

AQUEOUS ALTERATION OF BASALTIC LAVAS IN ICELAND: AN ANALOGUE FOR NOACHIAN MARS. B.L. Ehlmann¹, J.F. Mustard², D.L. Bish³, ¹IAS U. Paris-Sud XI ²Geological Sciences, Brown Univ. ³Geological Sciences, Indiana Univ. (bethany.ehlmann@ias.u-psud.fr)

Introduction: Orbital investigations of the basaltic terrains comprising Mars' earliest Noachian crust have revealed diverse assemblages of hydrated silicate mineral phases formed during aqueous alteration [1]. Most commonly detected are smectite clays, chlorites, prehnite, silica, and zeolite; hence, the rock record from early Mars preserves mostly evidence for neutral to alkaline pH environments. These include near-surface pedogenic and low-temperature/pressure hydrothermal systems [2-4]. In recent investigations of terrestrial Mars-analog sites, neutral to alkaline pH alteration of basalt has been neglected in favor of sulfur-rich, acidic systems. We began study of the near-neutral pH, near-surface alteration of basalt lava flows in Iceland as a geochemical and mineralogic analog for Noachian Mars [5]. This setting has provided a testbed for understanding synergies between different instrumental measurements used to infer past paleoenvironmental conditions and also provides an opportunity to study the habitability and organic preservation potential of crustal groundwater systems.

Appropriateness as an Analogue: Because the basaltic bedrock of Iceland is recently formed (<16Ma), with few localities of more highly evolved composition, and has poorly formed soils and sparse vegetation, ground and surface waters may be similar to those that might have existed on Noachian Mars. Iceland has a variety of geothermal spring systems of different temperatures and sulfur contents, each of which creates distinctive mineralogic assemblages. Here we have examined rocks collected from basalt flows that were in some places altered at the surface by pedogenesis and in other locations were hydrothermally altered by non-sulfurous groundwater circulation (low T, low S) as most analogous to Noachian Mars (Figure 1).

Site Name	Icelandic Basalts (Hvalfjordur, Berufjordur)
Location	61.3°N, 21.7°W and 64.8°N, 14.5°W
Areal Extent	Outcrops at tens to hundreds of meters-scale, with stratigraphy best-exposed in channels carved by fluvial erosion
Prime Science Questions	Do VNIR spectra accurately capture mineralogy, permitting paleoenvironmental determination? What are the synergies between XRD and IR techniques? Can these environments host and preserve evidence for life?
Analogous to	Most smectite-bearing terrains on Mars, especially as exposed by craters of the S. Highlands

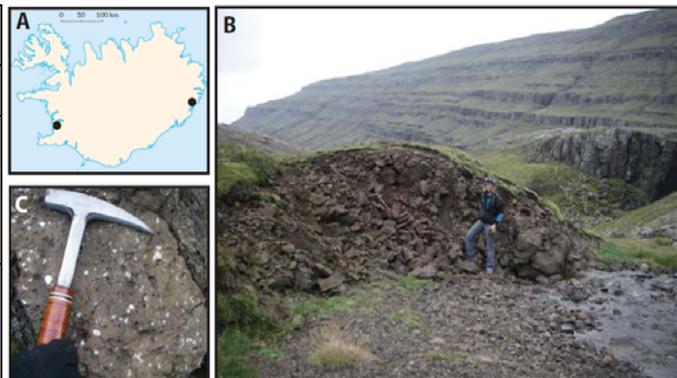


Figure 1. Sampling sites and study samples. (a) Rocks were sampled near Hvalfjordur (west) and Berufjordur (east). At both sites, massive basaltic flows exhibited evidence of alteration minerals filling veins and fractures. (b) Successive basalt flows eroded by glacial activity and a stream at Berufjordur, site of sample wtrfall016. (c) Outcropping of zeolitized basalt at Hvalfjordur.

Linking remote spectroscopic and in-situ mineral detections: Our sample characterization methods emulated orbital data from CRISM, OMEGA, and TES, which detect the infrared active components, linked to *in-situ* data such as will be measured by MSL's ChemMin instrument. Rock samples were surveyed in the field using a portable VNIR spectrometer. Altered and unaltered rocks that were typical for the locality were collected, as were altered rocks whose spectra were most similar to those measured by CRISM from Mars orbit (similar to the Al- and Fe/Mg clays at Mawrth Vallis as well as the smectite-zeolite-silica assemblages associated with Noachian cratered terrains). In RELAB, reflectance spectra from 0.4-25 μ m were acquired of dried particle-size separates (<150 μ m) derived from the bulk rock and from precipitated minerals extracted from vesicles and veins (Figure 2). X-ray diffraction (XRD) data were measured on the <25 μ m size fraction from 2° to 70° 2 θ with 0.02° 2 θ steps. Areas of the most

intense peaks from component minerals were measured, and the relative percentage of each constituent was determined using the reference intensity ratio (RIR) method [6]. Rietveld refinement was also applied, using the Topas Rietveld program, to determine the relative abundance of the well-ordered (i.e., non-clay mineral) components. Final mineral abundances (Table) represent wt. % obtained from the Rietveld method scaled to include the RIR-determined smectite abundances. To verify the presence of smectite and check for interstratified or non-expanding clays (e.g., chlorite, kaolinite), untreated samples with a (001) diffraction peak near 15Å were prepared as oriented mounts, dried, saturated with ethylene glycol, and then measured from 2-20° 2θ. Bulk chemistry of samples was measured with flux fusion/OES.

