

**ACIDIC ALTERATION IN A YOUNG BASALTIC LAVA FIELD: SULFUR-BEARING PRODUCTS AND IMPLICATIONS FOR MARS.** C. N. Achilles<sup>1</sup>, A. C. McAdam<sup>1</sup>, C. A. Knudson<sup>2</sup>, K. E. Young<sup>1</sup>, J. Bleacher<sup>1</sup>, D. Bower<sup>2</sup>, J. Eigenbrode<sup>1</sup>, C. Hamilton<sup>3</sup>, T. Hewagama<sup>2</sup>, C. Nixon<sup>1</sup>, J. Richardson<sup>2</sup>, S. Scheidt<sup>3</sup>, S. Sutton<sup>3</sup>, J. Voight<sup>3</sup>, M. Wasser<sup>4</sup>, N. Whelley<sup>2</sup>, P. Whelley<sup>2</sup>, <sup>1</sup>NASA GSFC, <sup>2</sup>University of Maryland/NASA-GSFC, <sup>3</sup>University of Arizona, <sup>4</sup>ADNET Systems/NASA-GSFC.

**Introduction:** Remote sensing observations and in situ chemical and mineralogical analyses have revealed the presence of sulfur-bearing rocks, soils, and dust across the martian surface [1]. Among the various S-bearing phases identified, sulfates have served as important minerals for constraining past pH, temperature,  $pH_2O$ , and  $pO_2$  conditions. Evaporative settings, groundwater diagenesis, hydrothermal alteration, and fumarolic alteration are among the various processes responsible for the production of sulfate on Mars. To understand the vapor and fluid conditions associated with basaltic alteration and sulfate formation, we explored fumarole-associated rocks and cave-like mineral deposits in a young basaltic lava flow

Terrestrial analogs are important for understanding the basaltic alteration conditions responsible for the formation of S-bearing minerals observed on Mars. To investigate early basaltic alteration products associated with fumaroles and meteoric waters, we studied S-bearing deposits in 4-year-old rocks from a basaltic fissure eruption in Holuhraun, Iceland. This young, remote volcanic field provides a unique opportunity to examine early S-rich alteration products and to monitor year-to-year changes under cold, dry conditions.

**Field Site and Samples:** The Holuhraun lava field, covering ~84 km<sup>2</sup>, was emplaced between August 2014 and February 2015 in central Iceland [2]. Primary and altered basalts were explored both inside the vent and

on the outer flanks during a 2018 Goddard Instrument Field Team (GIFT) field expedition. Within the vent, an alcove displaying yellow and white speleothems (Fig. 1a) and white ceiling deposits (Fig. 1b) were sampled to study the chemistry and mineralogy of the materials. Considered to result from the redistribution of S by percolating meteoric waters (initially products of volcanic exhalations and minor basaltic sulfides and/or glass), the alcove materials, altered ceiling basalt, and fresh alcove basalt (basalt results not shown) were acquired to investigate the role primary basaltic minerals play in the formation of these deposits. Additionally, numerous active fumaroles were observed within and outside the volcanic vent. Samples representing various degrees of vapor phase alteration were acquired to assess the type and abundance of secondary minerals formed. The alteration mineralogy for two fumarole-associated rocks are presented here: 1) HSP1 - basaltic alteration phases formed from interactions with fumarolic vapors and/or related fluids (Fig. 1c), and 2) HSP4 - condensate/encrustation phases and basaltic alteration products related to fumarolic vapors and/or related fluids (Fig. 1d).

**Mineralogy:** The mineralogy of sampled materials was determined from X-ray diffraction patterns acquired on a Bruker D8 diffractometer and analyzed by Rietveld refinement using MDI Jade software.

