

**BULK MINERALOGY OF SURFICIAL HYDROTHERMAL ACID-SULFATE DEPOSITS AT NÁMAFJALL, ÞEISTAREYKIR GEOTHERMAL FIELD, AND HENGILL VOLCANO, ICELAND: IMPLICATIONS FOR THE IDENTIFICATION AND INTERPRETATION OF HYDROTHERMAL DEPOSITS ON MARS.** S. R. Black<sup>1,2</sup>, B. M. Hynek<sup>1,2</sup>, L. J. McHenry<sup>3</sup>, C. Glenister<sup>3</sup>, B. I. Cameron<sup>3</sup>, T. M. McCollom<sup>1</sup>, J. Ludyen<sup>3</sup>, <sup>1</sup> Laboratory for Atmospheric and Space Physics, University of Colorado Boulder, 1234 Innovation Drive, Boulder, CO 80303; <sup>2</sup> Dept. of Geological Sciences, University of Colorado Boulder, Campus Box 600 UCB, Boulder, CO 80303; <sup>3</sup> Dept. of Geosciences, University of Wisconsin-Milwaukee

**Introduction:** Our ability to identify and interpret the geochemical conditions in relict Martian hydrothermal systems is dependent on our understanding of their terrestrial analogs. Parent rock composition influences secondary alteration assemblages [1,2]. Therefore, alteration of high Fe Martian basalts must be analyzed through the lens of high Fe terrestrial hydrothermal systems such as those at Námafjall geothermal field, Þeistareykir geothermal field, and Hengill Volcano in Iceland (Figure 1). We characterized the surficial alteration assemblages present at these sites, including three previously undescribed mudpots and a fumarole at Þeistareykir.

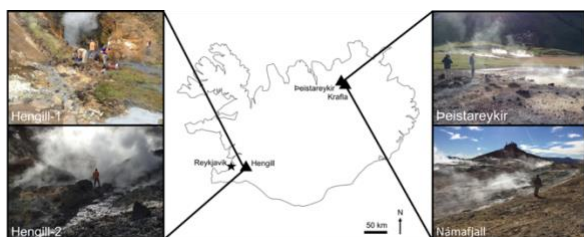


Figure 1: Sampling locations across Iceland

**Námafjall.** The Námafjall geothermal field is altering a Pleistocene basaltic hyaloclastite ridge [3] approximately 8 km south of the main Krafla caldera in northern Iceland. Alteration of primary basalts (10.05 wt % FeO<sub>T</sub>) at Námafjall is primarily through fluid-dominated mudpots and gas-dominated fumarole vents.

**Þeistareykir.** The Þeistareykir geothermal field is located ~4 km west of the Krafla fault system. The most active portion of this geothermal field is on and adjacent to the northern slope of Mt. Bæjarfjall (hyaloclastite) with surrounding lava flows emplaced approximately 10 – 2.5 kya [4]. The Þeistareykir geothermal field has been identified as one of the highest temperature fields in Iceland, with bedrock temperatures measured up to 380°C [5]. Our investigation focused on surficial alteration of parent basalts by mudpots (9.31 wt % FeO<sub>T</sub>) and a fumarole vent (11.48 wt % FeO<sub>T</sub>) located at 65.87174°N, 16.97193°W in the Þeistareykir geothermal field.

**Hengill.** The Hengill volcanic region sits atop the rift zone in southwest Iceland, just south of Lake Þingvellir. The Hengill volcanic complex includes one of the largest geothermal fields in Iceland [6,7]. Sampling at Hengill focused on alteration of primary basalt (11.80 wt % FeO<sub>T</sub>) at two locations on the grounds of the Nesjavallavir Power Plant. Location 1

(Hengill-1) consists of a fluid-dominated mudpot located at 64.09722°N, 21.27444°W. The nearby location 2 (64.08639°N, 21.27028°W, Hengill-2) consists of a complex fluid-dominated hot spring system with coalescing multicolored streams.

**Methods: Sample collection.** Fresh basalts were collected from the areas immediately adjacent to the primary alteration site to ensure that it was the parent substrate for the alteration process. Collection of alteration products focused on color and textural/morphological variations to ensure that all surficial mineralogical products were gathered.

**Sample analysis.** Primary basalts were analyzed with X-ray Diffraction (XRD) for bulk mineralogy, X-ray Fluorescence (XRF) for bulk elemental oxide chemistry, and Electron Probe Microanalyzer Energy-Dispersive Spectroscopy (EPMA-EDS) to quantify the composition of primary minerals. Secondary mineralogy was characterized using Visible Near-Infrared (VNIR) reflectance spectroscopy and bulk powder XRD, as well as Raman laser spectroscopy and Scanning Electron Microscopy Energy-Dispersive Spectroscopy (SEM-EDS) on select samples.

