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Glaciovolcanic hydrothermal environments in Iceland and implications for their detection on Mars

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Abstract

Volcanism has been a dominant process on Mars, along with a pervasive global cryosphere. Therefore, the interaction between these two is considered likely. Terrestrial glaciovolcanism produces distinctive lithologies and alteration terrains, as well as hydrothermal environments that can be inhabited by microorganisms. Here, we provide a framework for identifying evidence of such glaciovolcanic environments during future Mars exploration, and provide a descriptive reference for active hydrothermal environments to be utilised for future astrobiological studies. Remote sensing data were combined with field observations and sample analysis that included X-ray diffraction, Raman spectroscopy, thin section petrography, scanning electron microscopy, electron dispersive spectrometer analysis, and dissolved water chemistry to characterise samples from two areas of basaltic glaciovolcanism: Askja and Kverkfjöll volcanoes in Iceland. The glaciovolcanic terrain between these volcanoes is characterised by subglacially-erupted fissure swarm ridges, which have since been modified by multiple glacial outburst floods. Active hydrothermal environments at Kverkfjöll include hot springs, anoxic pools, glacial meltwater lakes, and sulfur- and iron- depositing fumaroles, all situated within ice-bound geothermal fields. Temperatures range from 0 °C - 94.4 °C, and aqueous environments are acidic - neutral (pH 2 - 7.5) and sulfate-dominated. Mineralogy of sediments, mineral crusts, and secondary deposits within basalts suggest two types of hydrothermal alteration: a low-temperature (<120 °C) assemblage dominated by nanophase palagonite, sulfates (gypsum, jarosite), and iron oxides (goethite, hematite); and a high-temperature (>120 °C) assemblage signified by zeolite (heulandite) and quartz. These mineral assemblages are consistent with those identified at the Martian surface. *In-situ* and laboratory VNIR (440 – 1000 nm) reflectance spectra representative of Mars rover multispectral imaging show sediment spectral profiles to be influenced by Fe^{2+/3+} - bearing minerals, regardless of their dominant bulk mineralogy. Characterising these terrestrial glaciovolcanic deposits can help identify similar processes on Mars, as well as identifying palaeoenvironments that may once have supported and preserved life.

1. Introduction

Hydrothermal environments driven by volcanism are prime targets for astrobiological exploration on Mars (for a review see Schulze-Makuch et al., 2007), and have many well-documented terrestrial analogues, e.g. Yellowstone National Park, USA (Bishop et al., 2004; Hellman and Ramsey, 2004; Marion et al., 2011), Cerro Negro volcano, Nicaragua (Hynek et al., 2011), and Iceland (Griffith and Shock, 1997; Nelson et al., 2005; Warner and Farmer, 2010). Fundamental to the generation of these environments is water, either as liquid ground water or seawater (as typical on Earth), or frozen water ice as found within the cryosphere of Mars (Clifford et al., 2010). Hydrothermal systems that are associated with fissure and hot spot basaltic volcanism in particular are analogous to past environments on Mars.

However, despite the ubiquity of both volcanism and a widespread cryosphere on Mars, widespread glaciovolcanic terrains have yet to be definitively identified (Keszthelyi et al., 2010). If these two processes have both occurred concurrently, then it is a challenge for future exploration to find unequivocal or diagnostic topographic, geomorphological, sedimentological and/or mineralogical evidence of glaciovolcanic interactions. Glaciovolcanism is proposed to have been widespread on Mars throughout its past (e.g. Chapman et al., 2000; Head and Wilson, 2002; 2007) ranging from lava flows that have interacted with ground ice, e.g. rootless cones in Athabasca Valles (Fagents and Thordarson, 2007; Jaeger et al., 2007) to volcanic eruptions into glaciers, e.g. tuya constructs at Chryse/Acidalia Planitia (Martinez-Alonso et al., 2011) and moberg ridges at Pavonis Mons (Head and Wilson, 2007). Glacial processes themselves have been widely documented on Mars throughout its history (Karhel and Strom, 1992; Neukum et al., 2004; Dickson et al., 2008), much of which has been in association with volcanic regions (Head and Wilson, 2002; Cousins and Crawford, 2011 and references therein). Likewise, it has been recently proposed that low-albedo sediments covering large areas ($> 10^7$ km²) of the northern lowlands of Mars are dominated by basaltic glass (Horgan and Bell, 2012), implying widespread explosive volcanism, such as that found during volcano – ice

interaction (Horgan and Bell, 2012). One recent terrestrial example of this process is the 2010 Eyjafjallajökull eruption in southern Iceland, which generated large volumes of ash as fine glass particles (Dellino et al., 2012).