Sample	description	VNIR mineralogy	XRD mineralogy
hvalfj011	gray, friable rock	HCP + Fe/Mg smectite + (chlorite?)	smectite 17% pyroxene 34% plagioclase 40% ilmenite 5% clinoptilolite 5%
hvalfj025	host rock from rock with vesicles with blue-green precipitate	HCP + hydrated phase (FeOH- bearing?)	smectite 11% pyroxene 38% plagioclase 49%
hvalfj054	host rock from rock with vesicles with whitish precipitates	HCP + Mg smectite	smectite 17% pyroxene 63% plagioclase 5% hematite 5% levyne 9%
icel009	massive brown rock with greasy feel	HCP + Fe/Mg smectite	smectite 23% pyroxene 26% plagioclase 49%
icel010	massive black rock with greasy feel	HCP + Fe/Mg smectite	smectite 20% pyroxene 28% plagioclase 49% ilmenite 3%
hvalfj017	reddish friable rock	montmorillonite + hematite	montmorillonite 79% hematite 10% plagioclase 10%
hvalfj023	blue-green precipitate in vesicle	celadonite	celadonite 38% silica 35% smectite 20% plagioclase 6%
hvalfj055	opaque white to cream precipitate in vesicle	thomsonite (+ other zeolite?)	scolecite/mesolite 36% thomsonite 30% stilbite/stellerite 26% smectite 8%
hvalfj057	transparent, white xlls precipitated in vesicle	analcime	analcime 55% smectite 33% stilbite/stellerite 11%
wtrfall016	white precipitate from vein	hydrated silica	quartz 91% cristobalite 3% plagioclase 2% clinoptilolite 4%

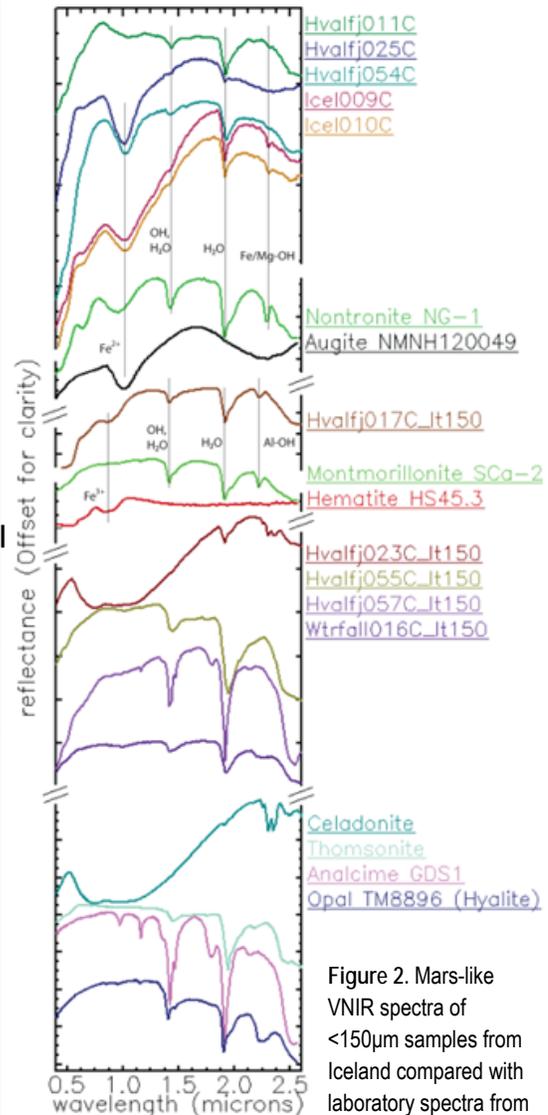


Figure 2. Mars-like VNIR spectra of <150µm samples from Iceland compared with laboratory spectra from USGS and CRISM spectral libraries

VNIR spectra of all samples show evidence for aqueous alteration, including the 1.9µm combination tone from the stretch and bend of the H₂O molecule (Fig. 2). OH and metal-OH overtones and combination tones are also visible near 1.4µm and over the 2.0-2.6µm region. Some minerals composing the sample, usually two or less, can be identified using the VNIR data (Table). Five samples have spectra consistent with high-calcium pyroxene and Fe/Mg smectite. One sample appears to be a mixture of hematite and montmorillonite, indicated by an Al-OH 2.2µm band. The four samples from rock veins and vesicles

appear to be celadonite-, thomsonite-, analcime-, and hydrated silica-bearing. XRD analyses confirm all of these identifications. In the bulk rock samples smectite is the most abundant alteration mineral. As little as ~10% smectite is observable in VNIR spectra of altered mafic rocks measured here. Zeolites in <10% abundance also occur in the host rock, although their presence cannot be determined from VNIR data. In samples extracted from veins and vesicles, alteration minerals other than smectite are most abundant phase. In these precipitates, some alteration minerals, e.g., analcime and celadonite in hvalfj057 and hvalfj023, respectively, mask in VNIR data the signature of substantial quantities of smectite.