**Fumarole-Associated Rocks:** Diffraction patterns of fumarole-associated samples showed both primary

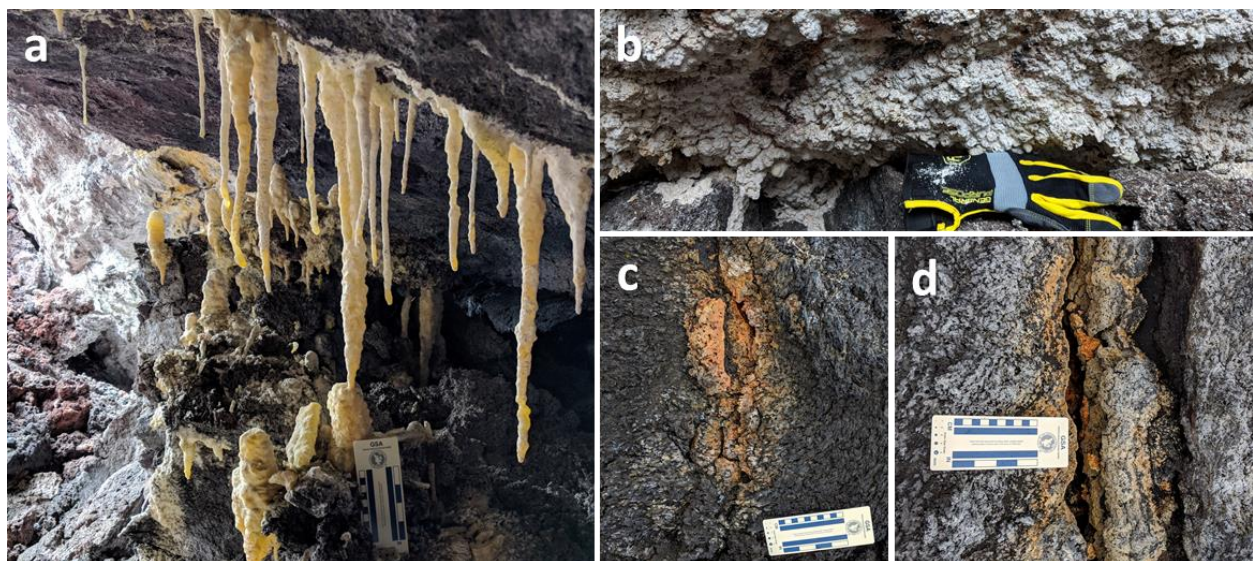


Figure 1. S-bearing deposits associated with the Holuhraun volcanic field. a) S-rich stalactites and stalagmites, b) deposits forming on the basaltic overhang, c & d) alteration near fumaroles

basaltic minerals and secondary phases (Fig. 2). Na-sulfate and natroalunite were the sulfates detected in HSP1. The presence of natroalunite indicates that acidic conditions persisted during at least one stage of alteration. Condensates and alteration phases identified in HSP4 consist primarily of elemental sulfur and Na-sulfate. Elemental sulfur is considered a direct precipitate of the vapor and Na-sulfate a product of basaltic alteration. The prevalence of Na-sulfate is notable and may be related to Na released during plagioclase dissolution.

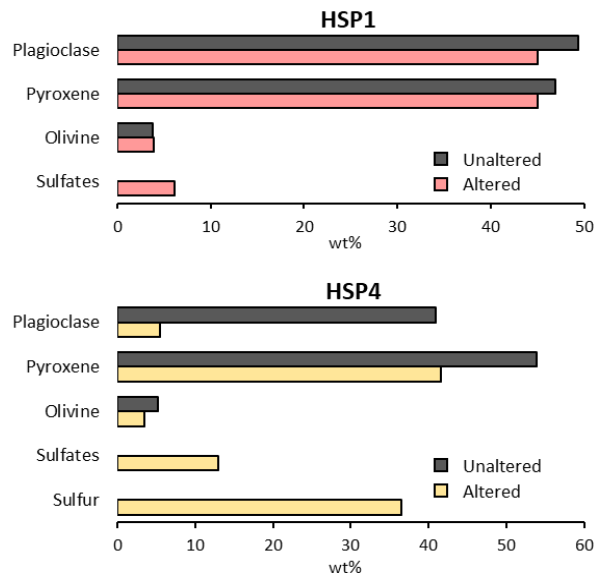


Figure 2. Mineralogy of fumarolic alteration samples and associated unaltered basalts.

