ALTERATION MINERALOGY AND THE EFFECT OF PARENT LITHOLOGY AT HYDROTHERMAL MARS ANALOG SITES: INITIAL RESULTS FROM HENGILL AND KRAFLA VOLCANOES, ICELAND.

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Introduction: Relict hydrothermal sites have been identified on Mars at Gusev Crater [1-5], Nili Patera [6], and Coprates Chasma [7]. The Mars Reconnaissance Orbiter's (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and the Mars Express (MEx) Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) instruments have shown areas containing phyllosilicates, sulfates, and hydrated silica in the aforementioned locations [1-7]. These mineral assemblages resemble those seen in terrestrial hydrothermal sites, and investigation of these sites can provide key constraints on the geochemical conditions of formation, which may have major implications for habitability. However, the true variability of hydrothermal alteration products and the effect of parent lithology on these products is not yet well understood. To improve our understanding of Martian hydrothermal environments and their geochemical conditions, we must first investigate relevant analog sites here on Earth.

Methodology: Our August 2016 field survey sampled sites in the Krafla region including Námafjall, Leirhnjúkur, and Þeistareykir. Hengill sites were located near the Nesjavellir power plant *(Fig 1)*. An initial site survey was conducted by McHenry et al. [8] in 2013. Hengill and Krafla were chosen for their high Fe content in unaltered basalts (17.00 and 16.27 wt % FeO_T, respectively) [8] – much higher than most terrestrial volcanic sites, and relatively close to observed Fe abundances in Martian basalts [eg, 9]. Sites contained a mixture of basalt-hosted high temperature gas-dominated fumaroles, and fluid-dominated hot springs, with pH ranging from ~0.5 to 6.

Sampling included all visible color and texture variations at each site. Collected samples were dried and analyzed with the TerraSpec4 High Resolution Visible Near-Infrared (VNIR) Spectrometer from ASD Inc. and the Olympus Terra portable X-Ray Diffractometer (XRD). In situ temperature and pH were recorded for each sample.

Fresh basalt samples were collected at each site and are representative of the primary rocks that are being altered. Polished thin sections were made for scanning electron microscope (SEM), electron microprobe (EPMA), Raman laser spectrometer, and petrographic analysis. Whole rock elemental compositions were measured for each fresh sample using X-ray fluorescence (XRF) at University of Wisconsisn-Milwaukee.

Results: *Námafjall:* Fresh hyaloclastite basalts at the top of the Námafjall ridge have moderate Al and some of the higher Fe and Ti abundances in this sample set *(Table 1)*. Fumarolic (up to 98°C) alteration on the slopes and summit of Námafjall is dominated by amorphous and crystalline SiO_2, sulfur, Fe- and Ti-

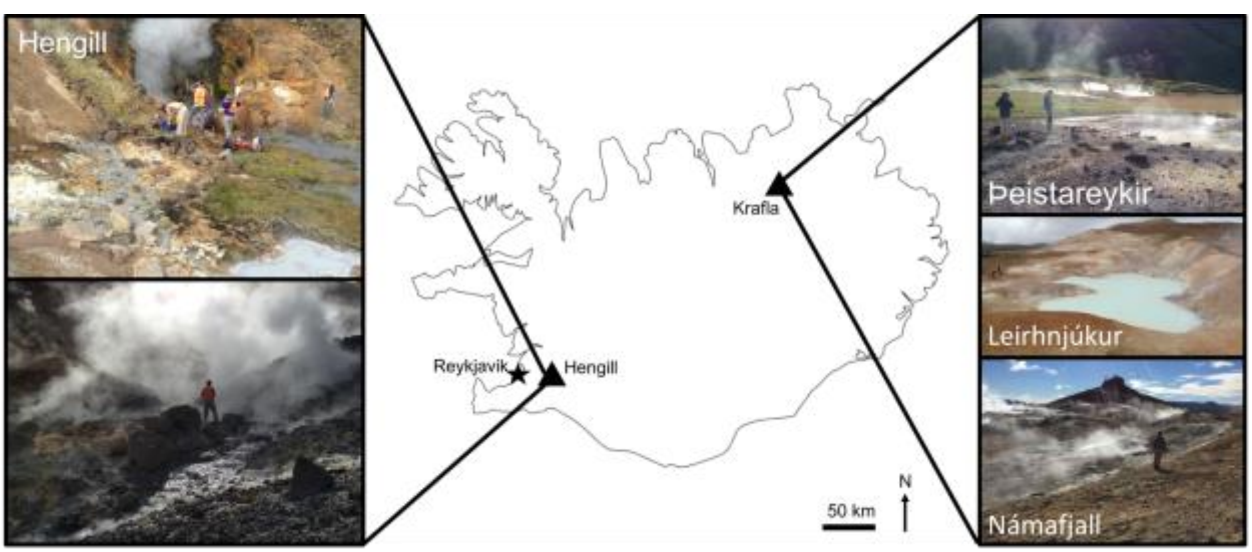

Figure 1: Sample locations at Krafla and Hengill Volcanoes, Iceland

oxides, gypsum, high Al natrojarosite (molar Fe/(Fe + Al) = 84-92), kaolinite, and the Ca/Al/Na zeolites epistilbite and heulandite *(table 2)*.