Nature of Alteration: Interestingly, bulk rock samples plot similarly in chemical diagrams in spite of different proportions of alteration minerals and, presumably, different amounts of removal and addition of ions by interaction with fluids. The most-altered bulk-rock sample in terms of mineralogy, hvalfj017, does not appreciably differ from less altered samples, suggesting the alteration may have been nearly isochemical (Figure 3). There is little progression along the typical terrestrial weathering trend towards the Al vertex. Most of the variation lies along the feldspar-olivine join with precipitates becoming either Fe-enriched or Fe-depleted. Variation along this line was also typical for low water:rock ratio acidic alteration on Mars (Hurowitz & McLennan, 2007). For these Icelandic environments of alteration, whole-rock elemental analyses only would lead to underestimation of the extent of alteration relative to the higher degree apparent from VNIR or XRD techniques, demonstrating the importance of knowledge of mineralogy in addition to chemistry in the exploration of Mars.

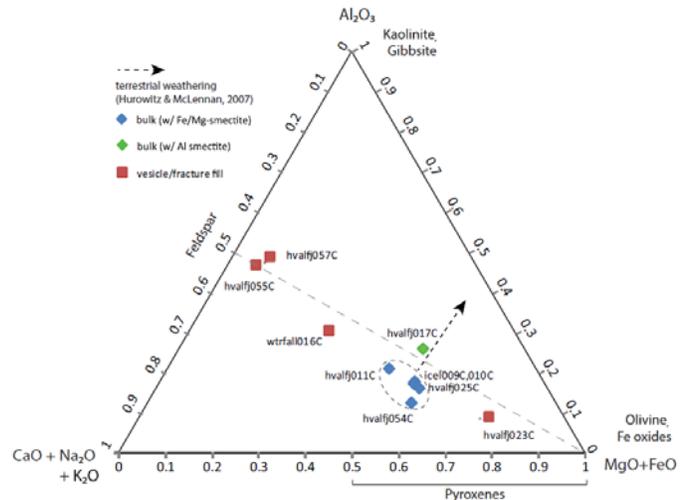


Figure 3. Ternary Al_2O_3 , $(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$, $(\text{FeO}_T+\text{MgO})$ diagrams, data plotted in mole percent. The bold black arrow indicates the direction of terrestrial weathering (after Hurowitz & McLennan, 2007). Light gray arrows indicate relationships between bulk rocks (blue diamonds for Fe/Mg smectite-bearing, green diamonds for Al smectite-bearing) and vesicle/fracture fill (orange squares) found within those bulk rocks.

Key Measurements and Questions on Earth and Mars: In Iceland, full sample mineralogy is not completely captured by spectroscopic data because of textural effects and masking of some minerals' signatures by others. Nevertheless, VNIR spectra capture the principal mineralogic diversity, and provide a means of rapidly assessing the nature of past alteration. Examination of whole rocks from Mars orbit, even at large scales, should yield similarly effective information on the mineral assemblages present on the surface. Presently, XRD is the only *in-situ* technique with which it is possible to characterize sample mineralogy quantitatively. But of all the mineralogic techniques, VNIR spectroscopy provides the most definitive information on the nature of the altered, smectite component due to its sensitivity to shifts in absorption band position that provide information on the octahedral cations even when smectites are at small abundances in bulk samples. Use of a combination of measurements to characterize the mineralogy of alteration on Mars lends confidence to inferences of past environmental processes.

As research proceeds on alteration in groundwater systems in basalt, a key future direction is biological: do these environments of aqueous alteration provide a habitat for microbial life? If so, for what quantities of biomass and via what metabolic mechanisms? Finally, are signatures of biological processes preserved through time? Synergistic study of the geochemistry, mineralogy, and biology of alteration of Icelandic lavas may help to reveal the nature and habitability of the first aqueous environments on early Mars.

References. 1. Mustard et al., 2008, *Nature* 454. 2. Murchie et al., 2009, *JGR* 114. 3. Ehlmann et al., 2009, *JGR* 114. 4. Ehlmann et al., in revision, *Clays & Clay Min.* 5. Ehlmann et al., *EPSL*, submitted. 6. Chung, F.H., 1974, *J. Appl. Cryst.*