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

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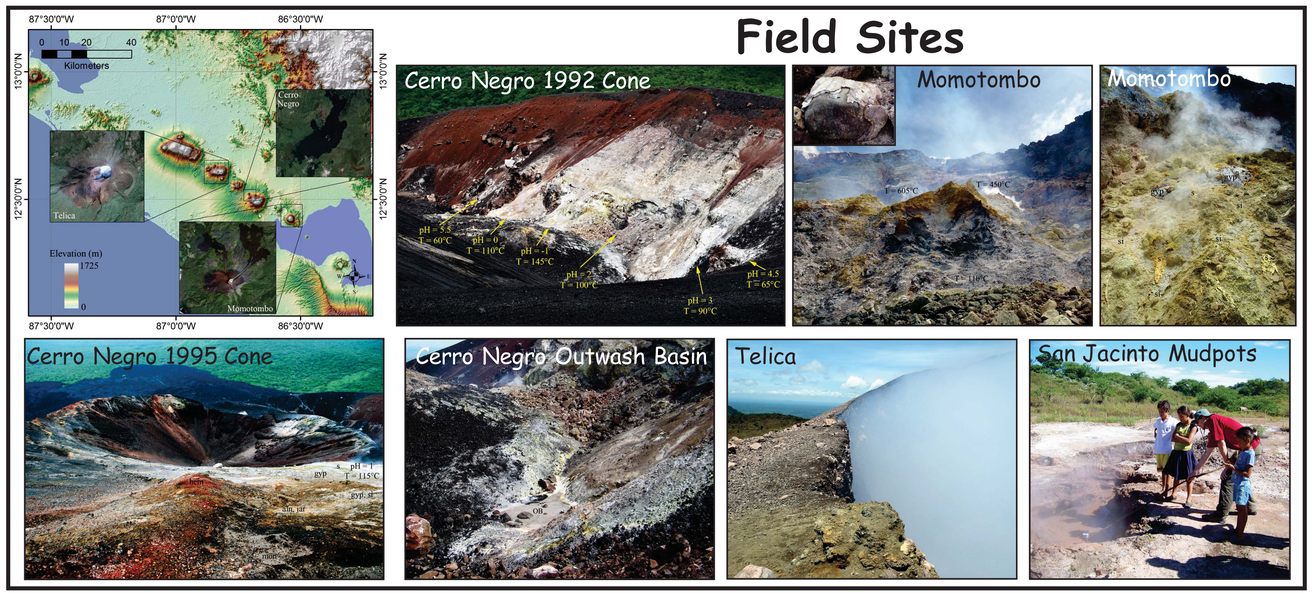
Introduction

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 orbiters 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 active acidic volcanoes in Nicaragua with similar parent lithology to Mars rocks to assess the controls on secondary mineralogy and elucidate the likely paleoenvironments of early martian hydrothermal systems [3-5].

Field Sites



Methods

- Major field campaign in August, 2012
  - Coordinated measurements of environmental parameters with field samples.
  - Characterized pristine to heavily altered materials.
- Measured *in situ mineralogy* with the CheMin equivalent Terra XRD/XRF instrument and CRISM and OMEGA-analog VNIR reflectance spectroscopy with ASD's TerraSpec 4 (see also Marcucci et al., this meeting).
- *Bulk solid/fluid chemistry* from XRF and IC-AES.
- Trace mineralogy from thin-section petrography, electron microprobe & SEM-EDS.

Aqueous Alteration Mineralogy

Table 1. Typical major, minor, and trace minerals identified in five types of environmental settings in Nicaraguan volcanoes.

	Major Phases	Minor Phases	Trace Phases
Fumaroles: pH = 1- to 1; T > 100°C	sulfur; Si (amorphous); SiO_2 (cristobalite and tridymite); gypsum ($CaSO_4 \cdot 2H_2O$);	hematite (Fe_2O_3)	muscovite; nontronite; montmorillonite
Fumaroles: pH = 4.0 to 5.5; T = 50°C-100°C	gypsum; Si (amorphous)	jarosite ($KFe^{3+}{}_3(SO_4)_2(OH)_6$); alunite ($KAl_3(SO_4)_2(OH)_6$); $Fe_2(SO_4)_3$; sodium alum ($NaAl(SO_4)_2 \cdot 12H_2O$); alunogen $Al_2(SO_4)_3 \cdot 17H_2O$); goethite (FeOOH); zeolites; montmorillonite	szomolnokite ($Fe^{2+}SO_4 \cdot H_2O$); mereiterite ($K_2Fe^{2+}(SO_4)_2 \cdot 4H_2O$); kieserite ($MgSO_4 \cdot H_2O$); hexahydrite ($MgSO_4 \cdot 5H_2O$); smectite; kaolinite
Fumaroles: pH = 6; T = 60°C	calcite ($Ca(CO)_3$)	gypsum	brushite ($CaHPO_4 \cdot 2H_2O$)
Outwash Basins: T = ambient	gypsum; alunite; goethite	pickeringite ($MgAl_2(SO_4)_4 \cdot 22H_2O$); zeolites	alpersite ($MgSO_4 \cdot 7H_2O$); mendozite ($NaAl(SO_4)_2 \cdot 11H_2O$); melanterite ($FeSO_4 \cdot 7H_2O$); epidote
Mudpots: pH = 1.5 to 4.0; T = 75°C-100°C	kaolinite; montmorillonite	despujolsite ($Ca_3Mn^{4+}(SO_4)_2(OH)_6 \cdot 3(H_2O)$); khademite ($Al(SO_4)F \cdot 5(H_2O)$); fibroferrite ($Fe^{3+}(SO_4)(OH) \cdot 5(H_2O)$); pickeringite; alunogen ($Al_2(SO_4)_3 \cdot 17H_2O$)	stilbite, aerinite, gobbinsite; FeOCl; potassium-alum; illite; chlorite; vermiculite