**Speleothems and Ceiling Coatings:** Sulfate minerals comprise the entirety of the materials sampled from the alcove overhang. Na-Mg-sulfate and Mg-sulfate were identified as the primary minerals in the stalactite (Fig. 3a). Na-sulfate and minor amounts of Na-Mg-sulfate, Mg-sulfate, and Ca-sulfate were identified in the stalagmite (Fig. 3b). The white ceiling deposits were similar in mineralogy to the stalactite with the addition of minor Na- and Ca-sulfates (Fig. 3c).

The mineral assemblages described above are unique compared to basaltic cave deposits sampled in Craters of the Moon (COM) National Monument, Idaho and Mauna Loa, Hawaii [3,4]. Porter (2000) observed Na-Mg-sulfate and  $\text{KMg}(\text{SO}_4)\text{Cl}\cdot 3\text{H}_2\text{O}$  in the Hawaiian Lae'apuki Cave (2 years-old at the time of sampling), similar assemblages to the Iceland speleothems. Porter described these minerals as transient phases which dissolve as the lava tube cools to ambient conditions and interactions with meteoric waters increase [4,5].

In both the COM and Mauna Loa caves, deposits are older than those described in Lae'apuki Cave and Holuhraun, Na-sulfates deposits were observed on the

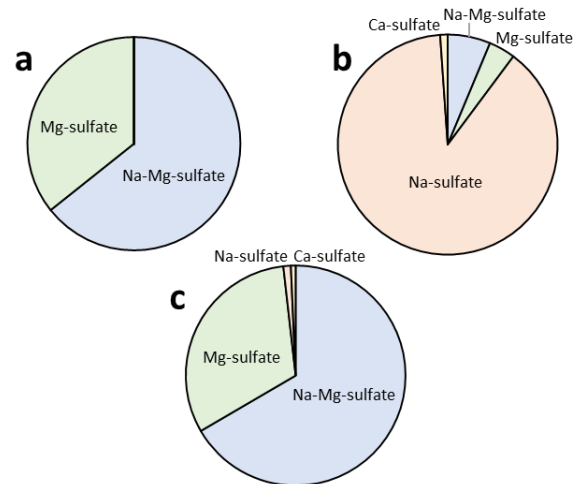


Figure 3. Mineralogy of alcove samples. a) stalactite, b) stalagmite, and c) overhang coatings

ceiling and floors of lava tubes. These phases are considered products from leaching of overlying basalt [3,4]. The stalactites and ceiling deposits observed in the Holuhraun vent have a significant Mg component, possibly implying early-stage alteration of the basalt, like observed in the Lae'apuki Cave, where highly soluble Mg-sulfates are preserved compared to less-soluble Na-sulfates observed in older basaltic cave deposits [6]. Annual sampling of the Holuhraun speleothems is planned in order to track the evolution of speleothem-associated sulfate phases with time.

**Implications for Mars:** The abundance of Na-sulfates observed in both fumarole and alcove samples would suggest the presence of Na-sulfates on Mars. Although these phases have yet to be confirmed on the martian surface, models show it is possible for Na-sulfates to precipitate from acidic, Na-, sulfate-, and chloride-rich solutions [7]. The presence of Na-sulfate phases in young, basaltic terrains and older caves and lava tubes, suggest these phases occur as early alteration products then persist in settings protected from exposure to destabilizing conditions (i.e. humidity, precipitation, etc.). If present on Mars, Mg- and Na-sulfates may occur in volcanic settings sheltered from major fluid interactions. These environments may be more common on Mars than Earth, especially in regions that hosted late volcanic activity during the "aridification" of Mars.

**References:** [1] King, P. L. and McLennan, S. M. (2010) *Elements* 6(2), 107-112. [2] Pedersen, G.B.M. et al. (2017) *J. Volcanol. Geotherm. Res.*, 340, 155-169. [3] Richardson, C. D. et al. (2012) *Planetary and Space Sci.* 65, 93-103. [4] White, W.B. (2010) *J. Cave and Karst Studies*, 72(2), 75-85. [5] Porter, A. (2000) *NSS News* 58, 10-17. [6] Spencer, R.J. (2000) *Rev. Min. and Geochem.* 40 173-192. [7] Tosca, N.J., McLennan, S.M., (2006) *EPSL* 241, 21-31.