ACID-SULFATE WEATHERING OF BASALTS AT CERRO NEGRO VOLCANO, NICARAGUA: AN EARLY MARS ANALOG. E. C. Marcucci[1,2], B. M. Hynek[1,2], T. M. McCollom[2], and K. L. Rogers[3], [1]Department of Geological Sciences, UCB 399, University of Colorado, Boulder, CO 80309, [2]Laboratory for Atmospheric and Space Physics, UCB 392, University of Colorado, Boulder, CO 80309, [3]Department of Geological Sciences, University of Missouri, 101 Geology Building, Columbia, MO 65211.

Introduction and Motivation: Recent observations from the Mars Express OMEGA and the Mars Reconnaissance Orbiter CRISM instruments have indentified numerous deposits of sulfate-rich bedrock in diverse geological settings [1, 2]. Additionally, the Mars Exploration Rovers (MER) Spirit and Opportunity have discovered sulfate accumulations at their landing sites [3]. While the specific formation mechanisms of the sulfates are debated and not well-constrained, it is generally accepted that some form of acid-sulfate weathering of basalt has occurred. One possible formation mechanism that has been proposed for some sulfate-rich deposits is high temperature alteration of Martian basalt by sulfur-rich vapors [1, 4]. It is conceivable that hydrothermal alteration was widespread early in Martian history from increased initial heat flux and transient heating from impactors. Understanding the geochemical pathways involved in the alteration of fresh, pristine basalts to heavily-weathered rock helps constrain the limits of the paleoclimate and environment, which in turn provides insight into the geological evolution and astrobiological potential of early Mars.

Cerro Negro as a Mars Analog: Cerro Negro, Nicaragua, is one of the youngest and most active volcanoes on Earth (Fig. 1). All 22 of its major eruptions have been observed and documented. It is a high temperature, low pH system with many solfataras (fumaroles which emit sulfur-rich gases). Many current and past Mars analogs have parent lithology that does not match that observed on Mars. Cerro Negro matches Martian meteorites and unweathered basalts examined by the MERs remarkably well (Fig. 2). Final weathered products and geochemical pathways depend on the composition of fluids, which in turn are controlled by the host-rock lithology [5]. Pristine basalt and alteration minerals seen at Cerro Negro are similar to those seen on Mars, as well as products predicted by geochemical computer modeling (Table 1).

Methodology: Owing to the usefulness of Cerro Negro, we can observe the acid-sulfate alteration process as it is occurring on numerous recent volcanic constructs. Our approach to the analysis of the Cerro Negro system is multi-faceted, with complementary analysis of field samples, laboratory experiments, computer modeling, and microbial studies.

Samples of varying degree of alteration were collected during three recent field campaigns from the 1999-2000, 1995, and 1992 eruptions. X-ray diffraction (XRD), thin-section petrography, and scanning electron microscopy (SEM) techniques were used to analyze rock samples, in order to characterize the chemical and mineralogical compositions of host rock and alteration minerals. Fluid and gas samples were also taken and analyzed with inductively coupled plasma atomic emission spectrometry. Laboratory experiments of acid-sulfate alteration of pristine Cerro Negro basalt are being conducted and analyzed with the same methods (see McCollom T. M. et al. abstract, this conference [6]). Theoretical geochemical modeling (EQ 3/6 and Geochemist's Workbench) of the weathering pathways and products are being used to aid in interpretation of field and experimental results.

The final component of our approach is the geomicrobiological analysis. S- and Fe-rich hydrothermal environments similar to Cerro Negro may have been widespread on early Earth and Mars and been the environment in which life originated. We are investigating the potential for habitability of these environments by exploring the phylogenetic and metabolic diversity of thermophiles found at the Cerro Negro fumaroles. During the field excursions, samples from a number of vents of differing temperature and pH were collected. Microbial studies include enrichment cultivation and culture-independent techniques, such as 16S rDNA phylogeny and epifluorescent microscopy.

Results: Cerro Negro basalt is phenocryst-rich and comprised of plagioclase (anorthite and bytownite), pyroxene (augite), and olivine within a glassy matrix (Fig. 3). Within a few years, the basalt can be pervasively altered, with plagioclase and olivine weathering out first. Secondary minerals are predominately Ca-, Fe-, and Mg-sulfates, including jarosite, and Fe oxides and hydroxides (Table 1). Clay minerals also appear in the alteration products. Large quantities of amorphous silica and sulfur are observed. Similar to Meridiani Planum and Gusev Crater bedrock, samples may contain up to 35% SO_3.

Analysis of field samples with XRD and SEM indicates that the predominate secondary products observed are gypsum and amorphous silica. Varying degrees of alteration are seen; for example gypsum forms as crystalline deposits on basalt and as more extensive, pure deposits. One curious result was the identification of black, spindle-like crystals of native selenium. Selenium is chemically similar to sulfur and is often found in sulfur compounds.

Experimental and theoretical studies of acid-sulfate alteration of Cerro Negro basalt [6] exhibit many similarities to the field samples, including the predominance of amorphous silica and gypsum as reaction products and the rapid reactivity of plagioclase phenocrysts. However, there are also some notable differences, including the occurrence of Al- and Mg-sulfate minerals in the experiments and models; whereas, they are rare in the field samples. These results indicate that the Mg and Al have largely been mobilized out of the natural system.