**Results:** Results are summarized below in Table 1.

Table 1: Alteration mineralogy of Icelandic hydrothermal sites.

		Amorphous SiO <sub>2</sub>	Crystalline SiO <sub>2</sub>	Fe-oxides/hydroxides	Mg-oxides/hydroxides	Ti-oxides	Ca-sulfates	Mg-sulfates	Na-sulfate	Al-sulfates	Fe# 61 Nitrojarosite	Fe-sulfates	Fe-sulfides	Kaolinite	Montmorillonite	Nontronite	Vermiculite	Zeolites	AlF <sub>3</sub>	Sulfur
Námafjall high F:R mudpots	35 – 90.6°C pH 1.5 - 3	*	*	t	*	*	*	t			*	*	*	t						*
Námafjall fumarole	~ 98°C	*	*	*	*	*	*	t	*	*	*	*	*	*	*	*	*	*	*	*
Þeistareykir high F:R mudpots	~ 80°C pH 3	t	*	*	t	*	*	*	*	*	*	*	*	*	t	*	*	t	*	*
Þeistareykir low F:R mudpots	~ 98°C pH 1.5	*	*	*	*	*	*	*	*	*	*	*	*	*	t	*	*	*	*	*
Þeistareykir fumarole	~ 40°C pH ~ 0.5	*	*	*	*	*	*	*	*	*	*	*	*	*	t	*	*	*	*	*
Hengill-1 high F:R mudpot	77 - 86°C pH 2.5 - 3	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Hengill-2 high F:R hot spring	22 - 55°C pH 3.5 - 6	*	*	*	*	*	*	*	*	*	*	*	*	*	t	*	*	*	*	*

F:R = fluid:rock; \* = mineral groups present at > 5 wt % in bulk powder XRD; t = < 5 wt %.

**Discussion:** In addition to the mineralogical characterization of new Mars analog sites, our results give additional insight into the formation of intermediate members of the alunite-jarosite solid solution series, and the influence of primary Fe on secondary mineral assemblages.

**Intermediate alunite-jarosite formation.** Until Fe-rich natroalunite was identified at multiple Nicaraguan [1,8,9], and Costa Rican [10,11] volcanoes, the only documented instances of alunite group minerals with moderate levels of Fe/Al substitution were of a 13% Fe alunite [12] (% Fe indicates the mole % Fe present in the B site in the alunite group formula  $AB_3(SO_4)_2(OH)_6$ ) and an 8% Fe alunite [13]. Our identification of 61% Fe natrojarosite at Námafjall in addition to the previously identified Fe-rich natroalunite [1,8-11] further supports the idea that Fe/Al substitution in the alunite-jarosite subgroup may be a common process in hydrothermal systems, and these intermediate products should be considered as a possible secondary mineral on Mars [9]. The combination of distinct natroalunite and natrojarosite peaks in our Raman spectra from sample Nama U4 (a mixture of natroalunite and 61% Fe natrojarosite per bulk XRD) (Figure 2) is suggestive of finely zoned or microcrystalline alunite and jarosite that is beyond the resolution ( $< 2 \mu\text{m}$ ) of the Raman instrumentation. Indeed, investigation of this sample with SEM-EDS suggests this intermediate chemistry is due to a chemically-variable microcrystalline ( $< 2 \mu\text{m}$ ) natroalunite-natrojarosite mixture (Figure 2).

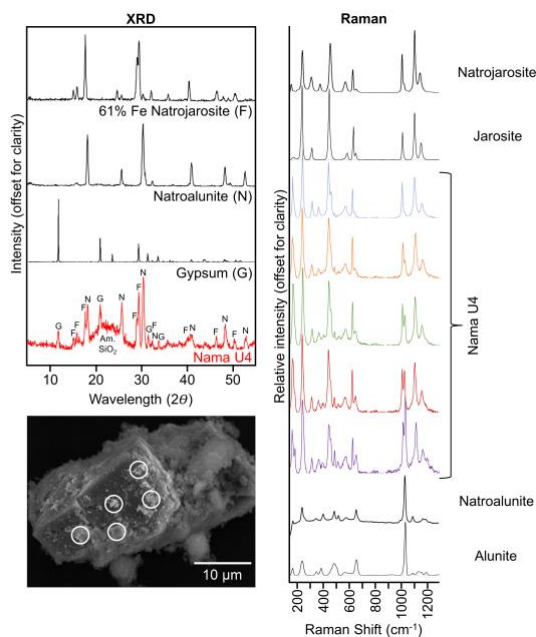


Figure 2 – XRD patterns (upper left) and Raman spectra (right) of sample Nama U4. SEM image in lower left shows areas (white circles) with EDS spectra consistent with Fe-bearing alunite group minerals.