Glaciovolcanic terrains are of relevance to astrobiology, as such systems may have provided a past habitat for microbial life on Mars due to the coupling of liquid water and geochemical disequilibria (Gaidos et al., 2004; Cousins and Crawford, 2011). In terrestrial systems this liquid water exists as subsurface cycling of hydrothermal fluids throughout the volcanic edifice, or as large volumes of subglacial meltwater (Björnsson, 2002). If released catastrophically this subsurface water forms a type of glacial outburst flood known as a “jökulhlaup” (Björnsson, 2002), of which the deposits and erosional features form a major indicator of glaciovolcanic activity. Aqueous floods have certainly played a major role in Mars surface processes (e.g. Warner et al., 2009), although the origin of these floods is often contested or uncertain (Baker et al., 1991; Baker, 2001). The megaflood features of Athabasca Valles in particular are temporally and spatially associated with volcanotectonic fissures (Burr et al., 2002), highlighting the important relationship between dike emplacement and the release of aquifers (Burr et al., 2002). Likewise, the formation of Aromatum Chaos has been attributed to volcano-ice interaction and subsequent release of subsurface water (Leask et al., 2006). However, both the Athabasca Valles floods and other chaos terrains (e.g. Iani Chaos) have alternative, non-volcanogenic explanations (Burr et al., 2005; Warner et al., 2011).

The mineral assemblages produced through glaciovolcanic hydrothermalism have yet to be fully incorporated into detection strategies. Mineral alteration terrains on Mars demonstrate a significant level of aqueous alteration of basaltic material, much of which may have been the result of hydrothermal activity (Bibring et al., 2006; Morris et al., 2008; Ehlmann et al., 2009). Mineral assemblages revealed by the instruments HiRISE and CRISM (Bibring et al., 2005; Carter et al., 2010; Ehlmann et al., 2011; Weitz et al., 2011) suggest a variety of environmental conditions spanning

acidic (typified by ferric oxides/oxyhydroxides and sulfates) to neutral – alkaline (typified by phyllosilicates and opaline silica) environments (Bibring et al., 2006; Chevrier et al., 2007; Ehlmann et al., 2011). Varying levels of water activity have also been proposed, ranging from ‘acid fog’ fumarole alteration (Tosca et al., 2004; Schiffman et al., 2006) to subsurface water circulation (Ehlmann et al., 2011). Terrestrial glaciovolcanism includes both of these contrasting mechanisms of hydrothermal alteration, and therefore alteration deposits associated with glaciovolcanic terrains have the potential to aid the future detection of such environments on Mars (Warner and Farmer, 2010), as well as provide a model for hydrothermal mineral deposition within cold, volcanic terrains.

Here, we assess (i) what specific mineral assemblages arise through the hydrothermal alteration of basaltic lithologies within glaciovolcanic environments, and how they correspond to the glaciovolcanic terrain in the Askja – Kverkfjöll region of Iceland, (ii) how these mineral assemblages compare to those on Mars, and (iii) the key environmental characteristics (temperature, pH, dissolved elemental chemistry) of the surface hydrothermal environments currently active at the Kverkfjöll volcano. Multi-instrument data products were acquired from natural glaciovolcanic deposits, including exposed pillow basalts and volcanoclastics, hydrothermal sediments, and hot spring mineral precipitates to provide a framework with which to identify glaciovolcanic terrains on Mars both remotely, and particularly with rover-deployed instruments. Combined, this study provides an overview of Askja and Kverkfjöll and their volcanic environments, with a call for these localities to be used as test grounds for future Mars research, from exploring microbiological processes to field-testing Mars rover instrumentation.

