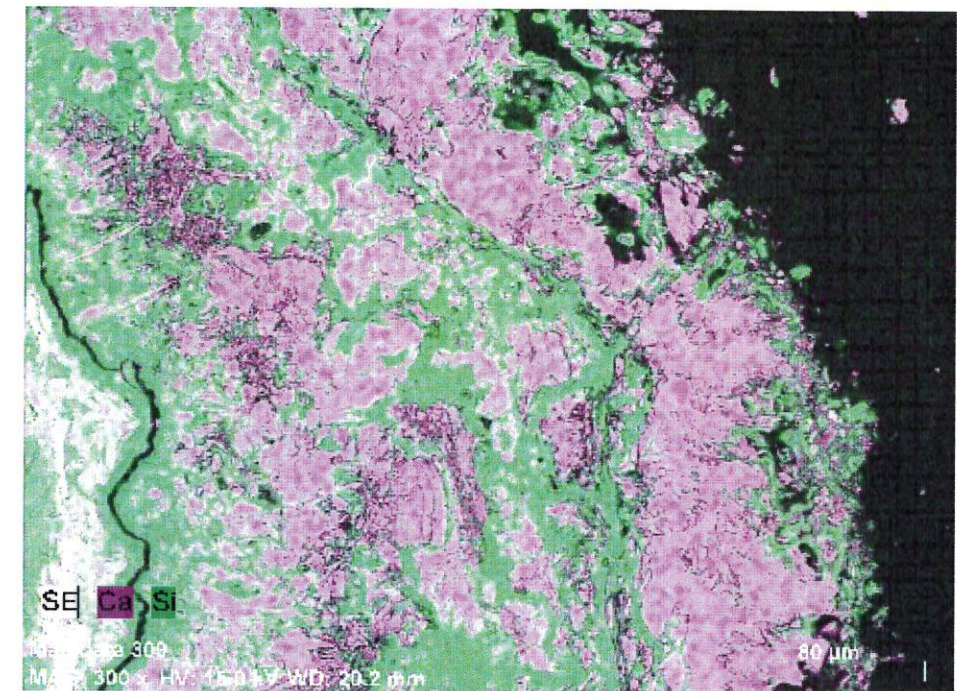


Figure 21. Deposition of silica and calcite layers in sample 15. Color overlay depicts concentrations of calcium (pink) and silicon (green).

Aqueous Geochemistry

Nine water samples are compared for this investigation (Table 6). Eight of the samples were collected for this investigation, seven from caves, one from a surface waterhole, and one collected from the National Atmospheric Deposition Program/ National Trends Network from Craters of the Moon National Monument (ID03) on Inferno Cone (<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=ID03>). The precipitation analysis is an annual mean weighted concentration from 2009. HCO_3^- was not reported, so it was assumed to be zero. The well analysis is from USGS scientific report 2010-5116. Though the USGS study analyzed many wells over time, the analysis chosen represents the general trend of well analyses from this report. Specifically, this

sample is from the 152 m depth, which is consistent with the inferred depth of the Snake River Plain aquifer at CRMO. The analyzed samples from our investigation were all undiluted, or at a 1:1 ratio. Figure 22 shows that cave interior waters group together even though some caves are kilometers apart. The cave waters are enriched in Na^+ and K^+ cations and HCO_3^- anions. The samples are very low in total dissolved solids. Pit Craters represents the only surface water sample. This sample is enriched in Ca and SO_4^{2-} in comparison to cave interior samples and depleted in Na^+ and HCO_3^- (Figure 22).

	Ca^{++}	Na^+	Mg^{++}	K^+	HCO_3^-	PO_4^{3-}	SO_4^{2-}	NO_3^-	Cl^-	pH
	(ppm)	(ppm)	(ppm)	(ppm)	(meq/l)	(ppm)	(ppm)	(ppm)	(ppm)	
Arco Tunnel 1	3.4	7.6	0.8	0.5	24.4	-	1.288	0.499	3.0	6.9
Arco Tunnel 2	3.2	4.9	0.8	0.3	24.4	-	3.664	7.615	1.3	6.6
Arco Tunnel 3	3.5	12.6	0.9	0.8	24.4	-	3.328	8.764	1.4	6.8
Beauty Cave	6.9	60.3	1.2	2.5	26.8	0.35	4.322	9.368	1.5	7
Boy Scout	6.0	13.1	1.3	2.7	30.5	2.336	6.694	21.39	6.4	6.8
Moonshine	7.4	8.0	1.0	0.9	30.5	0.413	4.676	7.322	2.0	5.9
Pit Craters	9.0	3.2	0.6	0.7	9.76	-	20.77	5.943	1.5	6
Surprise	5.6	6.3	0.7	0.4	30.5	2.561	4.131	5.537	1.4	6.8
CRMO Precip	0.46	0.708	0.036	0.046	-	-	0.76	0.48	0.58	5.74

Table 6. Aqueous geochemistry from caves, waterhole, and precipitation. Pit Craters represents a surface waterhole.

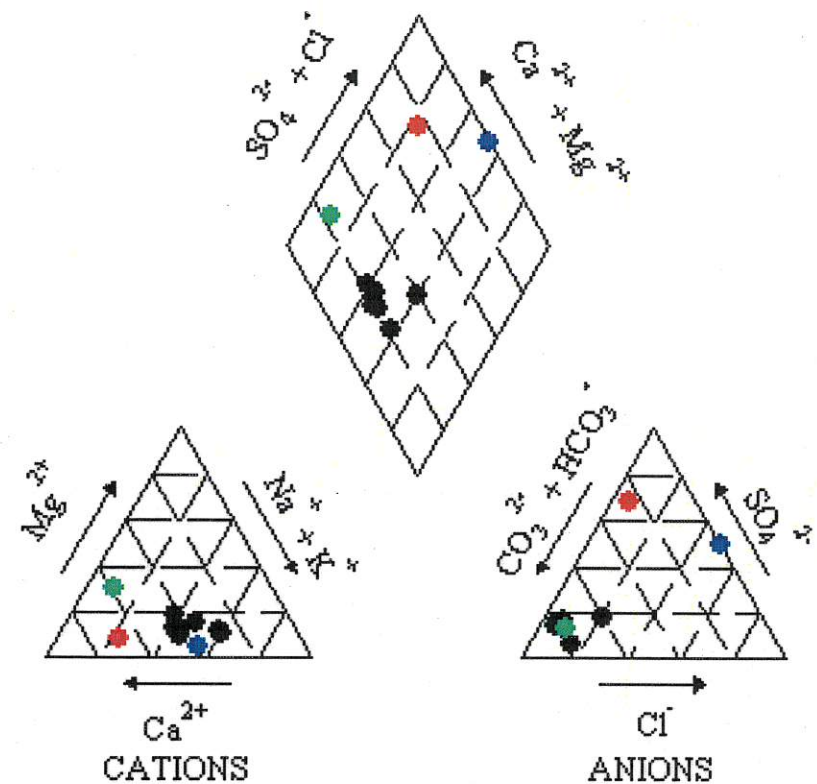


Figure 22. Major ion compositions of CRMO water sources. Samples include cave interior (black circles), surface waterhole (red circle), 2009 mean precipitation (blue circle) and a monitoring well (green circle). The gridlines are set to 20% intervals. Cave interior samples are relatively depleted in Cl^- , Ca^{2+} and have higher CO_3^{2-} and HCO_3^- .

Discussion

Basic Observations

The results detailed above present a complex pattern of primary igneous crystallization, diagenetic and secondary mineralization, and aqueous geochemistry. The XRD results provide a clear picture of the initial igneous composition, the secondary mineral assemblages, and the changes with cooling. XRF and EPMA data detail element mobility and the formation of new minerals at high to low temperatures in a system with a low water-rock ratio. The SEM data show the textural relationships, depicting the sequential formation and precipitation of minerals. The water data are consistent with the secondary mineralogy, where the sulfate abundance is lower in cave water than in rain and surface water. The cave waters are also enriched in Na^+ , K^+ , and bicarbonate, likely a product of leaching ions from the basalt or eolian dust deposited on the basalt.

Mineralogical and Geochemical Comparison between Unaltered Basalt, Substrate, and Coatings

Mineralogical (XRD) and geochemical (XRF, SEM) data show significant differences (and key similarities) between the unaltered Blue Dragon Flow basalt, the slightly altered substrate, and the surface coatings. All samples, including altered basalts and basaltic substrates, have less olivine than the unaltered basalt, a clear indication of alteration processes. Olivine is the least stable mineral in basalt under surficial

weathering conditions and is the first to break down (Reynold, 2008). The breakdown of Fe-rich olivine likely began at high temperature where it oxidized, allowing iron exsolution and the simultaneous enrichment in magnesium of the original mineral (Haggerty and Baker, 1967, Bandfield et al., 1990). The specular coating samples differ little in elemental composition from the unaltered basalt despite their lack of olivine (Figure 23). It is thus likely that these coatings are a product of in-situ basaltic alteration, where cations were not removed.

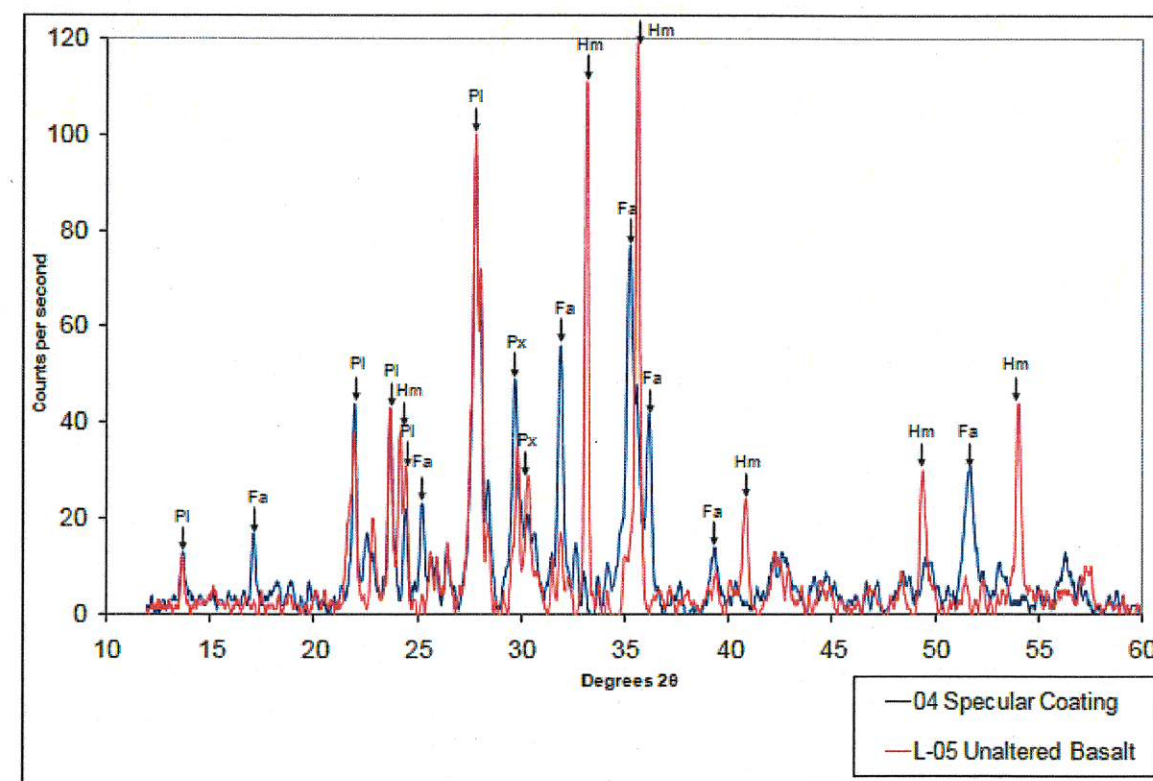


Figure 23. Comparison of XRD patterns from unaltered basalt (red) and specular coating (blue). Plagioclase (Pl) and pyroxene (Px) abundances are comparable, while the coating lacks olivine (Fa) and the unaltered substrate lacks hematite (Hm).

Element enrichment and leaching patterns relative to unaltered basalt help to constrain element mobility in the samples (Figure 24). Unaltered basalt shows the

general composition of the substrate before alteration, and the specular coatings have the same compositions since they were formed by in-situ alteration. The white coating sample shown in Figure 24 contains calcite and amorphous silica, and shows a corresponding enrichment in SiO_2 and CaO and decrease in all other elements because of dilution. The presence of calcite suggests that this sample is likely a product of ambient temperature meteoric precipitation in the cave rather than early, high-temperature processes (Forti, 2005).