Leirhnjúkur: Fresh basalts at the base of Leirhnjúkur have the lowest Ca and Al and highest Fe abundances relative to others in this sample set *(Table 1)*. Hot spring (pH 2, up to 80°C) and fumarolic (up to 97°C) alteration of these basalts results in amorphous SiO_2, anatase, Ca/Al/Mg/Fe-sulfates such as rhomboclase and alunogen, kaolinite, sulfur, and zeolites such as heulandite and maricopaite *(Table 2)*.

Þeistareykir: Þeistareykir's fresh basalts are the most Al- and Mg-rich, as well as being Fe-poor relative to the other substrates included in this sample set *(Table 1)*. Fumarolic (pH ~ 0.5, up to 40°C) alteration of these basalts results in amorphous SiO_2 and tridymite, sulfur, vermiculite, and sulfates such as gypsum, alunogen, natrojarosite, pickeringite, and rhomboclase. Nearby hot spring alteration (pH 1.5-3, 80-98°C) in the same basalts results in more diverse mixtures – including Fe- and Ti-oxides, Al/Mg/Fe-phyllosilicates, and Al/Mn/Ca/Fe-sulfates *(Table 2)*.

Hengill: The two Hengill locations sampled for this study were both located in basalts with lower Fe compositions than the previously reported 17.00 wt % [8]. This fresh substrate also had the highest Al and Ca abundances of those included in this study *(Table 1)*. Fluid-dominated (pH 2.5-3, 77-85.9°C at site 1; pH 3.5-6, ambient - 55.5°C, with dry areas up to 88.4°C at site 2) alteration of these basalts resulted in amorphous SiO_2, abundant Fe-oxides/hydroxides, anatase, Ca/Fe/Al/Mg-sulfates, Al/Mg/Fe-phyllosilicates such as kaolinite and vermiculite, sulfur, and the zeolite Philipsite-K *(Table 2)*.

Table 1: Fresh basalt compositions from each sampling location

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
Námafjall	49.85	2.25	13.56	14.17	0.23	5.21	10.63	2.27	0.28	0.25
Leirhnjúkur	48.43	2.02	12.71	15.92	0.24	5.59	9.92	2.29	0.34	0.20
Þeistareykir	47.36	1.57	13.86	12.76	0.20	8.60	11.53	1.78	0.22	0.18
Hengill	46.48	2.15	14.42	13.11	0.20	6.63	12.16	1.94	0.20	0.24

Discussion: Our initial results show increased Al/Ti/Mg in the primary substrate manifests itself through an increase in sulfates and oxides/hydroxides with similar chemistries in alteration products. The lack of Fe-oxides/hydroxides at Leirhnjúkur despite the high Fe abundances in the primary substrate may be due to sampling error. Alteration at this site is pervasive, and the fresh samples that were collected may not be representative of the primary substrate that is undergoing alteration. Our 2017 field campaign will further address this question. These initial results suggest alteration of Mars' Fe-rich basalts could result in a much higher abundance of Fe oxides/hydroxides, sulfates, and phyllosilicates than what is observed at terrestrial analog sites. However, further site investigation is needed to reconcile the Fe discrepancy at Leirhnjúkur. Additional investigation will also be conducted via laboratory experiments and geochemical modeling.

Table 2: Alteration mineralogy (identified with VNIR and XRD) for each sampling location

Mineralogy	Þeistareykir *Mudpots*	Þeistareykir *Fumaroles*	Námafjall	Leirhnjúkur	Hengill
			Silicates		
Amorphous SiO_2	X	X	X	X	X
Cristobalite	X		X		
Quartz			X		
Tridymite	X	?	X		
			Oxides/Hydroxides		
Amorphous Fe-ox	X				X
Hematite	X				X
Goethite	X				X
Magnetite	X		X		
Anatase	X		X	X	X
			Sulfates		
Anhydrite			X		
Gypsum	X	X	X	X	X
Jarosite	X	X			X
Al-rich Natrojarosite			X		
Alunite			?		X
Alunogen	X	X		X	X
Apjohnite	X				
Pickeringite		X		X	
Hexahydrite					X
Rhomboclase	X	X		X	
Sodium Alum					X
			Phyllosilicates		
Kaolinite	X		X	X	X
Pyrophyllite	X				X
Vermiculite	X	X			X
			Zeolites		
Epistilbite			X		
Heulandite			X	X	
Maricopaite	X			X	
Phillipsite-K	X				X
			Other		
Elemental Sulfur	X	X	X	X	X

References: [1] Morris et al. (2008) *JGR*, **113**; [2] Ruff (2015) *LPSC*, 1613; [3] Ruff et al. (2011) *JGR*, **116**; [4] Squyres et al. (2008) *Science*, **320**; [5] Yen et al. (2008) *JGR*, **113**; [6] Skok et al. (2010) *Nat. Geosci.*, **3**; [7] Weitz et al. (2014) *GRL*, **41**; [8] McHenry et al. (2016) *LPSC*, 1207; [9] McSween et al. (2009) *Science*, **324**