2. Regional Setting

The Kverkfjöll and Askja volcanoes in Iceland, and the subglacially-erupted fissure swarm that lies between them (Figure 1), represent both past and active hydrothermal environments and alteration. This region serves as an ideal Mars analogue for several reasons: (1) the region is dominated by

basaltic volcanism and near-surface hydrothermal activity; (2) a rain shadow cast by the Vatnajökull ice cap results in little vegetation and surface water; (3) its geographical isolation has resulted in little disturbance by people, animals, and development; and (4) as a result of factors (2) and (3), the preservation of hydrothermal features allows for multi-scale studies of mineralogical and lithological deposits. Individual field areas are described below.

2.1 Askja

The Askja ($65^{\circ}3.276'N$; $16^{\circ}30.480'W$) caldera lies within the Dyngjufjöll volcanic centre, and is dominated by a large subglacially-erupted hyaloclastite formation, comprised of basal pillow lavas, pillow breccias, and hyaloclastite tuffs (Brown et al., 1991; Sigvaldason, 2002). This subglacial terrain has been exposed by glacial retreat during the last 10,000 years (Sigvaldason, 2002), and has since been modified by more recent eruptions, including the explosive 1875 Plinian eruption producing Öskjuvatn (Askja lake) caldera (Hartley and Thordarson, 2012). The most recent activity at Askja was an eruption of subaerial basaltic lava to the north of the caldera ($65^{\circ} 3' 44.88''N$; $16^{\circ} 36' 58.61'' W$) in 1961 (Thorarinsson and Sigvaldason, 1962). Compositionally, eruptive products at Askja are largely basaltic, with the exception of rhyolite-producing eruptions at ~ 10 ka and in 1875 (Sigvaldason, 2002). The basaltic, glaciovolcanic terrain was the focus for this study.

2.2 Fissure Swarm

A Holocene fissure swarm extends northeast of Kverkfjöll (Figure 2A) towards Askja, and intrudes pre-Holocene bedrock (Hjartardottir and Einarsson, 2012). Hoskuldsson et al. (2006) infer that the pillow basalts within this fissure swarm were erupted beneath 1.2 to 1.6 km of ice during the last glacial maximum. These fissure swarms have since been eroded by catastrophic glacial outburst floods (jökulhlaups) originating from the northern Vatnajökull ice margin (Carrivick and Twigg, 2004; Carrivick et al., 2004a). Topography indicative of jökulhlaups includes a bedrock anastomosing channel pattern, which represents bifurcation of valleys separated by linear bedrock ridges or hills.

Further evidence is provided by streamlining of these bedrock ridges via flank erosion and tail (down-valley) extension due to deposition of pendant bars.

2.3 Kverkfjöll

Kverkfjöll lies above the Icelandic mantle plume (Sigvaldason et al., 1974; Wolfe et al., 1997), and is situated within the northern volcanic zone (NVZ), which marks the mid-Atlantic plate boundary in north Iceland (Hjartardottir and Einarsson, 2012). The Kverkfjöll central volcanic system comprises two dormant subglacial calderas (Hjartardottir and Einarsson, 2012), and is situated on the northern margin of the Vatnajökull ice cap ($64^{\circ} 38'6.92''\text{N}$; $16^{\circ}43'11.84''\text{W}$, see map in Figure 1). Kverkfjöll eruptive products are basaltic (Óladottir et al., 2011) with lithologies dominated by pillow lava, hyaloclastite, and fine-grained tuffs (Höskuldsson et al., 2006). Geothermal areas around the Kverkfjöll northern caldera have been previously described briefly by Ármannsson et al. (2000) and Ólafsson et al. (2000), and comprise high temperature fields around the northern caldera rim ($64^{\circ}40.176'\text{N}$; $16^{\circ}41.166'\text{W}$), and hydrothermal outflow environments at the glacial front (Karhunen, 1988). For the purpose of this study these are divided into four main areas: Hveradalur and Hveratagl at the summit of Kverkfjöll volcano, and Hveragil and an Ice Cave at northern margin of Kverkfjöll (Figure 2B). The proglacial area of Kverkfjöll is known as Kverkfjallarani and this area holds abundant geomorphological and sedimentological evidence of Holocene jökulhlaups (Carrivick and Twigg, 2004; Carrivick et al., 2004a; Carrivick, 2006; 2007a,b), which extend into the fissure swarm. The last recorded jökulhlaup at Kverkfjöll occurred in January 2002, and was caused by the catastrophic drainage of the geothermal lake “Gengissig” at Hveradalur (Rusmer, 2006; Figure 2B).