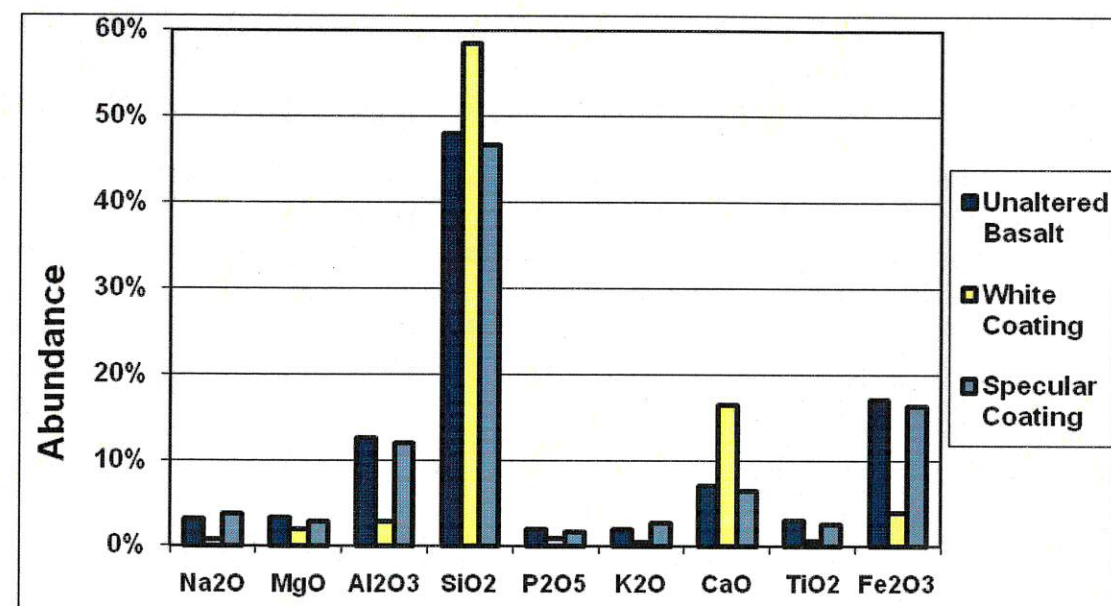


Figure 24. Comparison of elemental abundances of unaltered basalt, white coating (calcite and amorphous silica), and the specular coating. Note the similarity between the unaltered basalt and the specular coating, and the increase in SiO_2 and CaO in the white coating (dominated by calcite and amorphous silica).

SEM and EPMA data show many of the same compositional trends as XRF, but on a micron scale. The SEM images show the relationship between the basaltic substrate and the alteration products along the cave interior. For example, the hematite observed in the XRD patterns of the specular samples appears to be largely concentrated in a thin rim

(<10 μm). Iron from the basalt (especially the easily altered olivine) likely oxidized to form hematite as a discrete layer during high-temperature, possibly deuteric alteration, or alteration during solidification of the lava in contact with either exsolved or introduced water (Winter, 2010). This, and other potential models for hematite formation, are described in more detail in a later section.

The concentration of augite and apatite in vesicles and along cave walls is possibly a product of primary igneous cooling, where crystallization along the cave interior occurred more slowly because of continued heating from lava flow and gases within the tube. Devitrification of basaltic glass can also form surface pyroxene clusters, and can occur at elevated temperatures (Minitti et al., 2005). Sample 03S (the substrate of a Na sulfate sample) shows a higher degree of alteration, where both olivine and pyroxene have been destroyed yet plagioclase remains. Goethite is present in only two samples in very low amounts, and may have formed by the alteration of hematite or jarosite at low temperatures.

CRMO Aqueous Geochemistry

The aqueous geochemical data suggests that ion leaching is not a very productive process at CRMO, because there is not much variation in dissolved ions. The pH is also usually near-neutral, which lessens the ability of water to dissolve minerals and transport soluble ions. It is possible that our sampling resolution was insufficient, since few caves and only one surface pool were sampled. It is also possible that the water undergoes a significant change between the surface to the cave. The water could interact with the

basalt as it travels through, picking up sufficient ions and then precipitating them. The water pooling in the caves would then be representative of water that has recently precipitated secondary minerals and is now depleted in ions.

Adsorption to the surface of oxide minerals, including hematite, is a significant process and could cause the decrease in calcium and the increase in sodium from the surface due to replacement at adsorption sites on the surface. Surface area is directly related to the density of surface sites available for cation adsorption, and in hematite this plays a significant role in the aqueous geochemistry. The surface area of hematite is affected by crystal size and mass. (Langmuir, 1997; Davis and Kent, 1990).

PHREEQc modeling (Parkhurst and Appello, 1999) completed by Richardson et al. (*In review*) used the composition of dripping cave water in Blue Dragon lava tubes to determine saturation of minerals in this aqueous system. In these simulations, cave waters were allowed to equilibrate with CIPW-NORM calculated basaltic mineralogy, then allowed to evaporate (<10-20%). Calcite and a metastable Na-sulfate mineral, sodium heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), became oversaturated and precipitated. Thenardite and mirabilite can form from this metastable form during dehydration under ceratin conditions (Hall and Hamilton, 2008).

Hematite Formation

It is difficult to determine how the discrete hematite layer formed on the cave interior. Hematite cannot be a direct mineral phase crystallized from melt because oxygen fugacity and pressure conditions do not support its formation thermodynamically

(Catling and Moore, 2003). Freeze-thaw cycles or cryodesiccation of aqueous nanoparticle suspensions of hematite can form coarse-grained hematite, but this mechanism is not likely at CRMO due to lack of abundant standing water, and also because hematite occurs on ceilings and walls as well as floors (Madden et al., 2010). One possible model for its formation is that exsolved iron in this layer was mobilized by hydrothermal processes created by the high-temperature volcanic gases in the cave. This iron then quickly oxidized with exposure to the cave gases.

Another possible model for the formation of the hematite layer is the high-temperature oxidation of basaltic glass. Oxidizing conditions can cause "a coupled migration of divalent cations and charge within an oxidizing glass" (Minitti et al., 2005). Atmospheric oxygen oxidizes Fe^{2+} in the glass, and oxygen reacts with Fe, Ca, or Mg to form oxides on the surface. Fe^{3+} then migrates inward by transferring electron vacancies to interior Fe^{2+} cations, while Fe^{2+} cations move outward to form additional oxides (Cooper et al., 1996). Minitti et al. (2005) experimentally created hematite layers less than 1 micron thick, while those in the CRMO images are 2-3 microns thick. This difference in thickness could be a result of variation in the availability of Fe^{2+} or the length of time of exposure to high-temperature oxidizing conditions. This model does not require the presence of water to form hematite and is consistent with a volcanic origin. Cook and Cooper (2000) showed experimentally at 700°C that FeO concentrations above 1.9 weight % favors Fe migration over Ca and Mg migration. The presence of a Ca and Mg-rich pyroxene layer beneath the hematite layer in CRMO samples with specular coatings is consistent with this observation.

Experimental work has shown that hematite can form from the oxidation of fayalite over a wide range of temperatures approaching 1000°C (Banfield, 1990), which suggests that this transformation occurred at high temperatures. Further investigation into the presence of other olivine breakdown products must be conducted to specify a temperature range of oxidation for the olivine, but a high-temperature origin is likely. Additional specialized FTIR analyses on the hematite coatings (e.g. methods of Golden et al., 2008) could also help distinguish between high and low temperature hematite formation.

Carbonate and Silica Formation

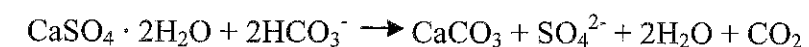
The sedimentary amorphous silica forming the outermost layers are also probably products of igneous mineral breakdown followed by precipitation, though this most likely occurred at lower temperatures. Olivine and pyroxene weathering releases Fe and Mg ions that can form oxides and sulfates, but excess silica is also a product of this weathering (McLennan, 2003). The precipitation of secondary silica does not require hydrothermal conditions, and it can thus form alongside calcite in a cave environment. Silica formation is not likely a product of acid-sulfate solutions leaching other cations (e.g. Chemtob et al., 2010) and leaving behind a silica-rich layer since the silica is often associated with calcite, a mineral easily leached by acidic solutions. It also occurs on top of the hematite layer, and acidic solutions have not been observed at CRMO.

Calcite formation is limited by the partial pressure of CO₂ in seeping meteoric water, which can be limited by the lack of soil above the lava tubes (Forti 2005). Small

amounts of eolian dust in cracks may provide carbonate for calcite formation. Calcite thus occurs in much lower abundances in the young CRMO lava tubes than it would in older lava tubes with a thicker soil cover or in limestone caves. Available Ca^{2+} ions can also decrease over time because of insufficient release from basaltic minerals. However, calcite can also be produced where gypsum is dissolving due of the common ion effect.

Sulfate Formation

Gypsum is a common product of groundwater precipitation, as is calcite. The preferential formation of calcite over gypsum in many lava tubes at CRMO could be a result of the common ion effect. Since gypsum is much more soluble than calcite, it dissolves, releasing Ca^{2+} cations. The water then becomes oversaturated in Ca^{2+} and precipitates calcite. This reaction (below) also releases sulfate anions into the water, which could be a source for the other sulfate minerals forming (Langmuir, 1997):



There could also be a near-vent constraint on these precipitates, since gypsum was found as a thick rind in a small spatter cone with an exposed chamber, while it was rare or absent in most other samples. Calcite was found as thin coatings in many locations within the basaltic flow. This may be a product of higher sulfur concentrations near the original volcanic vent. Examining more near-vent environments would help clarify this distinction.

The Na-sulfate and carbonate minerals are probably products of ambient-temperature ion leaching by percolating meteoric water. They are not direct weathering

products of authigenic basaltic minerals, because they occur as floor mounds with distinct contacts with the underlying basalt. This is corroborated by the water composition data, which shows an increase in Na^+ from the surface to the cave floor. The solutions likely become oversaturated in this ion and combine with leached sulfate and bicarbonate to form the various sodium-rich minerals. Richardson et al. (in review) determined (using PHREEQc) that the metastable mineral sodium heptahydrate ($\text{NaSO}_4 \cdot 7\text{H}_2\text{O}$) can precipitate from CRMO waters. This mineral could then alter into the observed assemblage of more stable sodium sulfate minerals.

The jarosite coating is the most difficult to explain. Jarosite forms under acidic, oxidizing conditions with low water:rock ratios, and while it can form under fumarolic conditions, it is often short-lived, breaking down rapidly into more stable iron hydroxide phases (Elwood Madden et al., 2004). Fine-grained jarosite would not be expected to last for 2,000 years in an environment with near-neutral, dilute fluids (Elwood Madden et al., 2008).

Jarosite was only observed once in this study, in a protected area on the cave ceiling near one of the highest points in Arco Tunnel. Low pH groundwater is an unlikely driver for the production of this mineral since precipitation, surface water, and water collected within the caves all have near neutral pH. The oxidation of Fe^{2+} bearing minerals under water-limited conditions can lead to localized acidic conditions, locally lowering the pH into the jarosite stability field (e.g. McHenry et al., 2011).

However, Fe^{2+} is not likely readily available at the surface of most CRMO lava tubes since the ubiquitous hematite layer contains oxidized iron. Glass or igneous minerals such as pyrite, pyroxene, or olivine beneath the hematite layer could be the

source of the Fe^{2+} , and local cracks or collapse features could expose them to oxidation, a process that can lower the pH (Tosca et al., 2008). If pyrite is leached the resulting fluids contain sulfuric acid, which can both lower the pH into the jarosite stability field and provide the Fe^{3+} and SO_4^{2-} needed for jarosite precipitation. However, pyrite was not identified by XRD or by casual inspection of CRMO basalt thin sections in this study. It is likely present, but not in abundance. Thus, the oxidation of other Fe^{2+} -rich phases were likely involved instead (or in addition), which would require a separate source for SO_4^{2-} . The relatively thin roof in this area may also provide for low humidity and high evaporation, leading to a low water:rock ratio, which is important for preserving jarosite. Microbial oxidation of Fe^{2+} can also explain jarosite formation (Daoud and Karamanev, 2006).

Peck (1974) interpreted a larger jarosite occurrence in a CRMO spatter cone chamber as the product of groundwater leaching of ions from basalt followed by precipitation. However, the 200+ meter depth of the water table at this site, coupled with the semi-arid environment and the extremely high conductivity of the basalt, make it impossible for the water table to reach the lava tubes. Interaction with water is limited to meteoric water from local precipitation or snowmelt percolating downward.

