CERRO NEGRO, NICARAGUA: A KEY MARS ANALOG ENVIRONMENT FOR ACID-SULFATE WEATHERING. B. M. Hynek[1], K L. Rogers[2], and T. M. McCollom [1] Laboratory for Atmospheric and Space Physics, Univ. of Colorado, 392 UCB, Boulder, CO 80309 [2]Woods Hole Oceanographic Institute, Woods Hole, MA. hynek@lasp.colorado.edu.

Motivation: Sulfate-rich bedrock has been discovered in many locations on Mars and has been studied by both orbiting spacecraft and landers (e.g., refs. 1-2, respectively). In most cases, these minerals are probably produced by acid-sulfate weathering of igneous rocks, which may have been a widespread process for the first billion years of Mars' history [1,3]. Acid-sulfate weathering often dominates the geochemistry of subaereal volcanic hydrothermal settings on Earth and assessing the biological potential of such environments is paramount in assessing the potential habitability of early Mars.

A wonderful terrestrial analog for acid-sulfate weathering of Mars-like basalts exists at Cerro Negro, Nicaragua. Here, a similar basaltic chemistry to that of Mars is being chemically altered in a solfatara-like setting (solfatara is a term applied to sulfur-rich volcanic fumaroles). We are studying this environment to better understand the astrobiological potential of Mars in these types of geochemical settings. Characterized by high temperatures, low pH, and high sulfur contents, these gas-dominated systems are the extreme of extreme environments and represent a unique and little explored microbial habitat.

Background: The Mars Exploration Rover (MER) Opportunity has returned close-up images of exposed bedrock from Meridiani Planum, as well as data on their chemical and mineralogical composition (e.g., refs. 2, 4-5). The rocks reflect extensive acid-sulfate weathering of basalt early in Mars' history. Water chemistry is mostly inferred from the presence of the mineral jarosite at Meridiani Planum. This mineral forms in specific geochemical environments; namely low pH (~1-3) and oxidizing conditions. The MER Science Team has interpreted the bedrock to be a result of acid-sulfate weathering via predominately groundwater processes [2] while McCollom and Hynek [6] proposed that the weathering occurred in a high temperature volcanic environment. Either way, both models identify acid-sulfate weathering of basalt as a predominant process on early Mars.

More recently, the Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité (OMEGA) investigation, onboard the Mars Express mission, has identified discrete locales of sulfate-rich bedrock around the planet [1,7]. Many of these are concentrated in the Valles Marineris in diverse geological settings [8], some of which may be a result of high-temperature alteration of basaltic crust on Mars. Indeed, the OMEGA Team has suggested that "sulfur-rich fluid circulation and the alteration of volcanic ashes into sulfates" may be a major contribution to the observance of sulfates globally on Mars.

These observations do not seem surprising when considering that the materials are >3 billion years old [1]. During this early time in Mars' history, volcanic/magmatic processes were rampant and liquid water was present in surface and near surface environments. The surface heat flux on early Mars was roughly a factor of eight higher than at present [9] and enormous amounts of crust were emplaced via volcanic and magmatic processes during the Noachian (e.g., ref. 10). Solomon et al. [11] argued that large-scale hydrothermal circulation likely operated throughout the Noachian epoch on Mars, which may be partially responsible for the widespread sulfate and clay minerals that have been identified around Mars.

A Terrestrial Analog at Cerro Negro Volcano, Nicaragua: From the above arguments, it is now quite likely that acid-sulfate weathering of basaltic rock was a dominant process on early Mars and undoubtedly some of this occurred at high temperatures. We are currently exploring a terrestrial analog environment that can provide great insights regarding the habitability of early Mars in this type of setting. Cerro Negro ("Black Mountain"), Nicaragua, provides an ideal field laboratory to investigate the process of acid-sulfate weathering of Mars-like rocks.