3. Materials and methods

Fieldwork was conducted during summer field campaigns in July 2007 and June 2011. Field sites were characterised *in situ* through a combination of field photography, GPS, Visible - Near Infra-Red (VNIR) field spectroscopy, and pH, temperature, dissolved oxygen (DO), and conductivity

measurements. Samples (including rocks, sediments, hot spring, and fumarole deposits) were collected from Kverkfjöll, Askja, and the fissure swarm, and laboratory analysed using VNIR reflectance spectra, X-ray diffraction (XRD), Raman spectroscopy, electron microprobe, scanning electron microscope (SEM) imaging, and light microscope petrography, all detailed below. A complete list of samples acquired in the field in both 2007 and 2011 is provided in Table 1. A summary of all sites and samples, and the instruments used to analyse them, are given in the Supplementary Material.

3.1 Remote sensing data

High resolution remote sensing data of Kverkfjöll and the fissure swarms were obtained to provide a detailed geomorphological context to the hydrothermal mineral terrains and environments explored for this work. Geomorphological characterisation and topography of Kverkfjöll and the fissure swarms were obtained via a Digital Elevation Model (DEM) produced using aerial photogrammetry (Carrivick and Twigg, 2004), and georeferenced airborne LiDAR data. Georeferencing firstly utilised differential Global Positioning System (dGPS) measurements of Ground Control Points (GCPs) across the study area (see Carrivick and Twigg, 2004). Secondly, occupation of an arbitrary static control point with a differential GPS 'base' receiver was maintained during the LiDAR overflight in August 2007. Both GCPs and the arbitrary static control point were precisely located with reference to permanent Icelandic geodetic dGPS receivers at Karahnjúkar and Höfn. The LiDAR 'point cloud' was interpolated using Inverse Distance Weighting (IDW) onto a regular grid. The resulting unprecedented topographic dataset for this part of Iceland has 2 m horizontal resolution and +/- 10 cm vertical accuracy. A composite digital elevation model (DEM) was created from a 2m grid resolution airborne LiDAR survey and from 5 m grid resolution photogrammetry. Google Earth SPOT-5 2011 2.5 m resolution images covering Askja and the fissure swarm were also used to image the Kverkfjöll – Askja transect.

3.2 Sampling and environmental measurements

Hydrothermal water samples from Hveradalur, Kverkfjöll were analysed to assess the dissolved aqueous composition of surface alteration fluids active at Kverkfjöll and to identify their relationship to the alteration minerals present in the surrounding sediments. It is presumed that surface hydrothermal environments are active during summer months, followed by annual freezing or desiccation over winter when air temperatures can drop to -15 °C. Samples were filtered using a Millex-AP prefilter to remove large particulate matter, and then filtered again using Millipore 0.45 µm filters. Duplicate 30 ml water samples were taken, one of which was acidified with nitric acid. Blank samples of dH₂O were also taken at Site 1, Site 4, Site 7 and Site 12. These were kept cold (~ 4 °C) prior to analysis.

Environmental measurements (pH, temperature, dissolved oxygen, conductivity) were acquired in July 2007 and June 2011. A Roche digital pH meter was calibrated to neutral (pH 7.0) and acid (pH 4.0) standards provided by the manufacturer. Random measurements were checked against pH indicator strips (Sigma-Aldrich). An Extech digital dissolved oxygen (DO) meter was calibrated to ambient air and adjusted for altitude prior to each set of analyses. DO measurements were made to a detection limit of 0.1 mg/l with an accuracy of ± 0.4 mg/l.