Karlo et al. (1980) invoke a fumarolic origin for the sulfate minerals, and their attrition through groundwater dissolution. This may be the case for some minerals (possibly gypsum), but is less likely for the most soluble minerals (such as the sodium sulfates). Some of the sulfate mounds we sampled had returned to full size (approx. 50 g) and "healed" our sampling scars in only 43 days. This suggests that these sulfate mounds are products of ongoing precipitation at low temperatures. CRMO sulfate mounds may be

seasonal features, since some specimens appeared smaller in October than in June of the same year (McHenry et al., 2010). A study of sulfur and oxygen stable isotope geochemistry could help define the sources of each.

A Mineralogical and Geochemical Comparison between CRMO and Mars

The geochemical and mineralogical patterns observed at CRMO are in part analogous to those observed at Meridiani Planum on Mars, and could provide insight into processes of formation. First, the results show that all substrate (including 19S) and unaltered samples are trachy-basalt based on the total alkali versus silica diagram, and the precursor Martian rock is basalt (Figure 25). The high iron concentrations of CRMO basalts make them an excellent Mars analog, since Mars basalts are similarly enriched in iron (Table 1, Figure 26) and since iron diagenesis largely controls the secondary mineralogy at Meridiani Planum (Squyres et al., 2004b). Hematite is an abundant secondary mineral at both sites, and jarosite is also observed at both (though more abundantly on Mars: Rieder et al., 2004). Secondary silica has also been observed at both Meridiani Planum and Gusev Crater on Mars (Squyres et al. 2004c).

However, there are also some major mineralogical differences between CRMO and Meridiani Planum. For example, Mg and Ca sulfates are abundant at Meridiani Planum (e.g. Christiansen et al., 2004) but absent at CRMO (except for occasional gypsum, mostly found near vents). The sulfate mineral assemblage at CRMO is instead dominated by Na sulfate phases, which have not yet been observed at Meridiani Planum. Minor amounts of Na-sulfates (along with Fe- and Mg- sulfates) have, however, been

proposed in Martian evaporitic basins based on spectral interpretation (McLennan et al., 2005; Zhu et al., 2006; Mangold et al., 2008) and possibly as a component of the Martian regolith based on chemical modeling (Tosca and McLennan, 2006). Calcite also appears to be rare on Mars (Fernández-Remolar et al., 2010).

A comparison between the chemical compositions of the calculated precursor basalt of the Burns Formation and CRMO basaltic samples is presented in Table 4 and Figures 25 and 26). The two have similar SiO_2 , MnO , CaO , and P_2O_5 concentrations. CRMO has higher concentrations of TiO_2 , Al_2O_3 , Na_2O , and K_2O , while the Burns Formation has higher Fe_2O_3 and MgO .

The significant differences in mineral assemblage between Meridiani Planum and CRMO can be attributed to many causes. First, the precursor basalts differ in composition. Second, alteration fluids at CRMO are near-neutral and dilute, whereas acidic brines are often invoked for Meridiani Planum (Squyres et al., 2006a). Third, while CRMO is considered semi-arid for Earth, it has much higher aqueous activity than would be expected for most if not all of Martian history. Finally, the Blue Dragon Flow is only 2 kya, while Meridiani Planum is likely well over 3.0 Gya (Squyres et al., 2005). Thus, slow alteration processes have had much longer to reach completion on Mars. Given these major differences in environment and history, it is perhaps more surprising that the two sites have as much in common mineralogically as they do.

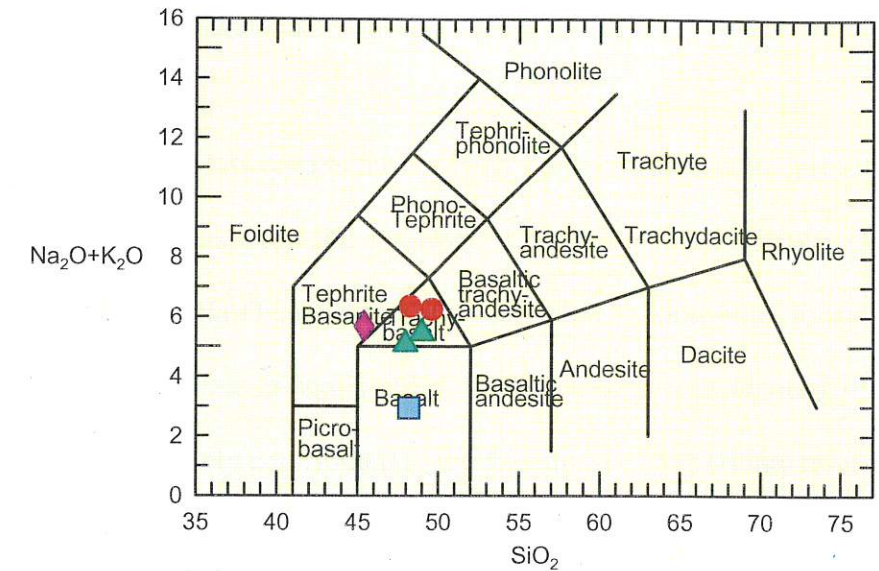


Figure 25. Total alkalis versus silica diagram in wt. %, with CRMO basalts as green triangles (L-05, 19S), specular coatings as red circles (04, 19), Maui basalt as a pink diamond, and calculated Meridiani precursor basalt as a blue square (OCBP-1). The CRMO basalt has a higher concentration of alkali elements than Meridiani but differs less than Maui in silica.

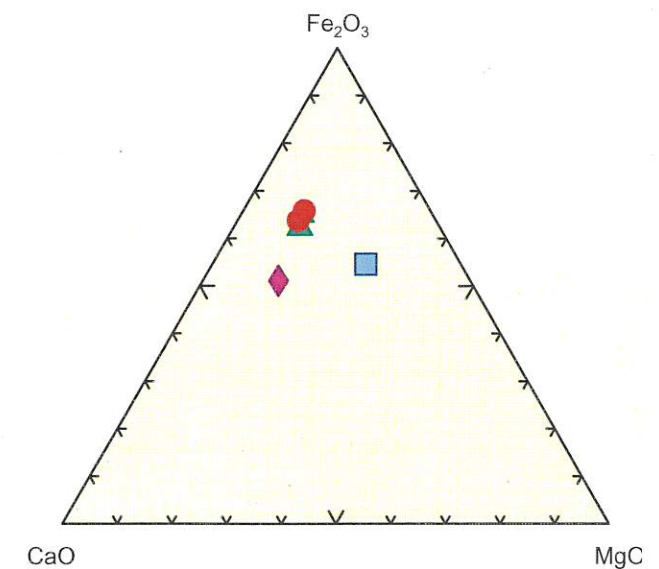


Figure 26. Ca-Fe-Mg Ternary diagram at 10% intervals. The CRMO basalts (green), specular coatings (red), and Meridiani Planum basalts (blue) have similar Fe_2O_3 proportions, but differ slightly in the relative concentrations of MgO . Maui (pink) differs in all three components. Symbols represent the same samples as in Figure 25.

Sulfate Minerals: CRMO vs. Mars

CRMO and Mars basalts have similar CaO concentrations, yet differ in their Ca-bearing alteration phases (calcite at CRMO, Ca sulfates at Meridiani). CRMO lavas have significantly higher Na₂O concentrations, which likely contributes to the formation of abundant sodium sulfate minerals. Higher MgO at Meridiani Planum, in addition to more acidic conditions, likely contributed to the formation of Mg-sulfate minerals (Glotch and Bandfield, 2006).

Experiments have yielded multiple possible explanations for the origin of jarosite on Mars. For example, Golden et al.'s (2008) experiments demonstrate that both hematite spherules and jarosite can form under hydrothermal conditions (Figure 8). In these experiments, Mg-Al-Fe-SO₄-Cl solutions precipitated minerals through forced hydrolysis with variable temperature and experimentation time. Hydronium jarosite formed in a 4-hour run from hydrothermal solutions at pH 1.2-1.5. At 150°C and a 16 hour run, both hydronium jarosite and hematite spherules formed. The initial hydronium jarosite is metastable, and it undergoes dissolution and precipitates an intermediate ferric hydroxide species that polymerizes into hematite. As the reaction series progresses, hydronium jarosite completely reacts to form hematite.

Golden et al. (2008) compared their experimental hematite spherules to natural spherules from Mauna Kea. They found compositional impurities in both. Their proposed model for Mars is that acid-sulfate solutions interacted with basalt at a low water-to-rock ratio, dissolving olivine and pyroxene and releasing Fe and precipitating jarosite. Hydrothermal conditions then dissolved jarosite to form hematite at

temperatures above 100°C, yet the reaction did not go to completion because jarosite would react completely if the reaction reached equilibrium.

Other models for jarosite formation are more consistent with our suggested analog (e.g. Elwood Madden et al., 2004). Simulating a wet Meridiani Planum using a sulfate-rich fluid with trace amounts of all cations and a generic basaltic mineral assemblage, their model predicted the formation of Na- or K- jarosite along with amorphous silica and an iron hydroxide phase. The minimum concentration of aqueous sulfate necessary to produce jarosite in their model was 0.96 mg/L, and our surface aqueous solution contains 20.77 mg/L. This would provide sufficient dissolved sulfate to produce jarosite in the CRMO system. The system also requires an oxygen fugacity above 10^{-50} . They also establish that a low water:rock ratio is needed to preserve the jarosite and gypsum weathering products, because progress towards equilibrium causes early-formed minerals to become unstable and be replaced by other Fe-bearing phases. This means that basaltic weathering on Mars likely did not go to completion (Elwood Madden et al., 2009). Basaltic weathering at CRMO has also not gone to completion, and jarosite is only present under specific conditions.

A water-limited environment on Mars also helps explain the presence of sulfate salts. Since they are highly soluble, they must have been deposited from an aqueous solution that evaporated and stayed dry until present day, preserving the salts. CRMO is a relevant analog in part because it is also water-limited, since it occurs in a high desert and water in the lava tubes is also limited. This has been integral for preserving soluble sulfates after aqueous deposition under semi-arid conditions, though annual variations in sulfate mineral accumulations at Craters of the Moon suggests a seasonal effect.

Hematite Formation on Mars vs. CRMO

Proposed hematite formation mechanisms for Mars include precipitation from iron-rich water (Christensen et al., 2001b ; Soderblom et al., 2004; Squyres et al., 2004b), hydrothermal activity (Catling and Moore, 2003), deuteritic alteration of lava, or burial-induced thermal alteration (Glotch et al., 2003). Oxygen fugacity in lavas on Mars is proposed to be similar to Earth or lower, and so primary igneous hematite is not possible (Catling and Moore, 2003; Christensen et al., 2001a).

Catling and Moore (2003) argue that their reconstruction of the Martian paleoatmosphere is consistent with slightly reducing conditions and thus not sufficiently enriched in oxygen to oxidize these extensive regions. Instead, they believe thermally dissociated water oxidized the iron in a hydrothermal environment. In hydrothermal systems iron solubility is positively correlated with temperature, and larger grain size precipitation is favored at high temperatures, approximately 100°C or higher (Kwak et al., 1986; Catling and Moore, 2003). This would be consistent with the specular hematite detected at Meridiani Planum (>5-10 μm) (Christensen et al., 1993).

Heat from burial and later exhumation and exposure is an unlikely heat source since kilometers of burial would be necessary to reach the needed temperatures. An impact could provide the needed heat, but the presence of sand-sized basaltic grains makes an air-fall origin unlikely as well (Christensen et al., 2001a). As detailed in the previous section, experimental hydrolysis above 100°C produced jarosite and hematite. Hydrothermal activity does not require standing surface water and requires only an iron-rich source, which could be the ferric sulfates.

This would be consistent with our hydrothermal model for the formation of the CRMO hematite. Hydrothermal fluids, in this case the result of percolating meteoric water heated by the fresh lavas, could have dissolved iron and precipitated the hematite-rich layer on the cave interior. It is also possible that the CRMO hematite formed without interaction with liquid water, as a result of oxidation of basaltic glass under high temperature conditions (e.g. Minitti et al., 2005). The possibility of a water-free formation of specular hematite in a high-iron basaltic environment at CRMO could suggest that liquid water was not required to form the Meridiani Planum deposits.

Habitability

One of the main objectives of the Mars Exploration Program (MEPAG 2008) is to determine the potential past habitability of Mars. Since water is required for all known life on Earth, evidence for past aqueous activity could indicate past or current habitable environments. The MER Opportunity landing site was selected in part because of the presence of specular hematite (detected from orbit), a likely indicator of aqueous processes. However, our results from CRMO suggest that similar hematite can form in a volcanic environment without liquid water. Together with experimental and other field-based studies of hematite and jarosite in volcanic environments (e.g. Golden et al., 2008), a volcanic interpretation (e.g. McCollom and Hynke, 2005) can be invoked for many of the mineralogical features observed at Meridiani Planum. While such volcanic environments on Earth are inhabited by extremophile organisms (Richmond et al., 1999;

Westall et al., 2002), such environments might not have been conducive to the origins of life (e.g. Knoll et al., 2005).