Cerro Negro is one of the youngest and most active volcanoes on Earth. It has been constructed from 22 major eruptions beginning with its inception in 1850. The eruption style has varied from effusive lava flows to explosive strombolian and sub-plinean activity with significant amounts of tephra. Importantly, this youthful volcano has a basaltic chemistry that is remarkably similar to many of the Mars meteorites and unweathered basalts studied on Mars' surface (Figure 1). To date, most Mars analogs have a different parent rock lithology such as Yellowstone (granitic/rhyolitic) and the Atacama Desert (andesitic). The Rio Tinto site that is being studied as an analog for acidic, sulfur-rich environments on Mars formed by oxidative weathering of metal sulfide ore deposits within intercalated slate, quartzite, sandstone and limestone. This type of lithological setting has not been observed on Mars.

Chemical Weathering at Cerro Negro Volcano, Nicaragua: At Cerro Negro, the basalts of Mars-like composition are undergoing extensive acid-sulfate weathering in a sulfur-rich fumarolic environment. The chemical weathering is predominately controlled by sulfuric acid that is produced by both

$$4SO_2 + 4H_2O = 3H_2SO_4 + H_2S$$

$$\text{and} \quad H_2S + 2O_2 = H_2SO_4$$

within the volcanic vapors.

On a reconnaissance excursion in late 2006, lava and tephra hand samples were collected from several recent eruptions at Cerro Negro (i.e., 1999, 1995, and 1992). Samples from pristine to heavily altered basalts were collected. Standard laboratory techniques are being applied including XRD/XRF, thin-section petrography, and S analysis to study the acid-sulfate alteration pathways of these Mars-like basalts. The pristine basalts are characterized by relatively large phenocrysts of clinopyroxene, plagioclase, and olivine, along with opaques in a dark matrix (Figure 2). The rocks have similar elemental chemistry to those explored *in situ* on Mars as well as the SNC meteorites (Figure 1). This fact is crucial since the geochemical pathways and final assemblage of weathered products relies heavily on chemical composition of weathering fluids, which can be largely controlled by variations in host-rock lithology (i.e., ref. 16).

In a few years, freshly erupted basalt can be converted into combinations of Ca-, Fe-, and Mg-sulfates, Fe-hydroxides, phyllosilicates, and free silica. Abundances of these groups can vary significantly. For example, ~80% free silica composed one of the most heavily weathered samples. Plagioclase and olivine are the first minerals to weather, freeing up cations for reaction with H_2SO_4 (Figure 2). The

