

**HYDROTHERMAL ACID-SULFATE ALTERATION OF A SYNTHETIC MARS COMPOSITION BASALT: SECONDARY IRON MINERALOGY AND THE ROLE OF PRIMARY BASALT COMPOSITION.** S. R. Black<sup>1,2</sup>, B. M. Hynek<sup>1,2</sup>, T. M. McCollom<sup>1</sup>, and J. F. Larsen<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> Department of Geoscience, University of Alaska Fairbanks, PO Box 755780, Fairbanks, AK 99775-5780

**Introduction:** Much of our understanding of Martian hydrothermal systems comes from the study of their terrestrial counterparts [e.g. 1-4]. However, as previous studies have noted, variations in parent rock composition have an effect on secondary mineralogy in hydrothermal systems [e.g. 2]. Most basaltic terrestrial analogs have much lower Fe than the martian crust (*Table 1*), potentially limiting their utility in understanding alteration mineralogy analogous to weathering processes on early Mars. Our goal is to determine what role the increased Fe in Martian basalts will have on secondary alteration products, and whether alteration of our lower Fe terrestrial basalts results in secondary mineral assemblages which are meaningful in our interpretation of Martian hydrothermal systems

*Table 1: Elemental compositions of unweathered Martian basalts and commonly-utilized terrestrial analogs*

Sample	SiO <sub>2</sub>	FeO <sub>T</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	TiO <sub>2</sub>
<i>Martian basalts</i>									
Adirondack, Gusev [5]	45.3	21.09	10.43	11.9	7.76	2.09	0.03	0.42	0.49
Backstay, Gusev [6]	49.4	13.1	13.1	8.3	6.0	4.0	1.02	0.25	0.93
Irvine, Gusev [6]	47.5	19.7	8.3	9.5	5.8	3.0	0.60	0.37	1.06
Algonquin, Gusev [6]	41.9	20.9	6.4	16.0	4.0	2.3	0.40	0.39	0.58
Bounce Rock, Meridiani [7]	50.8	15.6	10.1	6.4	12.5	1.3	0.10	0.43	0.78
Shergottite LA 1 [8]	49.1	21.2	11.2	3.53	10.0	2.22	0.24	0.45	1.30
Shergottite QUE 94021 [9]	47.9	18.5	11.0	6.3	11.4	1.58	0.05	0.45	1.84
Representative Basalt [10]	47.58	18.00	10.87	11.90	6.12	2.94	0.19	0.29	0.76
<i>Terrestrial basalts</i>									
Kilauea, Hawaii - Pu'u O'o [11]	52.32	10.77	13.48	6.90	10.99	2.05	0.41	0.17	2.44
Kilauea, Hawaii - '74 flow [11]	51.87	10.59	13.30	7.44	11.02	2.71	0.47	0.17	2.48
Cerro Negro, Nicaragua [2]	49.73	9.70	19.50	4.73	11.50	2.18	0.43	n.r.	n.r.
Momotombo, Nicaragua [2]	54.40	9.10	16.90	4.47	9.20	2.89	0.91	n.r.	n.r.
Telica, Nicaragua [2]	51.72	9.60	19.10	4.13	10.10	2.84	0.96	n.r.	n.r.
Poás, Costa Rica [1]	53.30	8.12	17.46	4.36	8.49	2.95	1.08	n.d.	0.78
Turrialba, Costa Rica [1]	54.14	7.59	16.30	6.02	9.22	3.12	1.43	0.01	1.05
Hengill, Iceland [12]	50.10	13.90	13.40	4.86	9.61	2.84	0.68	0.27	2.89
Krafla, Iceland [13]	48.54	11.58	15.29	8.80	12.71	1.83	0.11	0.18	1.11

n.d. = not detected; n.r. = not reported

**Methods: Synthetic Mars basalts.** Synthetic Mars basalts (SMB) were created from pure mixed oxides (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, and MnO) and carbonates (CaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>) at the University of Alaska Fairbanks experimental petrology lab. Bost's representative Mars basalt composition [10] (*Table 1*) was used as a starting point when mixing pure oxides and carbonates, with additional Fe<sub>2</sub>O<sub>3</sub> added to the powder mixture for crystalline basalt in anticipation of increased Fe diffusion into the Pt crucible due to an extended period at high temperature. The mixed oxides were fused at a temperature of 1330°C for 4-6 hours and then rapidly quenched in water to create the SMBgl starting materials. SMBxl runs were held at an initial temperature of 1330°C for 4 hours and then slowly cooled by 4°C per minute to a final temperature of 959°C, where they were then quenched in water. Observed Fe absorption was minimal, yielding FeO<sub>T</sub> abundances up to an Irvine-type 19.77 wt % FeO<sub>T</sub> in our crystalline SMB (SMBxl) and 17.03 wt % FeO<sub>T</sub> in our

glassy SMB (SMBgl) (*Table 2*). Oxygen fugacity ( $f_{O_2}$ ) for reduced basalt formation was set at  $\Delta IW + 1.73$  (+/- 0.12) log units to simulate calculated conditions from SNC spinels [14].