On the other hand, a low-temperature or hydrothermal origin for the CRMO hematite could indicate a more habitable environment. Hydrothermal systems have long been invoked (e.g. Orange et al., 2009; Konhauser et al., 2001) as potential early habitats for life on Earth, and their existence on Mars could indicate the presence of such habitable environments even if the Martian surface were cold and dry.

Conclusion

The purpose of this work was to determine the formation mechanisms behind secondary minerals on Earth that are similar to those at Meridiani Planum, Mars. We can conclude that:

- i) Formation of hematite at CRMO is likely the result of hydrothermal processes that were active while the flow was cooling. An oxidation mechanism not requiring liquid water is also possible.
- ii) Jarosite is rare at CRMO and is probably formed as a result of the oxidation of Fe^{2+} -bearing igneous phases in a low water:rock ratio environment. It is rare because the water at CRMO is generally near neutral (rather than acidic) and a specific, localized alteration process would be required to form it.
- iii) Calcite, silica, sodium sulfate, and sodium carbonate minerals formed at low temperatures, precipitating after the lava tube had completely cooled.
- iv) CRMO and Meridiani Planum both contain hematite, sulfate minerals, and amorphous silica in their alteration assemblages. However, the relative amounts of each, and the specific sulfate minerals present, are distinct because of differences in alteration conditions.
- v) The mineralogical similarities between this terrestrial analog and Meridiani Planum suggest that Meridiani could have had a similar diagenetic history, involving both high and low temperature aqueous processes, variable pH, and generally arid conditions.

These results also provide insight into possible variations in diagenetic environment at Meridiani Planum. CRMO caves contain minerals that were products of neutral and low pH precipitation, which is a direct result of local acidification of groundwater via oxidation of ferrous iron. These conditions may help us understand the complexity of the Martian groundwater system, which was not necessarily acidic throughout. It is possible that oxidation of iron and precipitation of minerals increased acidity in localized areas. Hydrothermal activity also could have fluctuated throughout time, affecting hematite formation. A further study of the hematite layer by VNIR or FTIR spectroscopy could help determine the temperature at which the hematite formed. A study of cave humidity could help constrain the jarosite formation, along with further sampling and fieldwork to locate more samples. Also, further investigation into sulfur in the CRMO samples will help understand its mobility and initial concentration.

A greater understanding of the mineralogy of Mars will also provide more refined conclusions about formation. The Mars Science Laboratory mission, which is scheduled for launch in late 2011, will analyze Martian samples using XRD and other methods and help us understand more about the formations present on the surface of the red planet.

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Appendix A

XRD Plots

JR-CM10-01

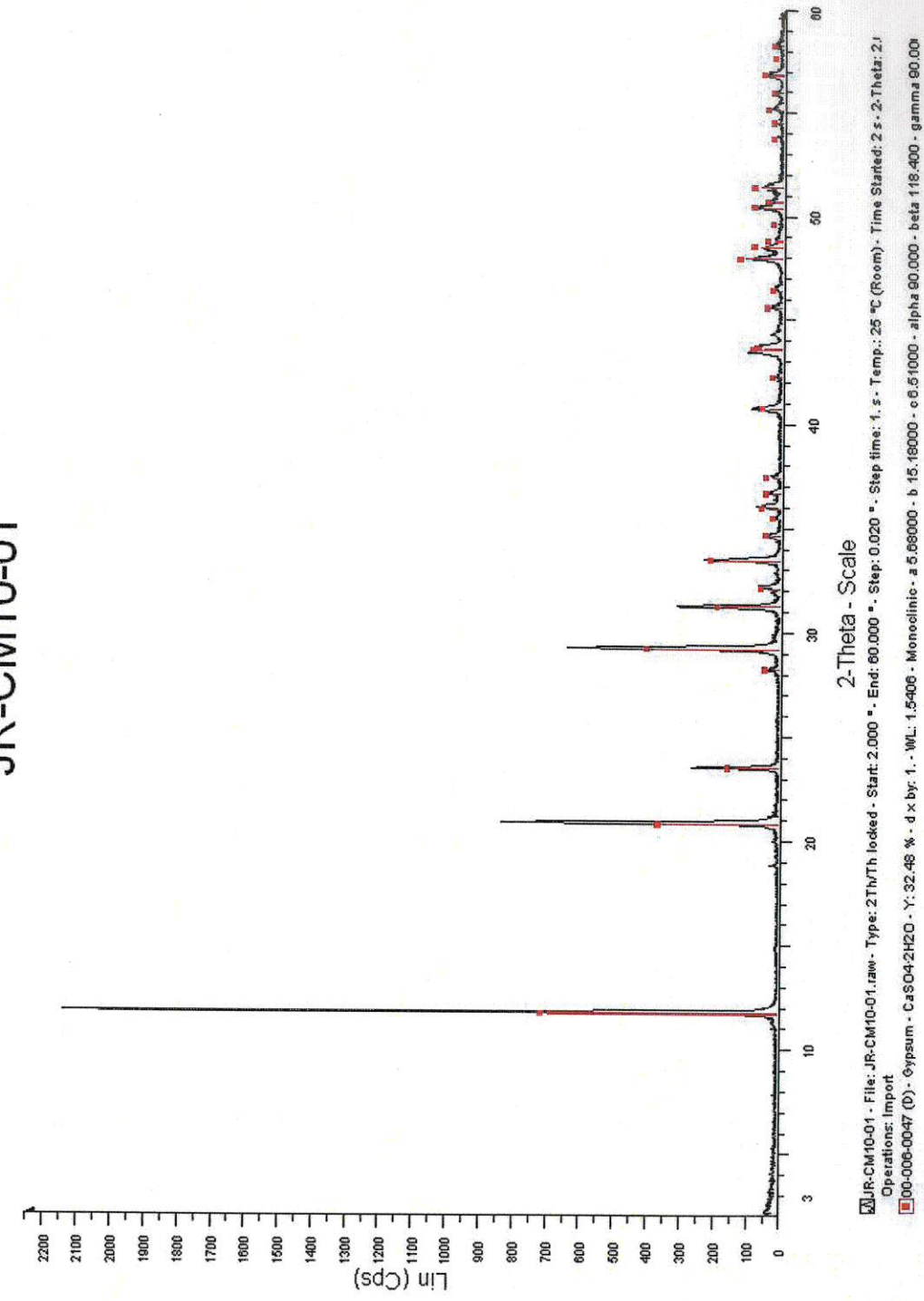


Figure 27. Sample 01: XRD pattern for gypsum.

JR-CM10-02

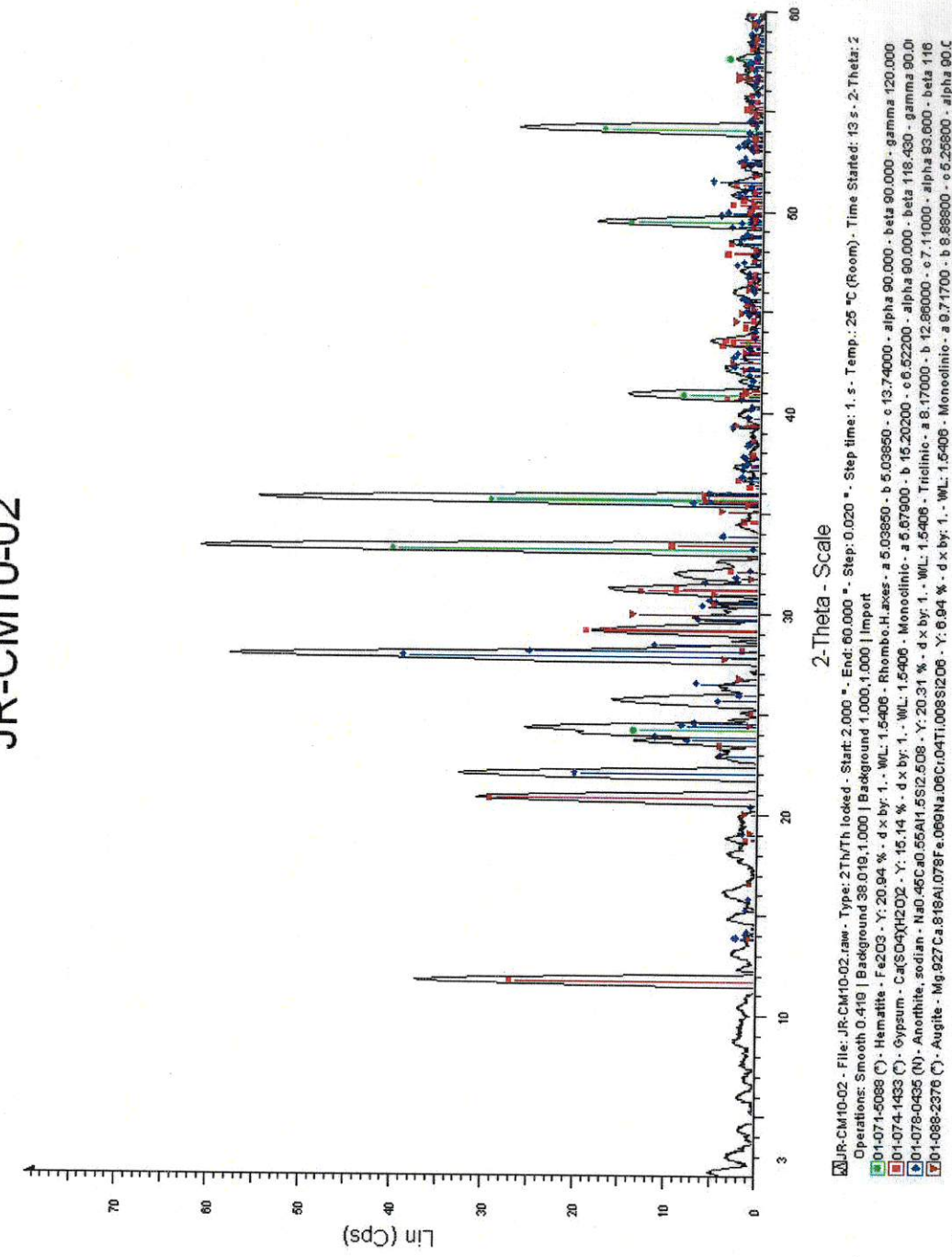


Figure 28. Sample 02: XRD pattern for altered basaltic substrate under gypsum coating.

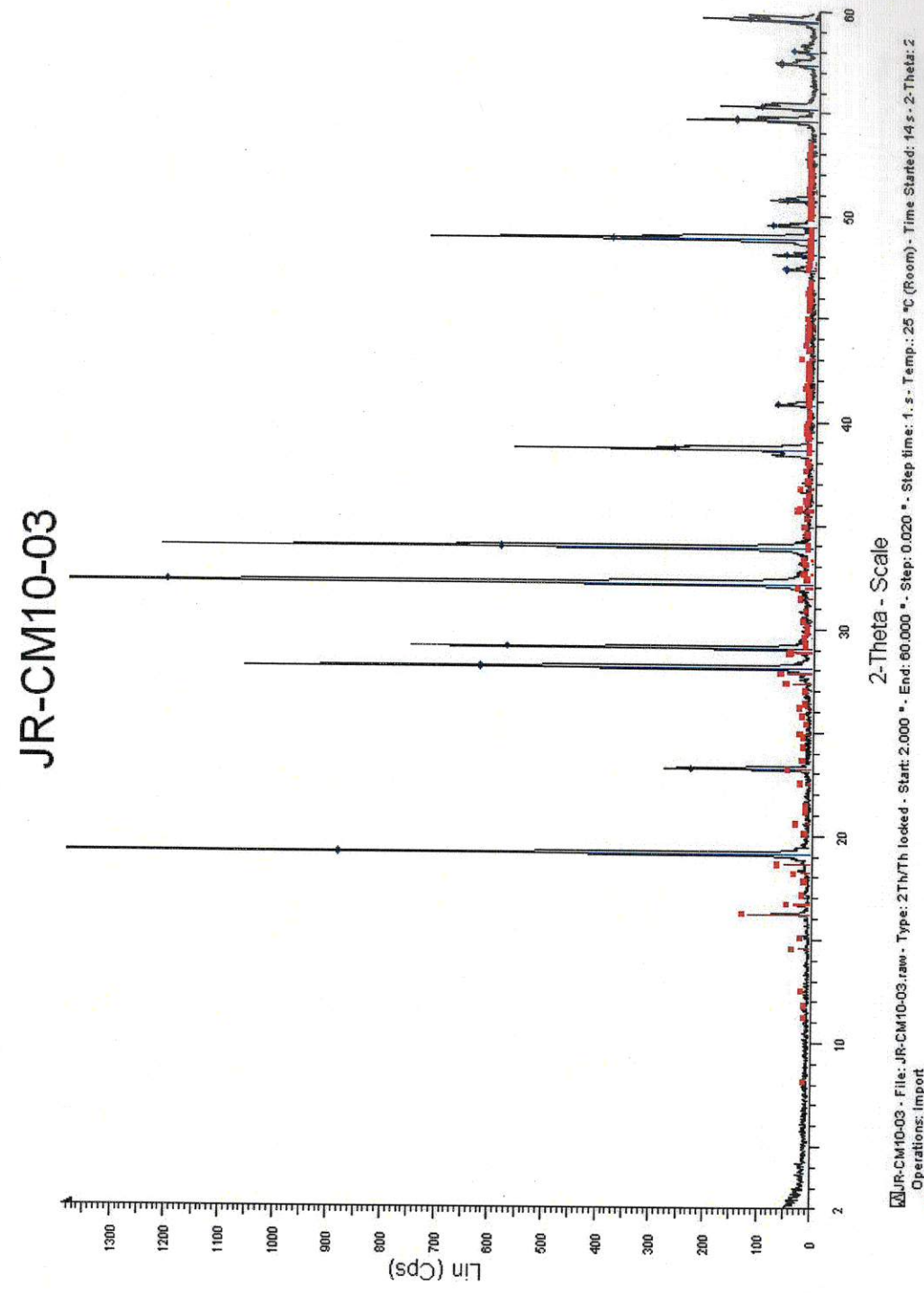


Figure 29. Sample 03: XRD pattern for Na-sulfate powders, dominated by thenardite.