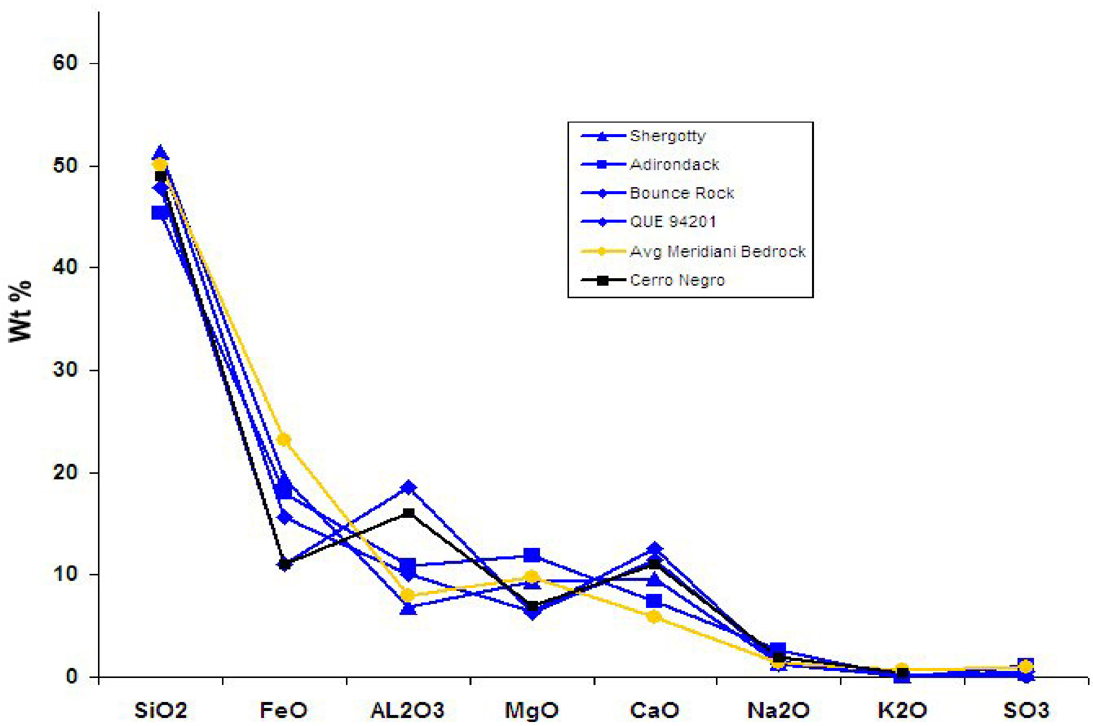

Figure 1. A comparison of Cerro Negro elemental chemistry from Walker and Carr [12] to Mars rocks. Data in blue are Mars meteorite compositions and rocks sampled by the MERs [13-15] and orange represents the average composition of Meridiani bedrock with the excess sulfur removed [6]. The fresh Cerro Negro basalts are a good proxy for the composition of the martian crust and the parent rocks that are inferred to have undergone chemical weathering.

altered rocks have up to 30 wt% SO_3 equivalent, which is quite similar to the Meridiani Planum bedrocks studied by Opportunity [5] and inferred in other sulfate-bearing bedrock on Mars. It is noteworthy that this is happening in an environment with limited water and on very short timescales (~10 yrs). Applying these results to an early, hot, outgassing Mars suggests that the water-altered minerals detected to date could form very quickly.

Geomicrobiological Analysis: Inherent to water-rock reactions in hydrothermal systems are chemical disequilibria among redox sensitive species, including those that are common in microbial metabolisms (e.g. H_2S, S^0, SO_4^{2-}, Fe(II), Fe(III), CO_2, CO, CH_4, and H_2). In fact, most extant thermophiles, as well as the hypothesized last common ancestor (LCA) of life on Earth, are chemotrophs, exploiting these disequilibria to drive their metabolisms [17-18]. The diversity and distribution of thermophiles are functions of the geochemical characteristics of hydrothermal systems, and these are often dictated by host rock composition [16, 19]. Solfatara environments like that of Cerro Negro are unique and little explored geothermal settings that are likely to host equally unique microbial communities.

Under these conditions, the predominant microbial metabolisms are based on S- and Fe-redox reactions, the latter being the case where Fe-bearing minerals are present, such as at Cerro Negro. Both S- and Fe- metabolizing thermophiles have been implicated in the origin and early evolution of life on Earth (e.g., refs. 18, 20), and are common in hydrothermal environments. Both Fe-oxidizers and reducers have been isolated from hydrothermal environments [20] and many exhibit some of the more outstanding biosignatures documented to date [21].

We are striving to establish the phylogenetic diversity of the microbial population at the Cerro Negro solfatara system. In addition to the rocks collected for mineralogical analysis discussed above, roughly ten sediment samples were collected within or in close proximity to active vents (Figure 3). Samples were collected that spanned a temperature range from 45-112°C. pH was measured when possible and hovered around 2. We took care to assess the diversity present by sampling half a dozen different vent systems with significant variations in mineralogy (Figure 3). The samples were collected in sterile Falcon Tubes and immediately capped and wrapped in Parafilm. All samples for microbiological analysis were placed in cold storage within four hours of collection.

Ongoing culture-independent techniques (i.e., 16S rDNA and epifluorescent microscopy) are expanding our understanding of the geochemical parameters that constrain life in solfatara systems. This work, coupled with theoretical geochemical

