ASSESSING ENVIRONMENTAL CONTROLS ON ACID-SULFATE ALTERATION AT ACTIVE VOLCANOES IN NICARAGUA: APPLICATIONS TO RELIC HYDROTHERMAL SYSTEMS ON MARS.

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Introduction: Hydrothermal acid-sulfate alteration of Mars' crust was likely widespread in ancient times, owing to the ubiquitous presence of water, widespread volcanism and high heat flow. Results from CRISM on MRO and the Spirit Rover attest to acidic, high temperature alteration of basaltic materials and secondary mineral assemblages include abundant sulfates, silica, and some phyllosilicates [e.g. 1–2]. Different suites of alteration minerals occur across Mars, which is likely a result of environmental variables including fluid and parent rock composition, temperature, pH, and duration of volcanic activity. Thus, the alteration mineralogy holds clues to the ancient environments and overall habitability of Mars. We studied two active acidic volcanoes in Nicaragua to assess the controls on secondary mineralogy to elucidate the likely paleoenvironments of early martian hydrothermal systems.

Field Sites: The Cerro Negro (CN) and Momotombo (MO) volcanoes in Nicaragua are active centers resulting from subduction of the Cocos plate. Both basaltic volcanoes were built from numerous effusive to explosive eruptions in historical times. Products are similar at each volcano and range from lavas with phenocrysts of plagioclase, pyroxene, olivine, and magnetite to glassy cinders and ash. Bulk compositions are similar to the martian crust [3]. Many fumarolic vents exist within the volcanoes and basalts are undergoing extensive acid-sulfate alteration over a range of temperature, pH, and gas composition.

Methods: We conducted multiple field campaigns at CN and MO, measuring local environmental variables and collecting samples. The fumarole vents ranged in temperature from 45°C to 450°C and pH from -1 to 6. We analyzed secondary mineral assemblages across this range of environmental conditions occurring in a uniform basaltic parent material with two similar but distinct gas compositions (MO had much higher HCl and 1.5× more S [4]). We used the MSL CheMin equivalent Terra XRD/XRF instrument as well as a VNIR reflectance spectrometer [5, this meeting] in situ for direct comparisons to Mars data. Additional laboratory analyses include XRD and thin-section petrography, bulk chemistry from XRF, raman, microscopic imaging with SEM and condensed gas analysis.

Environmental Controls on Acid-Sulfate Alteration: The highest temperature and lowest pH fumaroles consisted of relatively simple secondary mineral assemblages dominated by elemental sulfur surrounding the active vents, and an apron consisting of gypsum and amorphous silica (Fig. 1). Within a few years the primary basalts are entirely reduced to these products, with the S° precipitating from the gases, forming large crystals. The Si is a result of the wholesale leaching of the basalts and the mobilized Ca^{2+} combined with condensed H_2SO_4 leading to the gypsum crusts. Minor amounts of hematite, and the phyllosilicates nontronite and muscovite were occasionally present. The highest temperature sites also exhibited abundant cristobalite and tridymite, high temperature SiO_2 phases.
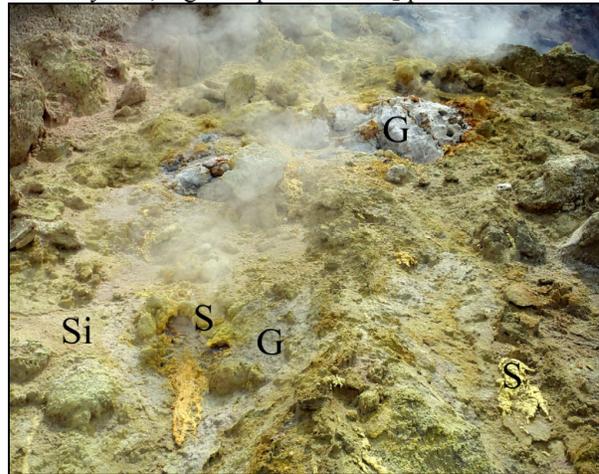

Fig. 1. High temp (150°C), low pH (-1) active fumarole at Momotombo. S = elemental sulfur around vents, G = gypsum, Si = amorphous silica. Image is ~2 m wide.

The alteration was slower at the moderate pH (4–5) fumaroles, occurring on decadal scales (reconstructed from eruption histories). Gypsum and amorphous silica were similarly abundant in these settings (Fig. 2). No elemental S was detected; instead this element was sequestered into a number of Al, Fe, Mg, and Ca sulfates including alunite (Al equivalent of jarosite), jarosite, $Fe_2(SO_4)_3$, szomolnokite ($Fe^{2+}SO_4 \cdot H_2O$), mereiterite ($K_2Fe^{2+}(SO_4)_2 \cdot 4H_2O$), kieserite ($MgSO_4 \cdot H_2O$) and hexahydrite ($MgSO_4 \cdot 5H_2O$). Fe also partitioned into goethite and hematite phases. Zeolites were present in some samples in minor amounts and phyllosilicate minerals were rare in XRD but easily detectable in VNIR data and included montmorillinite and smectite-kaolinite mixtures. Temperatures ranged from 45°C to 115°C, but this variable had little effect on the resultant alteration minerals and their abundances.