JR-CM10-03S

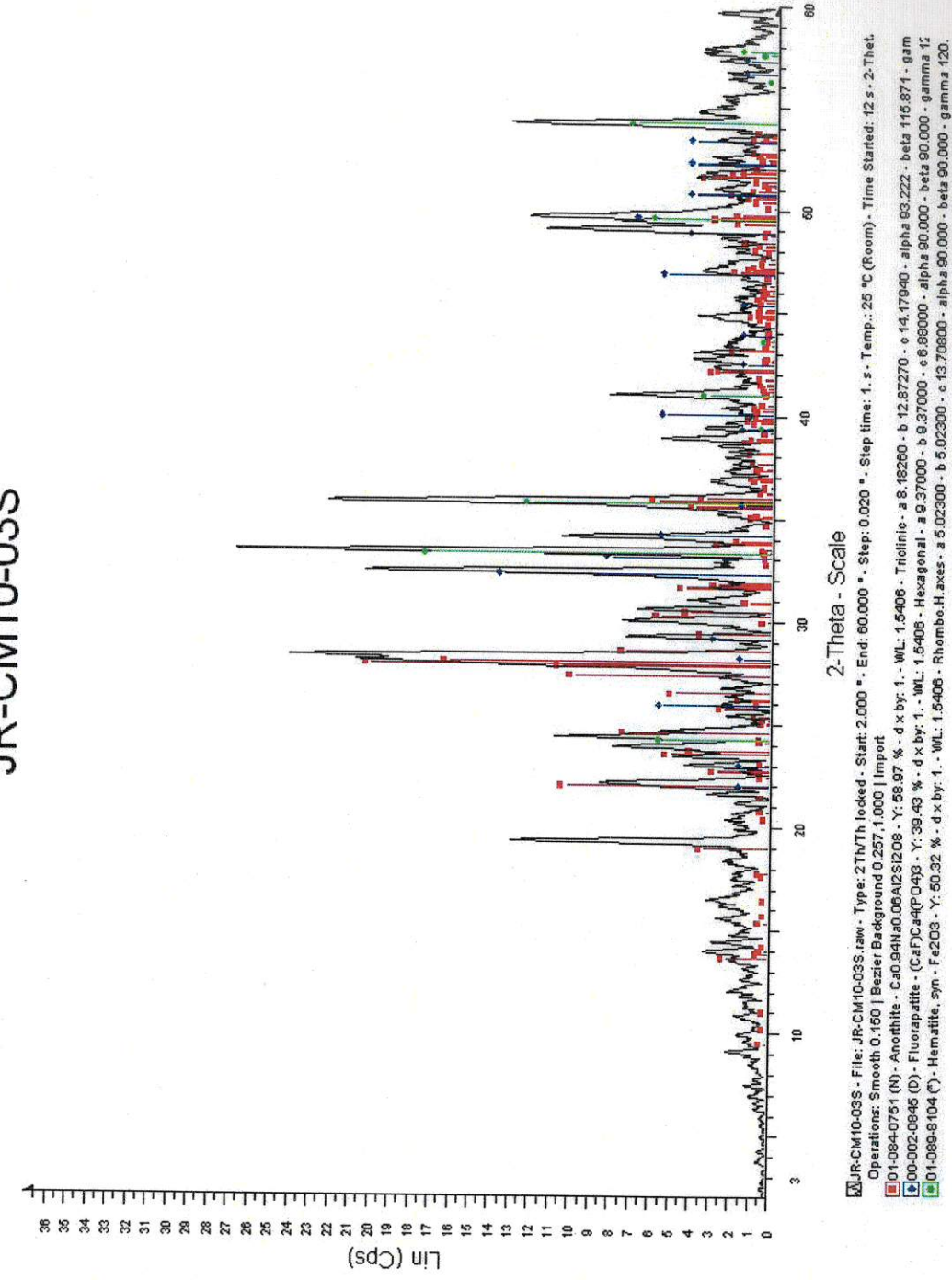


Figure 30. Sample 03S: XRD pattern for altered basaltic substrate under Na-sulfate powders.

JR-CM10- 06

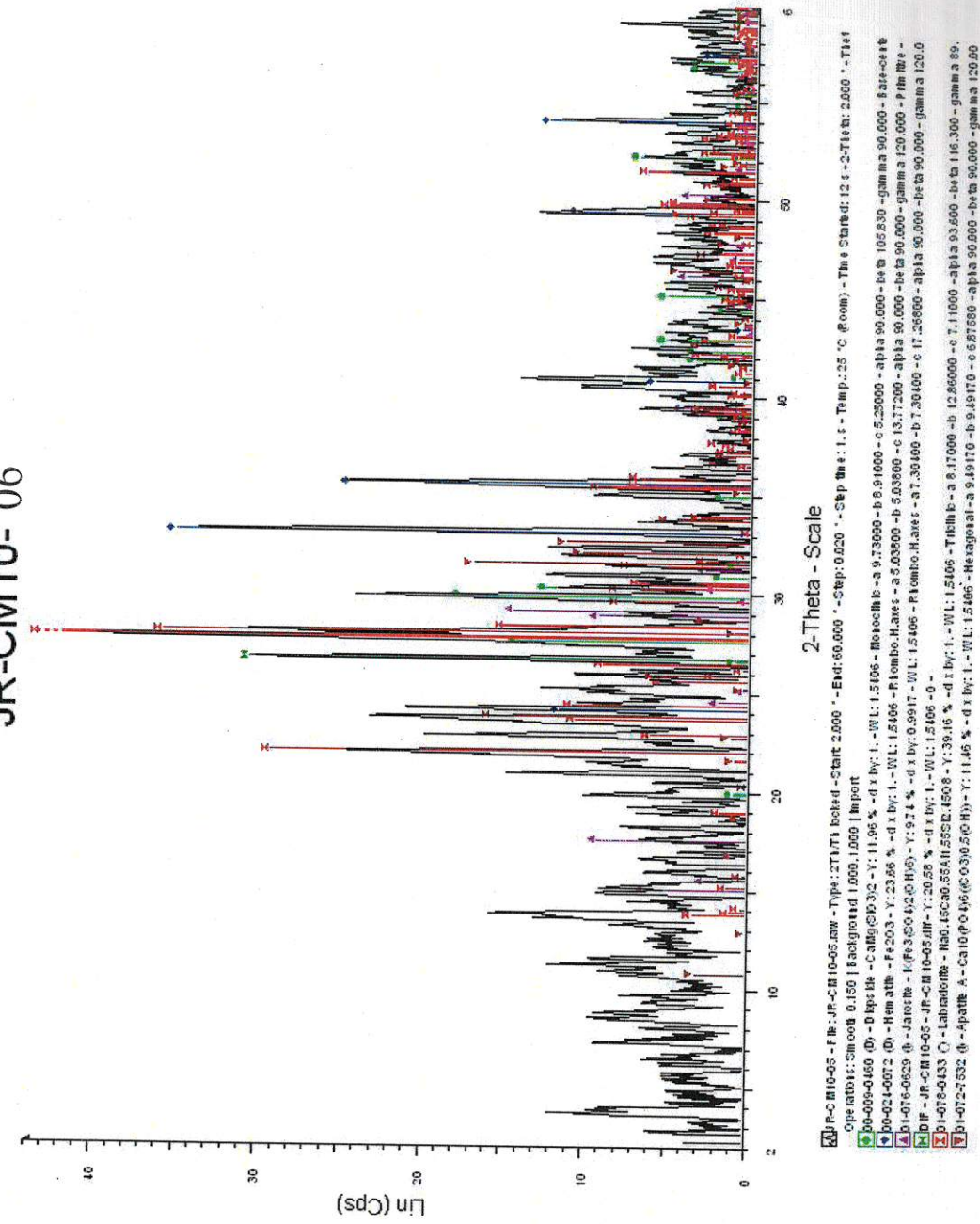


Figure 31. Sample 06: XRD pattern for jarosite sample with significant basalt contamination.

JR-CM10-10

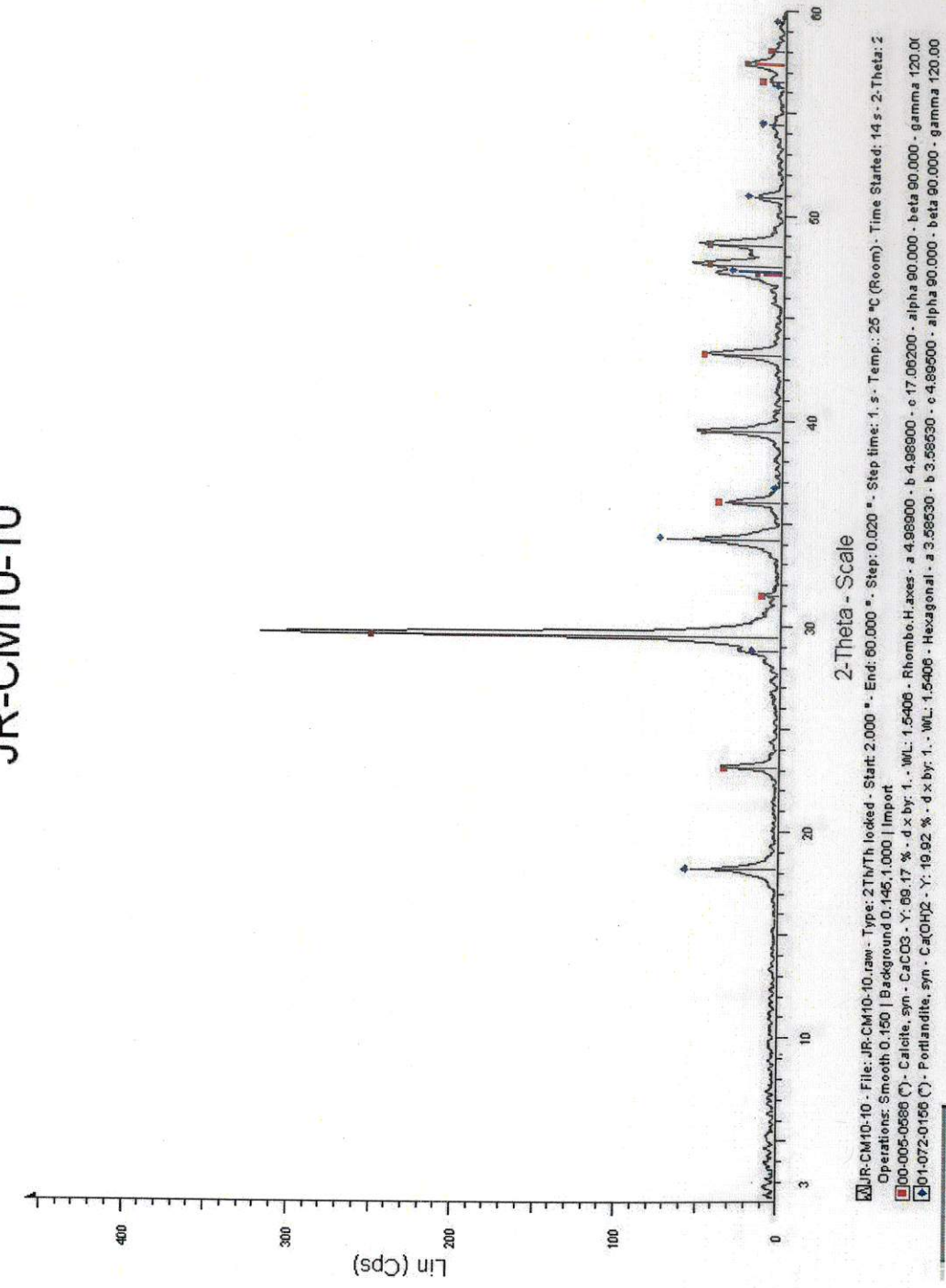


Figure 32. Sample 10: XRD pattern for calcite and portlandite.