*Table 2: Elemental compositions of parent materials measured by XRF analysis*

Sample	SiO <sub>2</sub>	FeO <sub>T</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MnO	TiO <sub>2</sub>
Crystalline "Mars" Basalt SMBxl	46.52	19.77	10.92	11.26	6.07	2.44	0.22	0.33	0.80
Glassy "Mars" Basalt SMBgl	48.17	17.03	11.35	11.53	6.29	2.59	0.24	0.33	0.85
Hengill basalt HN-BAS	46.48	11.80	14.42	6.63	12.16	1.94	0.20	0.20	2.15
Cerro Negro basalt CN-BAS	49.79	10.14	17.99	6.11	11.25	2.12	0.47	0.19	0.77
Turrialba basaltic andesite B. AND	54.14	7.59	16.30	6.02	9.22	3.12	1.43	0.01	1.05
Flagstaff andesite AND	69.30	2.50	16.51	0.99	0.36	0.37	5.48	0.03	0.29
Ruby Mt. rhyolite RHY	75.75	0.49	12.97	0.37	0.30	3.74	4.62	0.10	0.07
Millard County obsidian OBS	76.41	0.88	13.08	0.07	0.75	4.03	4.80	0.06	0.06

**Experimental setup.** Alteration experiments were run to simulate closed systems using both the SMB and terrestrial parent rocks (*Table 2*). Approximately 3 g of parent rock was ground to sand-size particles and placed in a Savillex Teflon reaction vessel. 1M H<sub>2</sub>SO<sub>4</sub> was added to achieve a 4:1 fluid:rock ratio by weight. Vessels were then sealed and placed in an oven at 95°C ± 5°C for 70 days. A second set of open system experiments were run with SMBxl and SMBgl parent rock. Approximately 4 g of sand-size parent rock were combined with 1M H<sub>2</sub>SO<sub>4</sub> at a 5:1 fluid:rock ratio, and kept at 95°C ± 5°C for 140 days. Every 14 days, alteration fluid was removed from the reaction vessel and kept for geochemical analysis. A small (~0.1 g) amount of solid and gel material was removed for mineralogical analysis, and new 1M H<sub>2</sub>SO<sub>4</sub> was added. The vessel was then sealed and returned to the oven.

**Sample analysis.** Upon completion of the experiment, alteration fluid was separated and saved for chemical analysis. Altered samples were then rinsed with ethanol and the Si-rich gel coating was separated from the solids. This step isolates products formed during the primary reaction phase (solids), and those formed from the subsequent dried gel. Both the solids and dried gel products were analyzed with Visible Near-Infrared (VNIR) reflectance spectrometry, bulk powder X-ray Diffraction (XRD), and Scanning Electron Microscopy Energy-Dispersive Spectrometry (SEM-EDS). Alteration fluids were analyzed for major element concentrations using an inductively coupled optical emission spectrometer (ICP-OES) and ion chromatograph.

**Results:** Closed-system alteration of our crystalline SMB resulted in a mixture of residual primary minerals (pyroxene, feldspar), with an abundance of secondary Mg-sulfates (hexahydrite/epsomite), large crystalline Fe-oxides/hydroxides (hematite, maghemite, goethite),

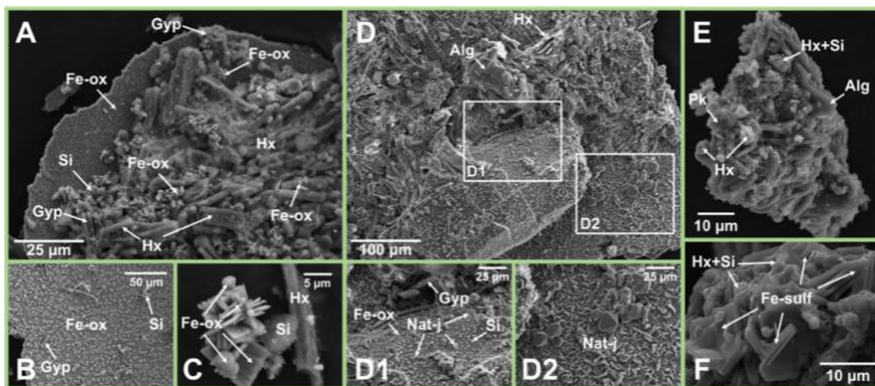


Figure 1: A-C) Solid alteration products from the closed-system SMBxl run; D) Solid alteration products from the closed-system SMBgl run; E and F) Evaporate products from the SMBgl separated gel material. Alg = alunogen; Hx = hexahydrite; Pk = pickeringite; Fe-ox = Fe-oxide; Gyp = gypsum; Si = amorphous SiO<sub>2</sub>; Fe-sulf = unidentified Fe-sulfate; Nat-j = natrojarosite