Fig 2. 1995 eruption cone at Cerro Negro (T ~100°C, pH ~4–5). Nearly all basalt has undergone acid-sulfate alteration. White colors include abundant gypsum, minor alunite, and traces of Mg-sulfates. Orange represents nanophase FeOx and Fe-sulfates, including jarosite. Red shows Fe-oxides, including hematite. Tans and grays are mostly amorphous Si. Image is ~75 m wide.

The highest pH site (~6) had a temperature of 60°C and was farthest from the central portion of the CN crater. Alteration at this site included white precipitate rinds on basalt cinders within actively steaming ground. Here, calcite was the dominant secondary mineral, with minor amounts of gypsum and traces of Ca phosphate.

Outwash basins. At both volcanoes, outwash catchments existed downslope from the active vents. At CN, "bathtub rings" were present and likely resulted from evaporation of ponded water that dissolved, transported, and precipitated altered products during rainfall events. Gypsum was a major constituent, owing to its high solubility. In addition, numerous hydrated sulfates were present that were not seen at the upslope vents including pickeringite ($MgAl_2(SO_4)_4 \cdot 22H_2O$), alpersite ($MgSO_4 \cdot 7H_2O$) mendozite ($NaAl(SO_4)_2 \cdot 11H_2O$), and melanterite ($FeSO_4 \cdot 7H_2O$). Additional products included zeolites and epidote. Interior to the bathtub rings, the main mineral phases were alunite and goethite, which were likely transported intact from the vent areas above.

Finally, the CheMin-equivalent XRD/XRF provided robust and quantitative in situ mineralogy (Fig. 3). However, VNIR measurements identified a number of minerals not seen in the XRD results [5]. Hematite and goethite often existed as thin surface coatings that could not be detected in XRD but were distinct in VNIR data. Also, many phyllosilicates were seen in VNIR, but not in XRD data without specific preparation for clays, limiting CheMin's ability for detecting martian clays. Thus, multiple techniques are required for characterization of hydrothermal sites on Earth and Mars.

Comparison between the two volcanoes. CN and MO have nearly identical parent lithology but vary in temperature (higher at MO) and gas chemistry, which results in MO having more vigorous steam emissions with lower pH from higher HCl and S. In general,

more high-temperature SiO_2 phases and amorphous silica were seen at MO, as well as a greater abundance of elemental sulfur. MO also had more zeolite minerals and a variety of muscovite phases.

Applications to Mars: Relic hydrothermal systems on Mars were likely widespread and represent a key target for future astrobiological missions – the origin of life on Earth may have begun in a Fe-S hydrothermal setting [e.g. 6]. Resultant martian alteration assemblages seen by rovers and orbiters can provide insights into the local paleoenvironmental conditions. Our work on basaltic hydrothermal systems undergoing acid-sulfate alteration over a range of pH, temperature, and gas compositions provides a framework for interpretation of existing and future results from Mars.

The fumarolic areas of CN and MO had a high diversity of alteration minerals over cm to a few meter scale, and similar variety is expected from relic martian systems. Existing orbiting spectrometers at Mars have spatial footprints significantly larger than the altered regions of CN and MO, and thus similar scale martian hydrothermal features may only be detectable by higher spatial resolution instruments or landers. Fluvial processes on Mars may have distributed acidic alteration products over a broader region, and our results suggest that these would contain a wealth of hydrated sulfates. While the long-term stability of all these mineral phases under cold-dry martian conditions is not known, the results provide an initial conceptual model for interpreting local conditions at martian fumarole sites.
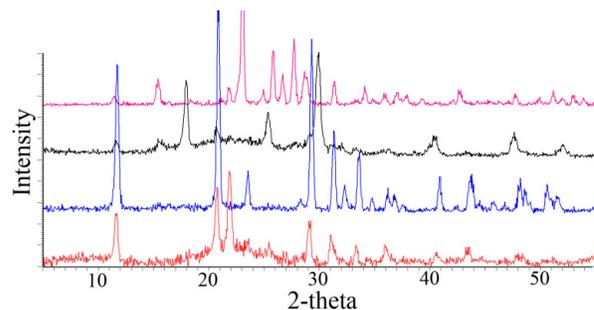

Fig 3. Examples of stacked diffractograms from Terra. From top to bottom: pure S; 79% natroalunite and 21% gypsum; pure gypsum; a mix of 40% gypsum, 40% christobalite, and 20% amorphous (broad hump from 18°–27° 2-theta).

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