JR-CM10-13

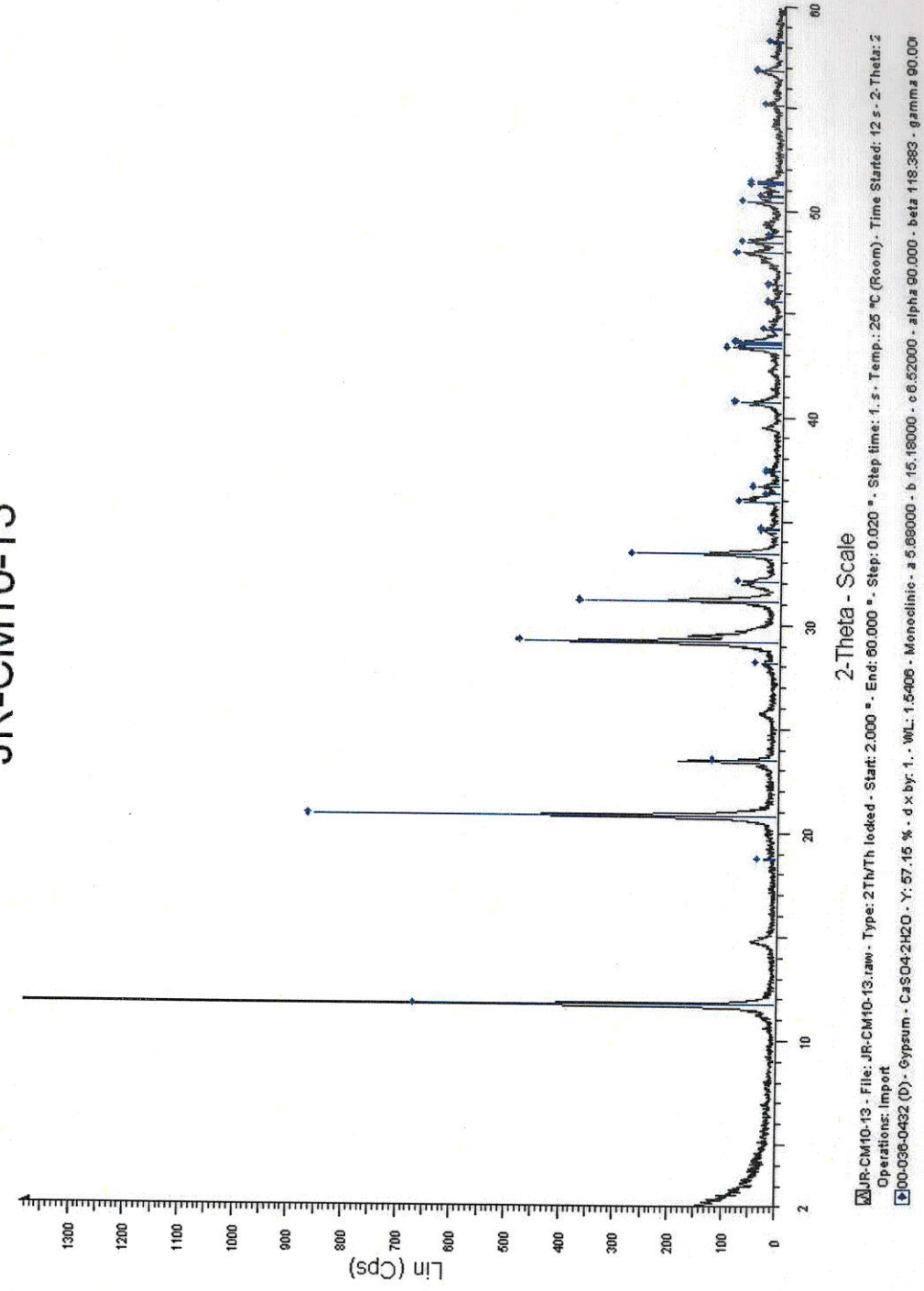


Figure 33. Sample 13: XRD pattern for gypsum.

JR-CM10-20

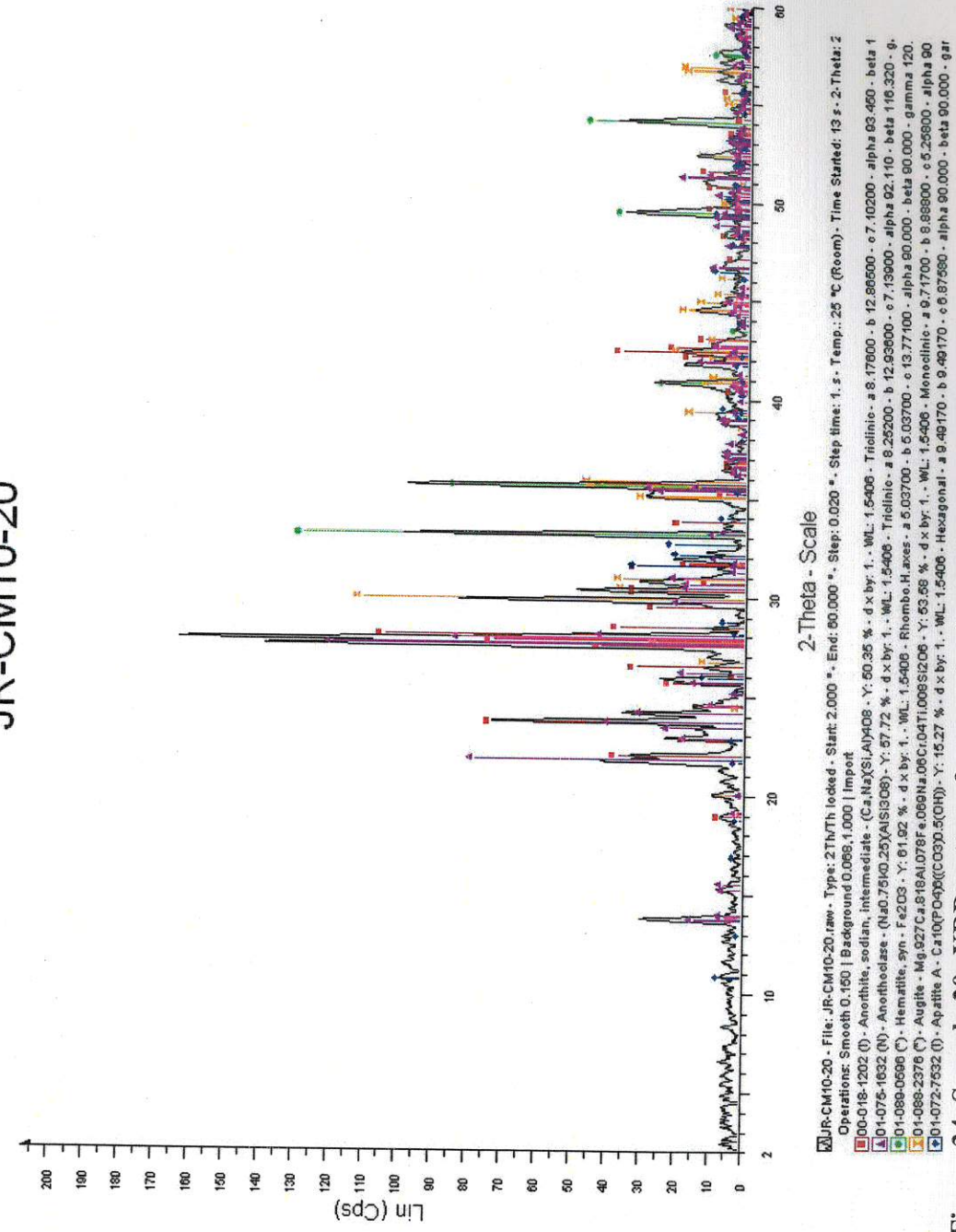


Figure 34. Sample 20: XRD pattern for specular hematite coating.

Appendix B
Supplementary SEM Images

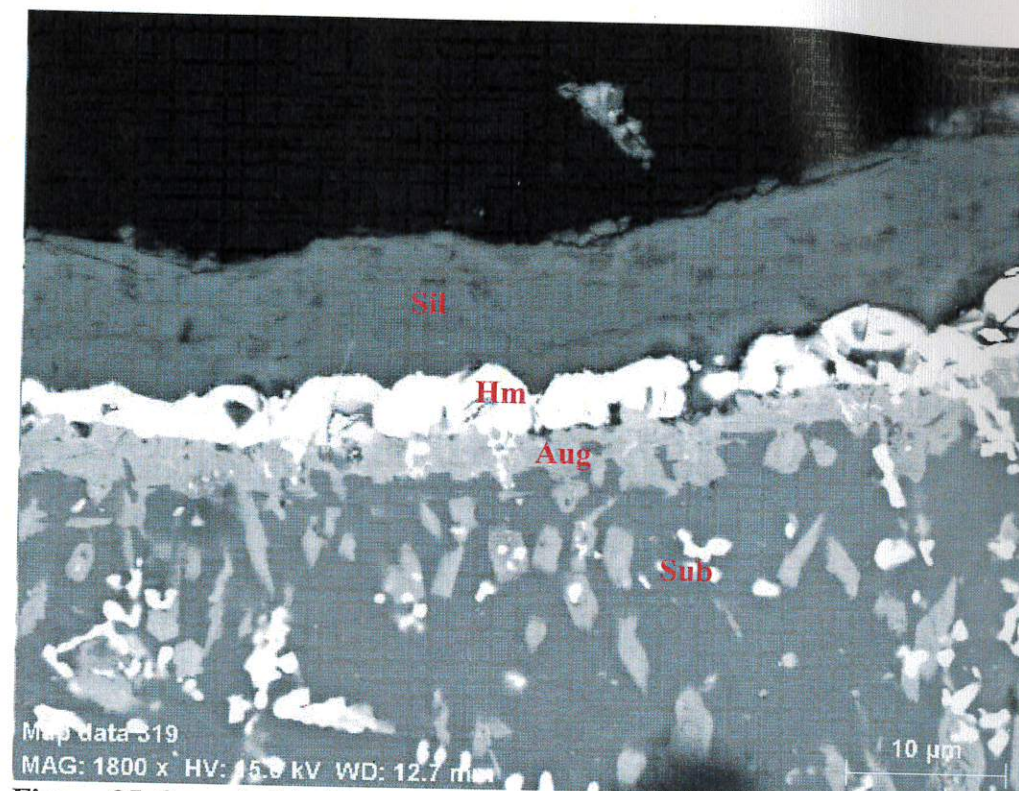


Figure 35. Sample 04: (From bottom up) Example of substrate (Sub) with augite (Aug), hematite (Hm), and silica layering (Sil)

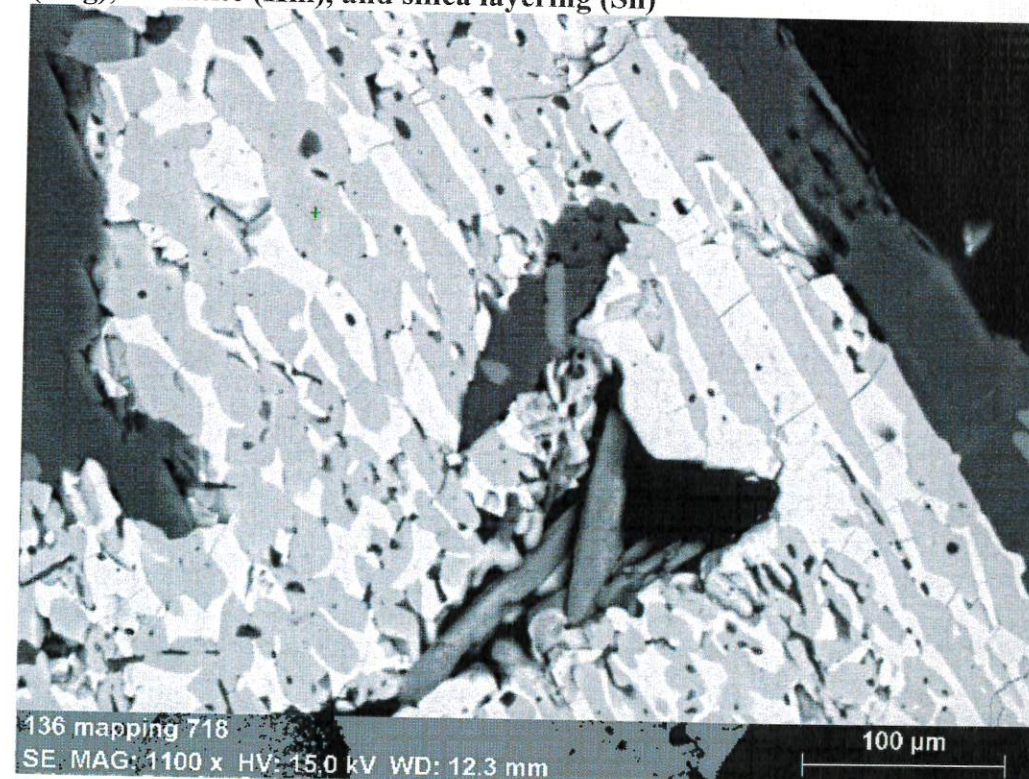


Figure 36. Sample 12: example of exsolution of what likely was titanomagnetite into Fe-rich (light gray) and Ti-rich (dark gray) segments.