Subglacially-erupted basalts were sampled from Askja and the NE-trending fissure swarm in 2007 (see Figures 1A and 1C). Sampling was focused on pillow basalt mounds, and outcrops of volcanoclastics. We use the term 'volcanoclastic' to encompass subglacial basaltic lithologies including hyaloclastite (a coarse-grained rock composed of mixed-sized basaltic glass clasts and scoria surrounded by finer palagonitized glass fragments), and hyalotuff (a generally fine-grained welded or loosely consolidated tuff composed of fine glass fragments, most of which have been palagonitized), as outlined by Jakobsson and Gudmundsson (2008). These samples, and others including

unconsolidated geothermal sediments, mineral crusts, hot spring sediment, and fumarole deposits, were collected within Whirlpak sample bags.

3.3 Reflectance spectroscopy

Within the context of Martian rover exploration, VNIR reflectance spectroscopy often provides the first putative composition and mineralogy of a nearby outcrop via multispectral imaging (e.g. Farrand et al., 2008). Panoramic cameras on the NASA Mars Exploration Rovers, NASA Mars Science Laboratory rover, and ESA planned ExoMars rover all have multispectral imaging capability, each mission using differing centre-wavelengths and bandpasses for the narrowband filters that provide the multispectral imaging capability (Cousins et al., 2012 and references therein). *In situ* VNIR field reflectance spectra (350 – 1100 nm) were acquired using a GER 1500 portable field spectrometer (loaned from the NERC Field Spectroscopy Facility, Edinburgh, UK). A spectralon white calibration target (also loaned from the NERC Field Spectroscopy Facility, Edinburgh, UK) was used at the time of measuring. Laboratory VNIR (400 - 1000 nm) reflectance spectra of freeze-dried, powdered samples (to homogenise samples for bulk analysis, using an alumina pestle and mortar; grain size <500 µm) were measured at Aberystwyth University using an Ocean Optics Jaz spectrometer with an ISP-REF integrating sphere probe (used in 8° incident / total hemispherical reflectance geometry) with a fibre coupled external lamp, and spectralon calibration reference.

3.4 Geochemistry

To assess currently active surface alteration fluids, dissolved ion chemistry of water samples collected from Kverkfjöll in 2011 and associated dH_2O blanks was analysed with a Dionex Ion Chromatograph and Horoba JY Ultima 2C ICP-AES for dissolved anion and cation analyses respectively, at the Wolfson Geochemistry Laboratory at Birkbeck/University College London (UCL). Standards were run during analysis. Cation results were taken as the mean of three repeat measurements, with standard deviations typically between 0.01 – 3.5 mg/l depending on the cation.

For mineralogical analysis, crushed rock and sediment samples from both Askja and Kverkfjöll were freeze-dried and homogenised to <500 µm grainsize using an alumina pestle and mortar prior to analysis with a Bruker D8 Advance XRD with a Vantec 1 detector at Aberystwyth University, calibrated using a corundum standard. Acquired sample spectra were compared to mineral spectra using the International Centre for Diffraction Data database, and the RRUFF database (Downs, 2006). SEM imaging of microtextures and mineralogy within Hveradalur (see Figure 2B) sediments and mineral crusts was performed using a Jeol Scanning Electron Microscope (JSM-6480LV) at University College London. Samples were gold-coated prior to imaging. Finally, Raman spectroscopy of samples was achieved from natural surfaces using a Renishaw InVia Raman Spectrometer with a 785 nm laser at UCL, calibrated to a pure silica standard.