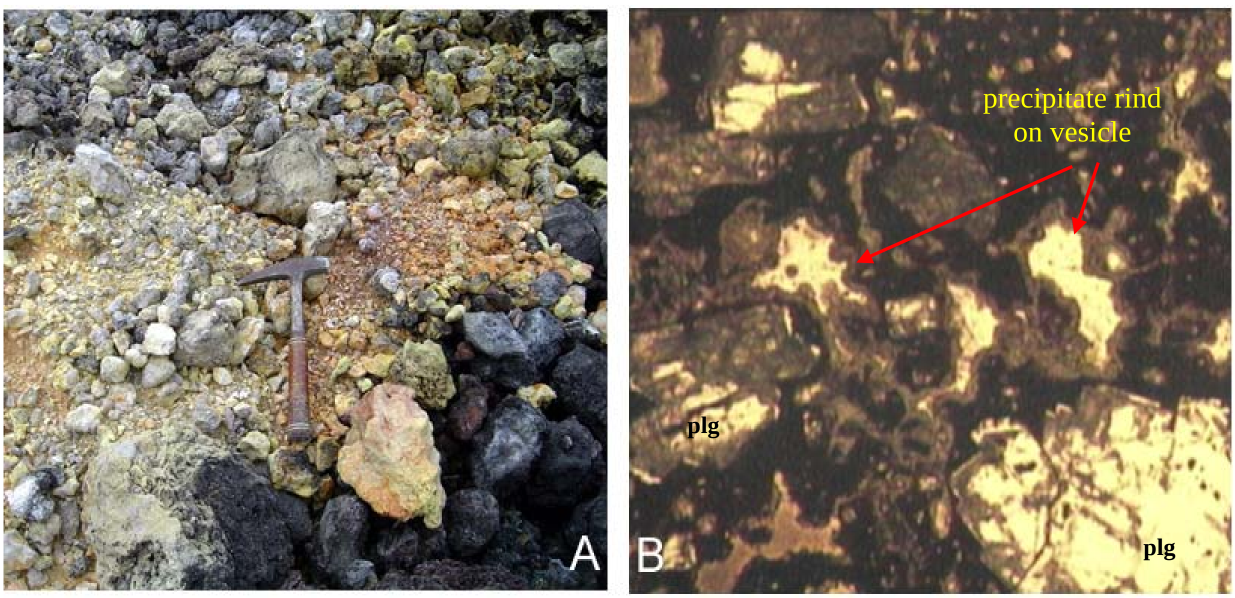

Figure 2. Cerro Negro context image (A) and thin section in visible light (B) taken from seven-year-old basalt that has undergone acid-sulfate weathering. Thin sections of pristine samples reveal basalt predominately composed of clinopyroxene, plagioclase (plg), and olivine phenocrysts in a dark matrix as well as opaques that likely represent Fe- and Mg-bearing materials. In (B), pervasive weathering of plagioclase crystals and precipitates rimming a vesicle are observed. Preliminary results from bulk rock analyses show that the altered samples contain abundant sulfates, iron hydroxides, minerals in the alunite/jarosite group, and up to 30 wt% SO_3.

modeling of such environments, is aiding in the prediction of the biological potential for life in similar systems on early Mars. To date, we have extracted 16S rDNA and are in the process of assessing the environmental population. Significantly less DNA is available, relative to hot spring environments with similar geochemical conditions. This is likely a result of the lack of resources available at solfataras; specifically a shortage of water and nutrients are thought to be paramount. Regardless of these deficiencies, microbes are thriving around these hot, acidic vent environments.

Summary: Recent chemical and mineralogical data from orbiters and landers show large locales of sulfates and smaller occurrences of hematite and phyllosilicates scattered across the martian surface. It is now understood that acid-sulfate weathering of basalt was a dominate process on early Mars and it is quite likely that many of these geochemical settings were characterized by low pH and high temperatures. Cerro Negro Volcano, Nicaragua, provides an ideal terrestrial analog environment for understanding processes that operated on early Mars and their potential for sustaining life. Chemical alteration of basalts with similar elemental chemistry to those from Mars is being studied to assess the geochemical pathways and reaction rates. In a few years, pristine basalt can be pervasively altered into predominately sulfates, clays, and free silica, which are similar to constituents observed at the Opportunity landing site and elsewhere on Mars. Additionally, the environmental population of microbes at this solfatara is being scrutinized to understand what organisms exploit this type of environment. This detailed characterization of the geological and biological settings at Cerro Negro is helping to elucidate the processes that occurred on early Mars and assess the habitability of these environments.

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Figure 3. Context photo showing several large-scale fumaroles at Cerro Negro, Nicaragua. Color differences relate to differing mineral assemblages and degrees of alteration. The arrow points to a person for scale.