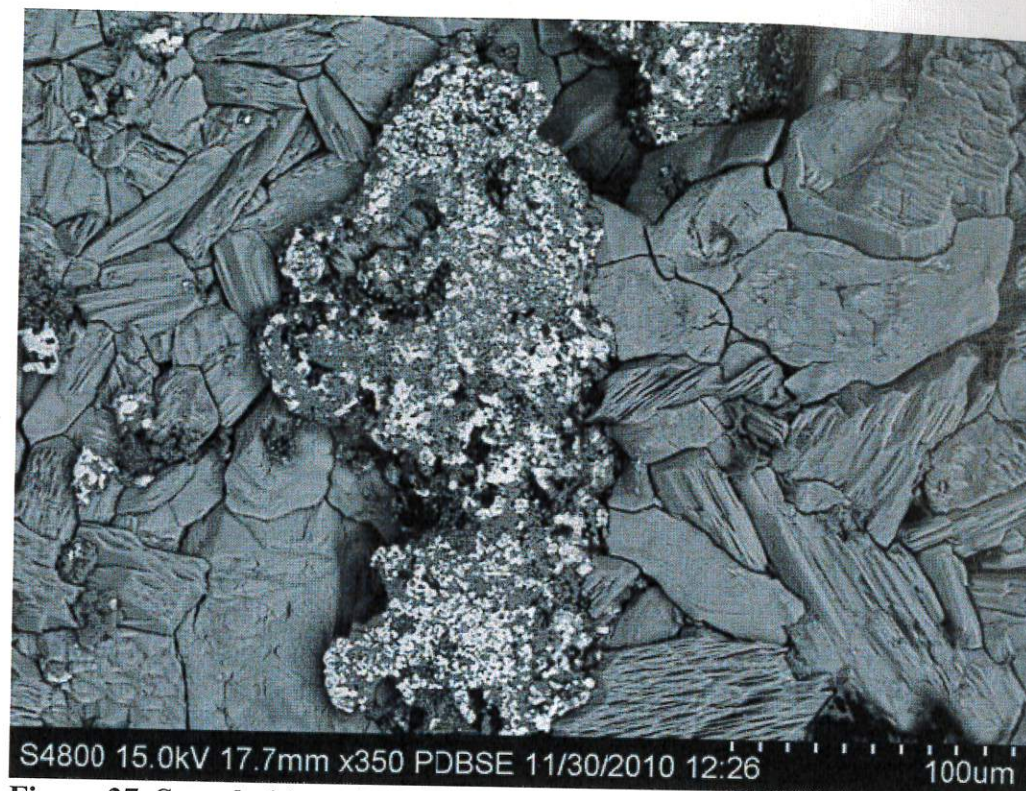


Figure 37. Sample 01: example of competency contrast between gypsum and substrate. Gypsum occurs as the striated material and substrate is in the center



Figure 38. Sample 12: example of exsolution of iron (white zones) from olivine grain (interstitial area with Mg enrichment in next figure)

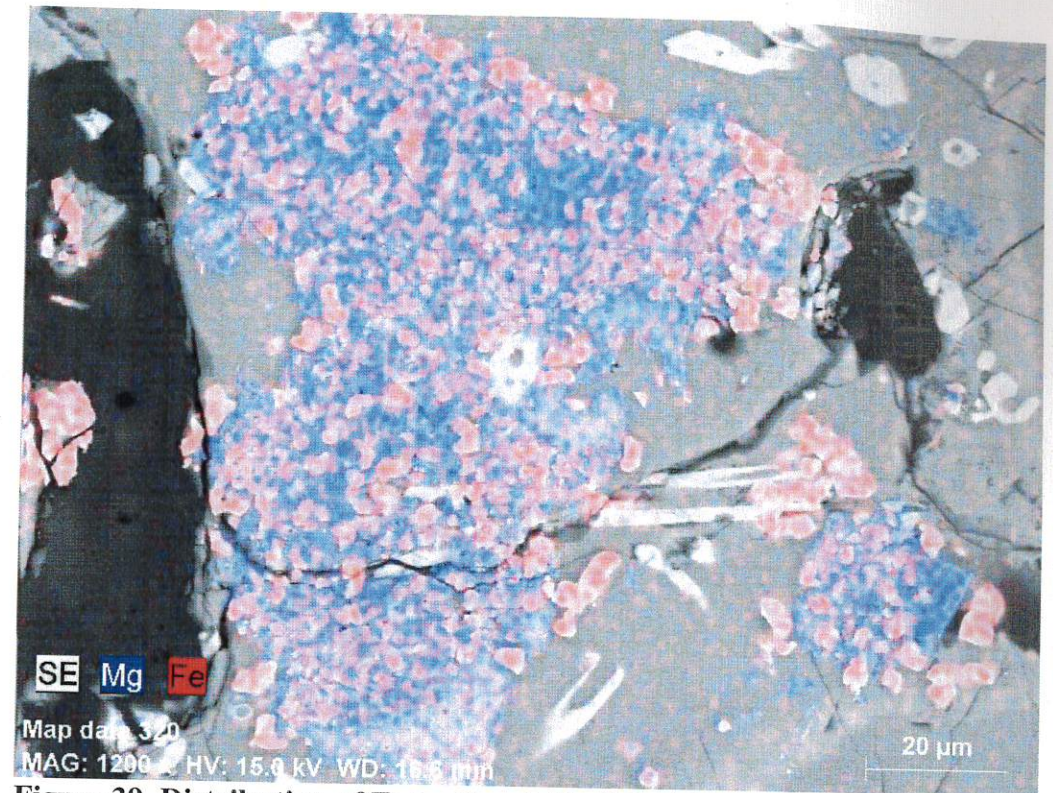


Figure 39. Distribution of Fe (red) and Mg (blue) in exsolved olivine. Mg is enriched in the olivine as Fe exsolves.

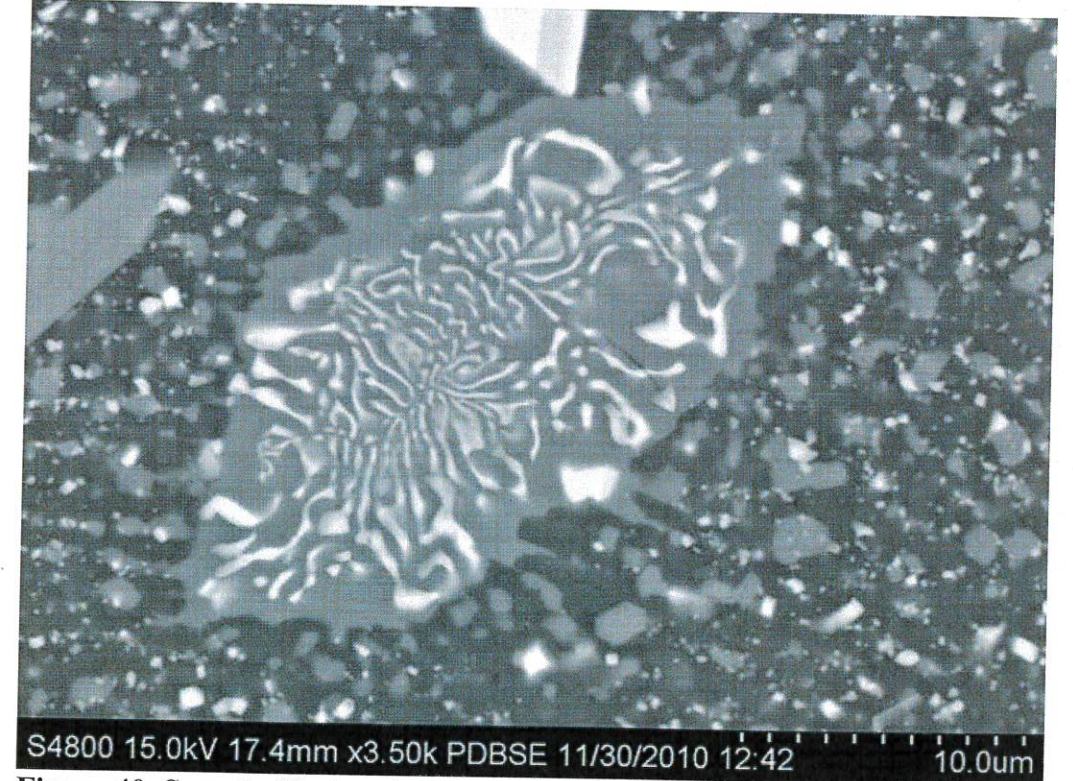


Figure 40. Sample 03. Another example of exsolution in olivine with apparent original olivine crystal shape.

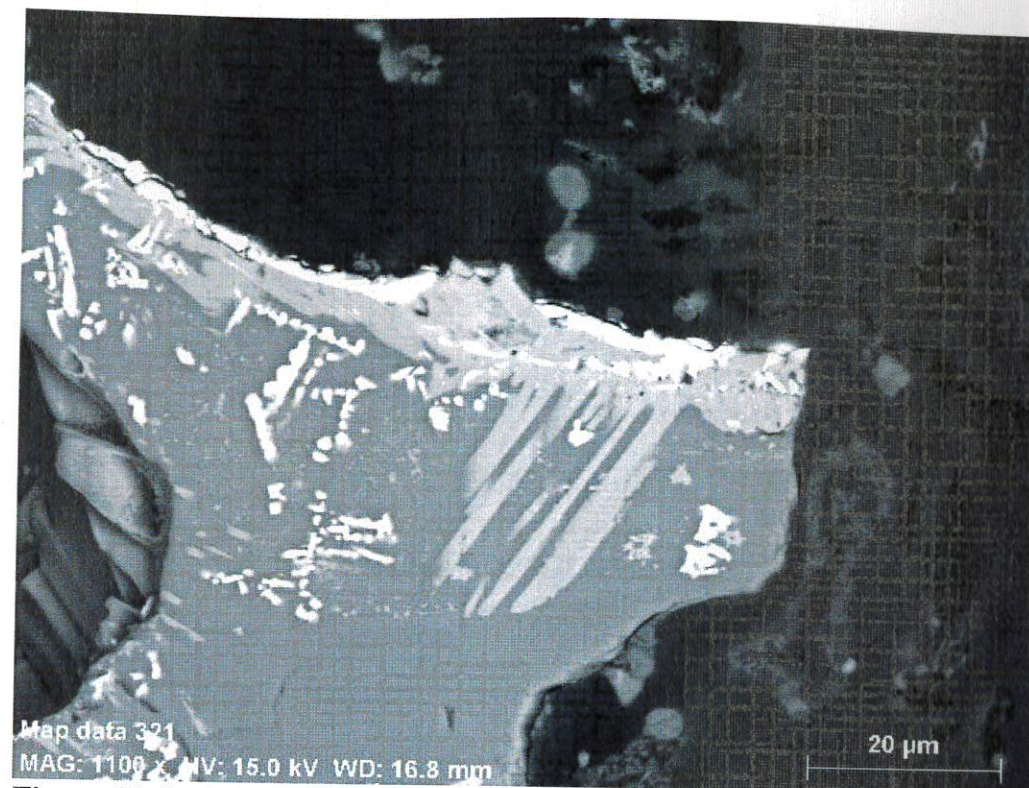


Figure 41. Sample 16: example of substrate, augite, and hematite. Voids in upper right were Na-sulfate and were mostly destroyed during sample preparation.