and amorphous SiO<sub>2</sub> (Figure 1a-c). Fluids collected from the reaction vessel contained 5.08x10<sup>5</sup> ppb Fe – five times higher than Fe concentrations in alteration fluids from HN-BAS (1.05x10<sup>5</sup> ppb), CN-BAS (1.97x10<sup>5</sup> ppb), and B.AND (1.01x10<sup>5</sup> ppb), indicating the potential for further Fe-bearing mineral formation upon complete evaporation of these hydrothermal fluids. SMBgl alteration products (Figure 1d-f) also contained hexahydrite/epsomite, as well as Al-sulfates (alunogen, pickeringite), Fe-oxides (titanomagnetite, and another unidentified Fe-oxide), an unidentified Fe-silicate and Fe-sulfate, amorphous SiO<sub>2</sub>, and abundant natrojarosite with ~84% Fe in the B site (alunite group: AB<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, with K/Na/Ca occupying the A site, and Al/Fe in the B site) as identified in bulk powder XRD, using McCollom et al's [15] solid solution series. Fluids collected from the SMBgl vessel contained 1.50x10<sup>6</sup> ppb Fe – an order of magnitude higher than all other samples. Alteration of terrestrial samples with lower parent FeO<sub>T</sub> also produced Fe-bearing secondary mineralogy (Table 3), however, in these cases secondary Fe is in the form of sulfates (primarily alunite group), and not Fe-oxides/hydroxides.

Table 3: Secondary Fe mineralogy in closed system reactions

	SMBxl	SMBgl	HN-BAS	CN-BAS	B.AND	AND	RHY	OBS
20% Fe Natroalunite								X
25% Fe Natroalunite			X	X				
84% Fe Natrojarosite		X						
Jarosite			X					X
Ferrinatrite								X
Unidentified Fe-sulfate		X						X
Hematite	X							
Goethite	X							
Maghemite	X							
Titanomagnetite		X						
FeSi		X						
Total wt % Fe-bearing mineralogy in XRD	22	31	23	30	25	11	4	< 1

**Discussion:** Field analog studies of basalt-hosted hydrothermal systems in Iceland [16] and Costa Rica [1] reveal a trend of increasing abundance of secondary Fe-bearing mineralogy as parent rock Fe increases [16]. Alteration of our SMB continues to follow this trend (Figure 2a). However, natural field sites such as those in Iceland and Costa Rica [16] rarely operate as true

closed systems, and results from our terrestrial parent rock closed-system experiments indicate slightly different trends (Figure 2b). Our experimental results suggest a negligible increase in overall abundance of secondary Fe-bearing mineralogy as basalts become increasingly enriched in primary Fe, although the mineralogy itself appears to vary (Fe-oxides/hydroxides vs. Fe-sulfates). We therefore expect alteration of Fe-rich Martian basalts to produce secondary assemblages in the range of ~15 – 35 wt % Fe-bearing minerals – similar to deposits we encounter at terrestrial analog sites.

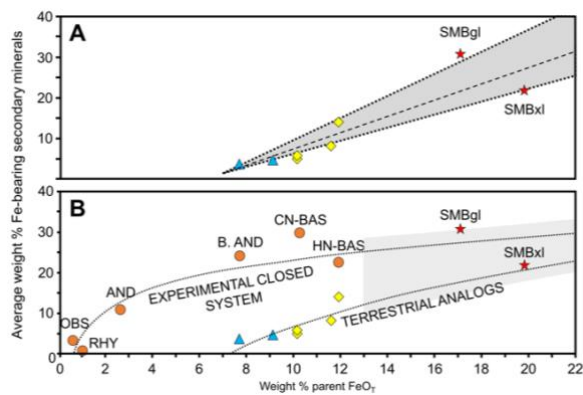


Figure 2 – A) Projected abundances of Fe-bearing secondary mineralogy from Black et al. (this meeting) [16], and B) for altered Fe-rich Martian basalts in closed and terrestrial systems (grey envelope). Red stars = our closed-system altered SMB products; Blue triangles = altered samples from Costa Rica [1]; yellow diamonds = altered samples from Iceland [16].

Data analysis is underway for open system reactions and results will be presented in March.

**References:** [1] Black and Hynek (2017), *Icarus*, in press. [2] Hynek et al. (2013), *JGR: Planets*, 118. [3] Marcucci et al. (2013), *JGR: Planets*, 118. [4] McCollom et al. (2013), *JGR: Planets*, 118. [5] McSween et al. (2006), *JGR*, 111. [6] Ming et al. (2008), *JGR*, 113. [7] Reider et al. (2004), *Science*, 306, 1746-1749. [8] Rubin et al. (2000), *Geology*, 28, 1011-1014. [9] Lodders (1998), *Met & Plan. Sci.*, 22, A183-190. [10] Bost (2012), *Ph.D. dissertation*. [11] Chemtob and Rossman (2014), *JVGR*, 286, 41-54. [12] Tronnes (1990), *JGR*, 95, 15893-15910. [13] Nicholson and Latin (1992), *J. of Pet.*, 33, 1105-1124. [14] Herd et al. (2001), *Am. Min.*, 86, 1015-1024. [15] McCollom et al. (2014), *Am. Min.*, 99, 948-964. [16] Black et al. (2018), *LPSC*, 49, Abstract # 1643.