**Effect of primary Fe on secondary mineralogy.** Our bulk powder XRD results show that the abundance of Fe-bearing secondary minerals generally correlates with wt % Fe in the parent basalt (Table 2). Alteration deposits at the Peistareykir mudpots are significantly enriched in Fe-bearing minerals, potentially due to additional Fe influx, extensively leached from a subsurface high-temperature region [e.g. 14], and are therefore excluded from our analysis.

Table 2: Parent Fe and average abundance of secondary Fe-bearing minerals

	wt % parent Fe <sub>T</sub>	Average wt % Fe-bearing secondary minerals
Hengill	11.80	14.4
Peistareykir fumaroles	11.48	8.6
Námafjall mudpots	10.05	5.4
Námafjall fumaroles	10.05	6.2
Peistareykir high F:R mudpots	9.31	14.6
Peistareykir low F:R mudpots	9.31	28.4
Poás, Costa Rica [10]	9.02	5.3
Turrialba, Costa Rica [10]	7.59	4.1

Despite the anomalously high values at the Peistareykir mudpots, the overall trend is clear, showing increasing average abundance of Fe-bearing secondary minerals with increasing parent rock wt % Fe. Additional data from Costa Rica [10] are also shown in Figure 3, and fit the trend observed in the Icelandic field sites from this study. From this trend, we expect alteration of Fe-rich Martian basalts to produce alteration assemblages with an average of ~10 – 40 wt % Fe-bearing minerals (Figure 3).

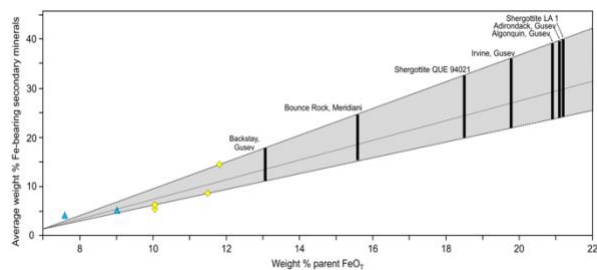


Figure 3 – Projected abundances of Fe-bearing secondary mineralogy for altered Fe-rich Martian basalts. Blue triangles = samples from Poás and Turrialba, Costa Rica [10], yellow diamonds = this study. Unaltered Martian basalts and their observed weight % parent Fe<sub>T</sub> (Backstay [15], Bounce Rock [16], Shergottite QUE 94021 [17], Irvine [15], Algonquin [15], Adirondack [18], and Shergottite LA1 [19]) are shown. We expect alteration of these primary basalts to produce mineral assemblages with an average Fe-bearing mineral abundance within the gray envelope.

**References:** [1] Hynek et al. (2013) *JGR: Planets*, 118. [2] Hynek et al. (2014) *LPSC*, Abstract #2172. [3] Ármannsson et al. (1987) *Jökull*, 37, 13–29. [4] Sæmundsson (2007) *Iceland GeoSurvey*. [5] Óskarsson et al. (2013) *Procedia Earth Planet. Sci.*, 7, 644–647. [6] Marty et al. (1991) *Chem. Geol.* 91, 207–225. [7] Hernández et al. (2012) *Bull. Volcanol.* 74, 2435–2448. [8] Marcucci et al. (2013) *JGR: Planets*, 118. [9] McCollom et al. (2013) *JGR: Planets*, 118. [10] Black and Hynek (2017) *Icarus*, in press. [11] Beckerman (2016) *MS Thesis, CU Boulder*. [12] Brophy et al. (1962) *Am. Min.*, 47, 112–126. [13] Alpers et al. (1992) *Chem. Geol.*, 96, 203–226. [14] Hui (2013), *UN University*. [15] Ming et al. (2008), *JGR*, 113. [16] Rieder et al. (2004), *Science*, 306, 1746–1749. [17] Lodders (1998), *Met. & Plan. Sci.*, 33, A183–A190. [18] McSween et al. (2006), *JGR*, 111. [19] Rubin et al. (2000), *Geology*, 28, 1011–1014.