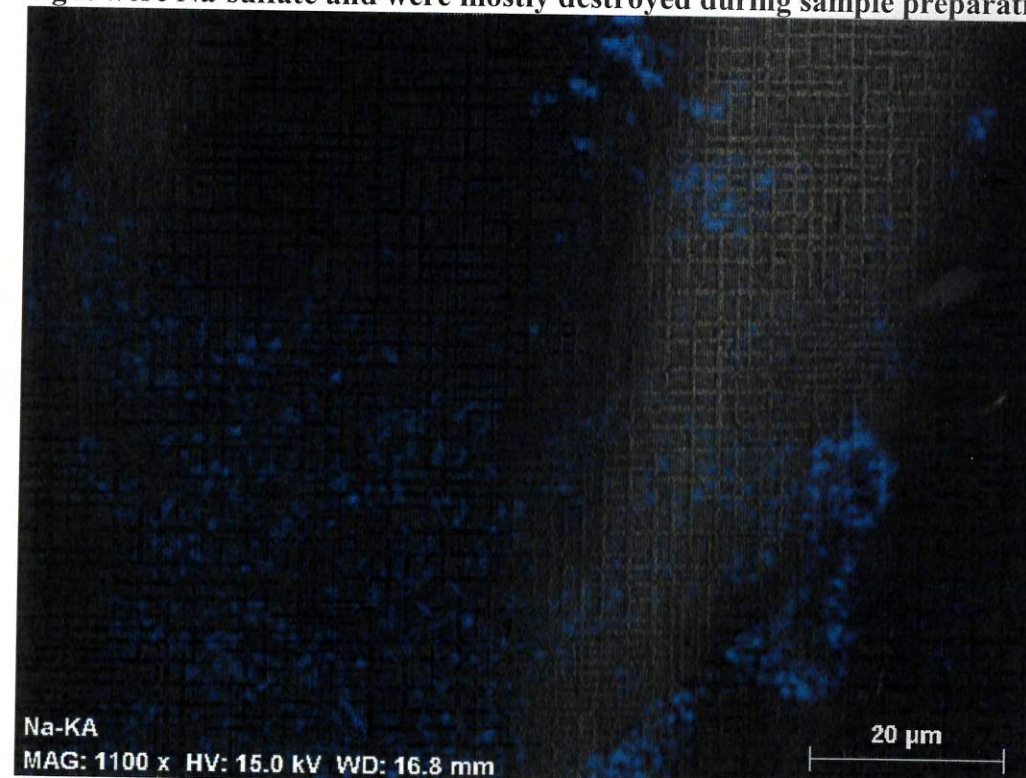


Figure 42. Sample 16: Na distribution. Enrichment of Na in voids shows some Na-sulfate presence

Appendix C

Arco Tunnel Sampling Map

ARCO TUNNEL Craters of the Moon National Monument Surveyed 2/4/94 - 4/2/94 Total Length 5805.6'

Surveyed by:
Serge Allen, Erik Fowler, Bruce McMurray
Bekie Baldwin, Don Griffin, Carter Mackley
Emma Baldwin, Dean Killian, Scott Nelson
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Scott Earl, Ryan McBride

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Scale: Feet
-50 0 50 100 150 200 250

LEGEND

- Cave Walls
- Nondescript Breakdown
- Individual Rocks
- Drop or Ledge
- Floor Slope
- Ceiling Height (in feet)
- Direction of Lava Flow
- Depth below surface @ entrance (in feet)

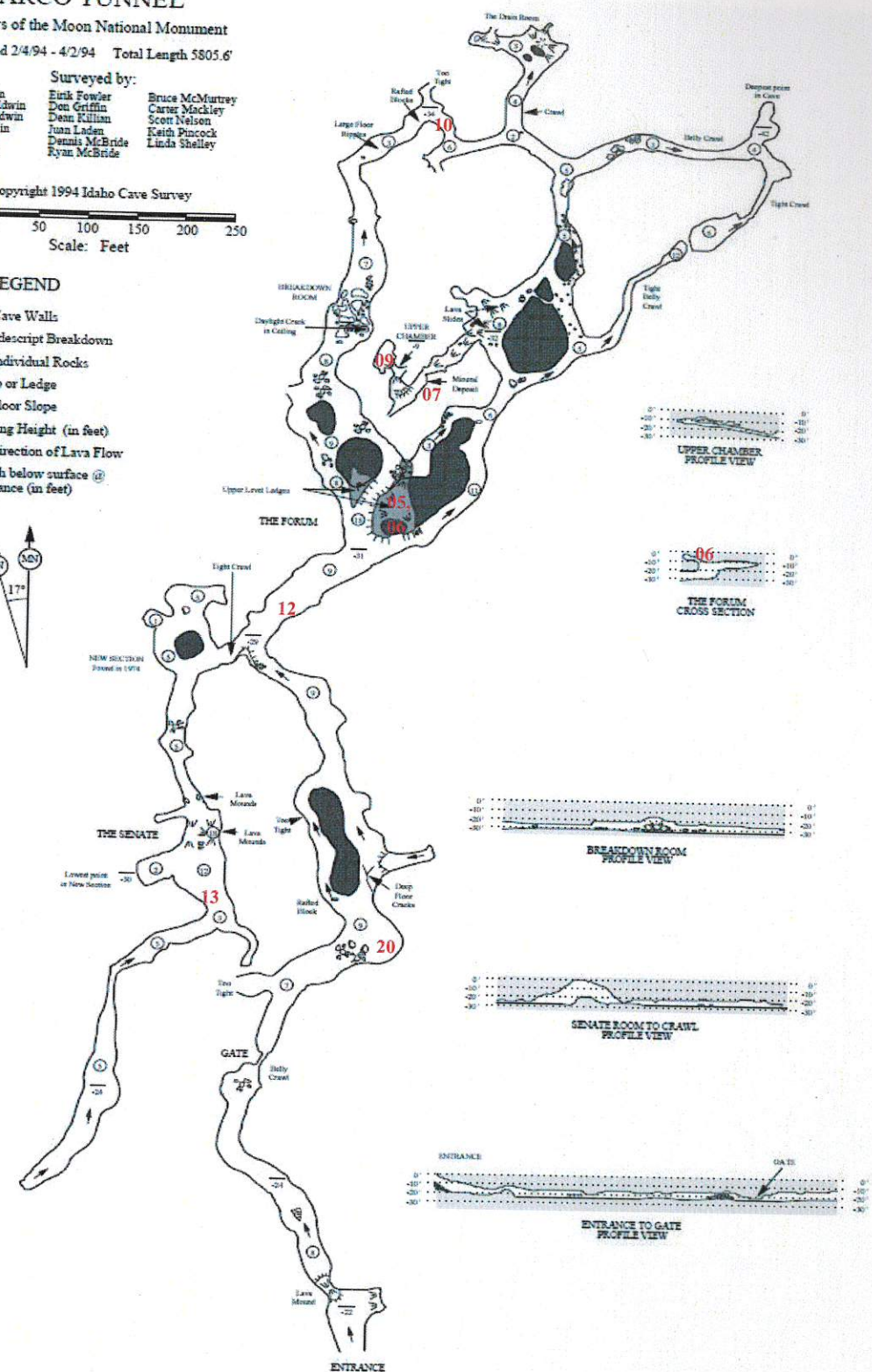
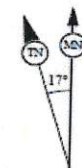


Figure 43. Samples from Arco Tunnel. Upper Chamber and Forum profile views on the right show areas that contained jarosite (sample 06) (Baldwin et. al., 1994)

Appendix D

GeoCorps Waterhole Sampling Protocol

Waterhole Sampling Protocol

Calibrate pH Meter and Conductivity Meter before leaving office and double check on last site # used. Pre-fill enough Nalgene® jars with isopropyl to equal to the maximum number of waterholes you plan to visit that day and take 1 extra empty jar for backwashing net.

Equipment List: Park Radio; First-Aid Kit; Plenty of Water; Measuring Tape(s) and Folding Rule; GPS; Digital Camera; Compass; Field Forms, Clip Board, and Writing Instruments; pH/Conductivity/Temperature Meter; thermometer (air); Invertebrate sampling equipment; Sharpie to write on Jars; and Topo-Sheet if available.

What to do and what to record on the waterhole sampling form.

Upon Arriving: Use measuring tapes to determine the surface dimensions of the waterhole. To do this, establish a base line of the long dimension (if possible) and measure transects perpendicular to it, record the dimensions (m) and create a plan view of the water hole using a sheet of graph paper (be sure and include a North Arrow and scale). If there is evidence of a high water mark (HWM) that has a different surface area than the current pool, measure and sketch the HWM on your diagram and label line as "HWM". If the pool is dry and there is enough evidence, sketch the HWM and label. ***If it can be safely done***, take a series of depth measurements along the long axis to create a bottom profile and make sketch on the graph paper. ***Make sure site # and date are written on the Sketch Map.***

Site #: Sites will be numbered sequentially. **If the site is being revisited do not give it a new #, record original #** **For a revisit--** Make a photocopy of the original sketch map to take in the field with you, so you can measure the water depth in the same place as before to look for change. Also, make a copy of the whole original form for comparison of animal sign, etc.

Investigators: List field party members

Time: List arrival time at site

Site Name: If the site has a Formal Name, e.g., Moonshine Cave, Yellowjacket Waterhole, etc., list it here, otherwise leave blank.

Revisit: If yes put a "Y" or "N" for no.

Date: Record M/D/Y

Photo Point:

1. Try several vantage points before establishing the Photo Point; point should provide the best view of the waterhole and the immediate surroundings; supplemental photos will show the water hole in the larger context of the surrounding area
2. Record the UTM location of the point using the NAD83 datum (be sure GPS unit has been averaging for at least two minutes or 120 points)
3. Use a digital camera with a 35mm equivalent focal length lens of 50mm, which is equivalent to what the human eye takes in. Most likely the camera will be equipped with a zoom lens, set it to a 50mm equivalent focal length {be sure and consider the crop factor of the camera sensor, i.e., you may need to set the lens at 30mm for a 1.6 crop factor (Canon) or 35mm for a 1.5 crop factor (Nikon) for it to be about equivalent to 50 mm focal length}.
4. If the shot contains a high % of black rocks set the exposure compensation to minus 2/3 stop to correct for the light meter adjusting exposure to middle grey.
5. Record image # from the camera and the azimuth along which the shot was taken
6. Mark "PP" for "Photo Point" on the sketch map and record the distance from the water on the sketch along the azimuth taken.
7. Take some overview/surrounding area shots aid in relocating the photo point on a revisit and have one of the party members stand on the photo point. Be sure and log these shots in the supplemental photo section of the field form.

Depth of Water: measure the water depth in cm using the folding rule and mark the location with a "WD" on the sketch map; if currently dry, write dry (with the WD marked on the sketch map the same spot can be measured on a revisit to determine any change). *Note: it may not be safe, e.g., ice floor, or practical, i.e., soaking your hiking boots, to measure the water depth too far from the edge.* Note if it represents an average water depth, maximum depth, or what was accessible on the form.

Depth at High Water Mark: Add the difference between the current pool level and the HWM to your depth of water measurement to get this #.

Evidence for HWM: Circle or describe how you are interpreting this.

Water Temp: Record measurement

Conductivity: Record measurement

pH: Record measurement

Ice Floored: If you can see ice mark "Y", otherwise "?"

Air Temp./Winds/Cloud Cover: Record as indicated on the form

Evidence of Cultural Use: Describe and photograph (record photo #'s)—*Report to Park Archeologist—Do not collect or relocate items!*

Evidence of Animal Use: Describe and photograph (record photo #'s)

Invertebrate reconnaissance sampling (note under Evidence of Animal Use):

- (1) Use aquarium net to collect samples—push, pull, and drag the net along the bottom, against and under rocks, and through the water column to collect organisms.
- (2) Dump contents of net into sample tray (use empty jar you brought to backwash net with water from pool)
- (3) Use forceps to carefully transfer organisms to Nalgene® jar with Isopropyl (be careful not crush or break off any body parts); *thank the organisms for giving their lives to further our knowledge.*
- (4) Label Jar: Invert and with WH# (e.g., **Invert WH12**); be sure lid is on tight

Samples Taken: Do not collect unless needed to make a positive ID back at office--Describe and list sample (# as follows: WH Site #--spl #, e.g., for Site13 and the second sample, it would be WH-13-2)

Supplemental Photos: Photo # and brief description