Sediment and condensed fluid samples were used in enrichment cultures targeting sulfur-, thiosulfate- and sulfate-reducing thermophiles and sulfide oxidizers at acidic conditions. To date nearly 4 dozen positive enrichment cultures incubated at 80°C have been identified from 9 sites and all tested metabolisms are represented. Positive enrichment cultures include both autotrophic and heterotrophic sulfur reducers, as well as aerobic sulfur oxidizers. Thiosulfate and sulfate were also reduced under anaerobic, acidic conditions. Ongoing studies will continue to characterize these microbial communities and their energy sources to assess the habitability of early Mars in similar environments.

Conclusions: Cerro Negro, Nicaragua is an ideal terrestrial analog to understand the geochemical pathways involved in acid-sulfate weathering. SO_2 is emitted from vents in the volcanic field and interacts with water to make sulfuric acid and hydrogen sulfide. This vapor condensate alters the freshly erupted basalts, resulting in large increases of sulfur, mainly as sulfates, and silica, as well as some Fe oxides and clays. The products observed in field samples, experiments, and computer models match those observed by spacecrafts and landers on Mars. Abundant Ca-sulfate is explained by the release of Ca^{2+} during plagioclase weathering. Similar release should yield Al-, Mg-, and Fe-sulfates, but they are not as prevalent in Cerro Negro samples, indicating there may be some loss from the system. Ongoing evaluation of microbial communities is providing information on what organisms can thrive in this type of environment.

References: [1] Gendrin A. et al. (2005) *Science, 307,* 1587-1591. [2] Murchie, S. et al. (2009) *JGR, 114,* E00D07. [3] Squyres S. W. et al. (2007) *Science, 316,* 738-742. [4] McCollom T. M. and Hynek B.M. (2005) *Nature, 438,* 1129-1131. [5] Tosca N. J. (2004) *JGR, 109,* E05003. [6] McCollom T. M. et al. (2010) LPSC XXXXI, this meeting. [7] Walker J.A. and Carr M.J. (1986) *USGS Bulletin, 97,* 1156-1162. [8] Lodders K. (1998) *Meteoritics and Planet. Sci., 33,* A183-190. [9] Rieder, R. et al. (2004) *Science, 306,* 1746-1749. [10] McSween S.M. et al. (2004) *Science, 305,* 842-845.

Figure 1: Context photo showing several large-scale fumaroles at Cerro Negro, Nicaragua. Differences in color relate to differing mineral assemblages and degrees of alteration. The arrow points to a person for scale.

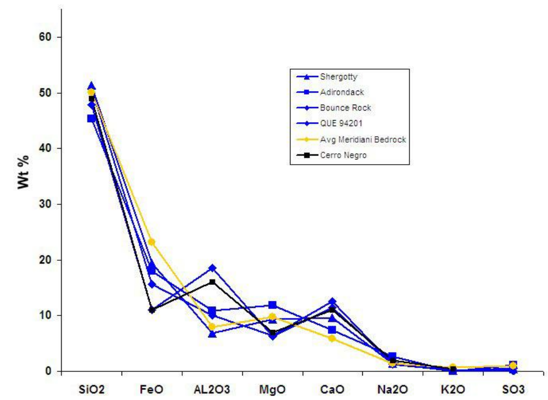

Figure 2: A comparison of Cerro Negro fresh basalt elemental chemistry from [7] and Mars rocks. Data in blue are Mars meteorite compositions and rocks sampled by the MER ([8], [9], [10]) and orange represents the average composition of Meridiani bedrock with the excess sulfur removed [4].

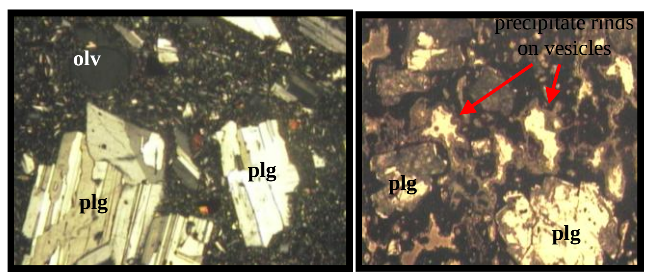

Figure 3: Cerro Negro thin sections of fresh and altered samples. (A) Polarized light thin section. Plagioclase (plg) and olivine (olv). (B) Visible light thin section of acid-sulfate weathered sample. Plagioclase is one of the first minerals to weather, freeing up Ca^{2+} for formation of Ca-sulfates.

Table 1: Acid-sulfate mineralogy of theoretical geochemical models, Cerro Negro alteration products, and materials at the MER landing sites.

	Theoretical models [6]	**Cerro Negro**	**Mars Rovers (i.e. [3])**
Sulfate/salts	Alunite, anhydrite, Mg-sulfates	Alunite, anhydrite, gypsum, Mg-sulfates	Gypsum, Mg-sulfates, halite
Fe minerals	Hematite	Bernalite ($Fe^{3+}(OH)_3$), jarosite	Hematite, jarosite, unidentified Fe3D3 mineral
Clay minerals	Kaolinite	Amorphous clays, smectites	Unidentified clays kaolinite? allophone?
Silicon	Quartz	Opaline, amorphous silica	Opaline, amorphous silica