3.5 Thin section petrology and microprobe analysis

Thin sections of pillow lava and hyaloclastite were optically imaged with an Olympus BX61 light microscope at the Geophysical Laboratory, Carnegie Institution for Science, USA. Major element analysis of glass compositions from volcaniclastics and pillow lavas was obtained with a Jeol JXA8100 electron microprobe with an Oxford Instrument INCA energy dispersive system (EDS) at UCL/Birkbeck, using an accelerating voltage of 15kV and analysis count time of 100 seconds at a working distance of 40 mm. Elemental standards for instrument calibration were: wollastonite (Si, Ca), corundum (Al), orthoclase (K), olivine (Mg and Fe for oxides), rutile (Ti, O), Apatite (P), Pyrite (S and Fe in sulfides), USGS BCR2 glass standard (Na), and pure metals for Mn, Ni, Cr, Zn, and Cu.

4. Results

4.1 Field observations at Askja

The subglacial terrain around Askja is dominated by hyaloclastite and hyalotuff deposits, in addition to occasional pillow lava exposures (Sigvaldason, 2002). Some volcaniclastic outcrops were observed

to have sub-meter scale depositional features comprising of finely layered welded hyalotuffs and friable, unconsolidated material (Figure 3A), likely from deposition of fragmented material within the meltwater lens that typically forms during a subglacial eruption (Jakobsson and Gudmundsson, 2008). All hyaloclastite outcrops are heavily palagonitized throughout, exhibiting buff-colouration, contrasting to the darker, unaltered basaltic terrain of the surrounding subaerial lava flows. This distinction however was largely obscured within the SPOT-5 images (Figure 1C) by more recent rhyolitic pumice deposits (Sigvaldason, 2002). Likewise, hyalotuff depositional bedding was not evident within the 2.5 m/pixel resolution images.

4.2. Fissure swarms and the Kverkfjöll proglacial environment

Pillow basalt mounds (Figure 3B) dominate the subglacial bedrock lithology of the fissure swarm, which follows the strike of the rift between Kverkfjöll (with which the fissure swarm is associated; Hjartardottir and Einarsson, 2012) and Askja (Figures 2A and 2C). Pillow mounds are typically comprised of unconsolidated scree slopes at the base, with preserved pillows near the top. These preserved pillow layers can be distinguished in the SPOT-5 imagery (Figure 1C) from their eroded counterparts, but the definitive identification of individual pillow morphology is not possible at the given resolution (2.5m/pixel). The mounds are surrounded by dry, loose basaltic sand, and individual pillows range from ~30 cm diameter at site ASK09 to up to 1 m at Site KV02. Columnar jointing, indicative of rapid cooling, can also be identified along the fissure swarm (Figure 2D).

These fissure swarms extend into the proglacial region at Kverkfjöll (Kverkfjallarani), which is dominated by extensive sedimentological deposits and geomorphological features from jökulhlaups originating from Kverkfjöll (Carrivick et al., 2004a,b), as well as glacial moraine deposits (Carrivick and Twigg, 2004). Erosional landforms here include 'streamlining' of the pillow basalt and hyaloclastite fissure swarm ridges, gorges, smoothing of lava flows, and scours on basalt surfaces (Carrivick et al., 2004a). Depositional features are similarly extensive, and include outwash fans

preserving palaeoflow lines (Figure 4B), depositional terraces and valley-fill sediments (Figure 4C), boulder clusters, and fragmented hyaloclastite (Carrivick et al., 2004b). These proglacial glaciofluvial deposits exhibit a wide variety of glaciofluvial sedimentary facies, ranging from coarse-grained matrix-supported facies indicative of jökulhlaups, to fine-grained clast-supported gravel facies with multi-directional clast orientations indicative of varying flow energy and an ablation-fed braided river flow regime.

To the NE of Kverkfjöll, Hveragil gorge (Figures 2 and 3C) contains a hydrothermal outflow stream. This stream deposits calcium carbonate from near-neutral CO₂-rich (500 – 600 mg/l) spring fluid (Ólafsson et al., 2000), and has previously been found to have temperatures of up to 62 °C, with an average temperature of 50 °C (Ólafsson et al., 2000). Hveragil probably formed subglacially during the last glacial maximum (Carrivick, 2005). To the west along the glacier front, the river Volga emerges from the Kverkjökull glacier and runs northwards, and is thought to be of subglacial origin (Friedman et al., 1972; Ólafsson et al., 2000). Along the western edge of the Kverkjökull glacier tongue, the river Volga has carved out a large ice cave; ice caves such as these are unstable, and this particular cave collapsed in summer 2010.