Acknowledgements
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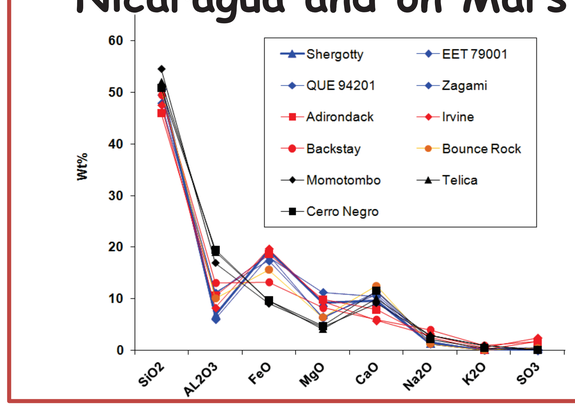
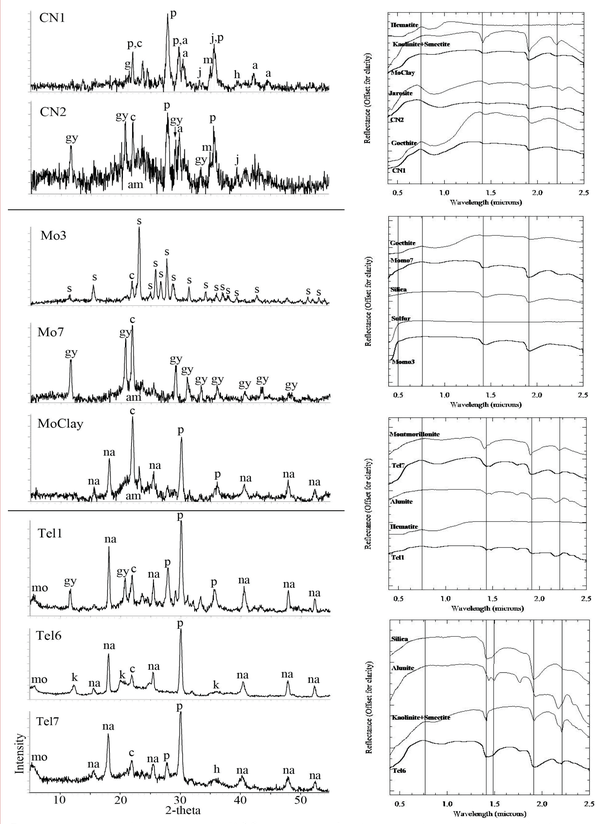
Fresh Basalts in Nicaragua and on Mars

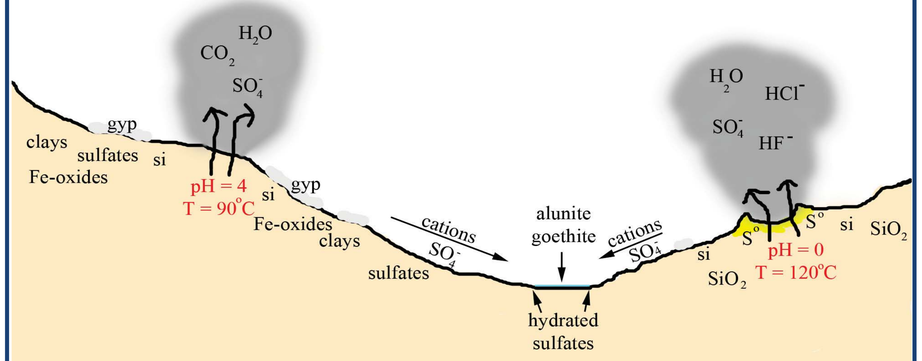


XRD and VNIR Data of Alteration Products



Some concordance and differences between the two techniques. VNIR captures more iron and clay mineralogy while XRD discerns trace phases. a = augite; am = amorphous silica hump; c = cristobalite; g = goethite; gy = gypsum; h = hematite; k = kieserite; p = pyroxene; m = melanterite; mo = montmorillonite; na = natroalunite; s = sulfur

Geochemical Model



Schematic of Nicaraguan fumarolic systems with moderate and extreme acidity and their major alteration products and distributions. si = amorph. silica, SiO_2 represents high temperature phases, and gyp = gypsum.

Conclusions

- Field work was conducted at five acid-sulfate volcanic environments in Nicaragua to characterize the geochemical pathways of mineral alteration.
  - Mars-relevant instrumentation was used and VNIR and XRD give similar, yet different, results.
  - Environmental parameters were correlated with alteration mineralogy to assess the controls on weathering.
- Alteration mineralogy is similar to findings from Mars.
- pH ~ 0 and highest T (>130°C) fumaroles resulted in high-T SiO_2, amorphous Si, S^o, and some gypsum.
- pH ~ 4, T ~ 100°C fumaroles led to amorphous Si, abundant sulfates and substantial phyllosilicates.
- pH ~ 6, T ~ 60°C fumaroles yielded calcite & gypsum.
- High fluid:rock ratios lead to numerous hydrated sulfate phases and widespread phyllosilicates.
- Many clay minerals can form under acidic conditions.
- *The results serve as a conceptual model for interpreting hydrothermal paleoenvironments on early Mars.*

References
[1] Gendrin A. et al. (2005) Science, 307, 1587-1591. [2] Murchie S.L. et al. (2009) JGR, 114. [3] Hynek B.M. et al. (2013) JGR, (in review). [4] Marcucci E.C. et al. (2013) JGR, (in review). [5] McCollom T.M. et al. (2013) JGR, (in review).