4.3. Field observations at Kverkfjöll hydrothermal fields

Environmental measurements of active hydrothermal springs, pools, streams, fumaroles, and geothermal ground were made in 2007 and 2011. pH measurements taken from the hydrothermal environments investigated at the summit of Kverkfjöll (Hveradalur and Hveratagl - Figure 2B) show them to cover a broad range between acidic – neutral (pH 2 to 7.5). Likewise, a wide range of temperatures from near 0°C to 94.4°C (boiling point at the 1750m elevation) were observed. These are shown in Figure 5, and individual measurements given in the Supplementary Material. A previous study by Ólafsson et al. (2000) of fumarole gas measured between 1992 - 1998 showed CO₂ to be the dominant species (80 – 97% of the gas emitted), with both H₂ and H₂S accounting for 1 –

12% each. Active environments and lithological deposits present at the geothermal field Hveratagl (64° 41.117' N; 16° 40.550' W), the proglacial ice cave (64°43.326'N; 16°39.445'W) with its outflow river (Volga), and the geothermal field Hveradalur (64° 40.173' N; 16° 41.100' W) were investigated in detail, and are described below.

4.3.1 Hveradalur

The Hveradalur geothermal area (64°40.176'N; 16°41.166' W) is dominated by two glacier-dammed meltwater lakes, which lie on the caldera's western rim (Figure 2B). Lake "Gengissig" was formed during a geothermal steam explosion in 1959 (Gudmundsson and Hognadottir, 2009). The geothermally-heated ground maintains a relatively warm lake temperature of ~10 – 20 °C, as measured in June 2011 (see Figure 5). This lake is thought to have drained catastrophically as jökulhlaups at least five times in the past 30 years, in 1985, 1987, 1993, 1997, and 2002 (Gudmundsson and Hognadottir, 2009). The nearby lake, "Galtarlón" lies to the northwest, and is thought to be more stable (Gudmundsson and Hognadottir, 2009). Adjacent to the NW shore of the lake "Gengissig" is a geothermal field (Figure 3F) entirely enclosed on all sides by ice, which gradually recedes during summer. This geothermal field is characterised by a number of boiling (or near-boiling) hydrothermal pools, sulfurous fumaroles, hot springs, and geothermal sediments (Figure 3D). Apart from small, boiling mud pots, which typically have a low pH (~2 - 3), aqueous environments here are maintained around a pH of 4 - 6 (Figure 5), and have variations in dissolved oxygen (<1 - 10.4 mg/l DO), and temperature (3.0 - 53.2 °C) (Table 2).

4.3.2. Hveratagl

Hveratagl (64° 41.122'N; 16° 40.562'W) lies ~ 2 km north of Hveradalur, and sits at the top of a north-south trending hyaloclastite ridge. This geothermal field is characterised by meltwater pools fed by glacial and snow melt during spring and summer. Over winter, the site becomes covered in thick snow, which melts away variably every summer. Pools here typically lie within shallow surface

depressions (Figure 3E), with an underlying layer of fine, soft sediment, suggesting these pools form in the same location annually. Additionally, a collapsed ice-cave was also observed at Hveratagl in 2007, out of which a subglacial outflow stream emerges. Temperature and pH measurements taken in 2007 are shown in Figure 5, and again show aqueous environments to also be acidic (pH 3 - 4).

4.4 Petrology of Askja and fissure swarm pillow basalts and hyaloclastites

Askja hyaloclastite samples ASK03, ASK04, and ASK07 are heavily palagonitized, with randomly orientated glass fragments (Figure 6B) surrounded by an amorphous palagonite matrix plus nanocrystalline oxide phases (Figure 6C). Many glass fragments have alteration rims where the glass has begun breaking down along clast boundaries. All alteration boundaries are smooth, and do not display any 'bioalteration' textures often found in seafloor basalts (Furnes et al., 2007). In sample ASK04, larger glass clasts are typically highly vesicular (Figure 6A). Secondary mineral alteration in all three hyaloclastites does not extend beyond palagonitisation. Zeolites and any other secondary phases are not seen. Pillow basalt KV02 is typified by large (2 -4 mm) plagioclase phenocrysts, surrounded by a fine-grained groundmass of fine plagioclase laths. However there are no signs of aqueous or hydrothermal alteration within this sample. Finally, pillow basalt ASK09 is dominated by a fine-grained groundmass primarily made up of small (approx. 10 x 100 μ m) plagioclase laths, typical of rapidly-cooled lava. This basalt is vesicular, with vesicles entirely or partially in-filled with secondary alteration minerals (Figure 6F), including iron oxides, silica, and sulfates (Figures 6D, G, and H).

Major element composition of glass fragments and rims within the hyaloclastite and pillow basalt samples (Table 3) show compositions to be typically basaltic, with SiO₂ content ranging from 48.60 (KV02) to 52.33 wt. % (ASK07). Total Alkali – Silica (TAS) classification of the Kverkfjöll samples show them to plot alongside Martian surface measurements and rocks, lying between basaltic and basaltic andesite in composition (Banfield et al., 2000; McSween, 2009).

4.5 Water chemistry at Hverdalur, Kverkfjöll

Aqueous environments are dominated by dissolved sulfate (up to 227.3 mg/l). Highly mobile cations such as Si^{4+} , Na^+ , Ca^{2+} , Mg^{2+} , and K^+ make up the remaining bulk of the dissolved load after sulfate, sourced from the underlying local basaltic bedrock, buffering pH (Table 2). Streams with little active hydrothermal input (Sites 12 and 15) typically had very low levels of dissolved sulfate and mobile cations in comparison to the other sites, but similar nitrate and chloride levels. The two lake samples (Sites 7 and 21) had increased levels of dissolved Ca^{2+} and Mg^{2+} reflecting the higher pH of these two sites (pH 6.0 and 5.0 respectively), and lower concentrations of all other dissolved species.

4.6 Mineralogy

Mineral compositions of basalts and geothermal sediments are given in Table 4. Figures 7 - 9 show the XRD patterns of bulk, homogenised sediments from Hveratagl, Hveradalur (including VNIR spectral targets), and the fissure swarm samples. Sediments from Hveradalur and Hveratagl vary in their individual composition (see Table 4). Heulandite (Ca/Na zeolite) and smectite (Fe/Mg phyllosilicates) are especially prevalent in sediments. Other alteration minerals identified include gypsum, quartz, sulfur, jarosite, and pyrite. Pillow basalt samples KV02 and KV07 are dominated by peaks for primary basaltic minerals pyroxene and plagioclase, as is the unaltered component of sample KS03 (a welded tuff, see Table 1) from Hveradalur. Figure 10 shows Raman spectra from spot targets on samples KV07, KS03, and a red mineral crust from Site 6. White mineral deposits within the vesicles of pillow basalt KV07 are identified as gypsum. The surface alteration of KS03 and the mineral crust from Site 6 are identified as hematite and goethite respectively, although sample fluorescence masks much of the Raman signal. Likewise, sample fluorescence meant XRD analysis was not feasible for these last two samples, and it is possible other mineral species are also present. Figure 10 also shows a Raman spectrum for sample I_9C, which shows peaks for jarosite. For comparison, XRD shows this sample to comprise of a mixture of sulfates (jarosite, alunogen), and

other minerals including pyrite, smectite, and heulandite. Sample mineralogy was also identifiable in sediments under the SEM (Figure 11), showing sediments to comprise of cubic pyrite, smectite, heulandite, and vesicular basaltic fragments. Finally, Askja volcanoclastics comprise of unaltered glass, nanophase iron oxides, and amorphous palagonite. These amorphous phases are difficult to detect using standard XRD techniques (Bishop et al., 2002), and their presence is identified from thin section (Figure 6).

4.7 VNIR reflectance spectra

4.7.1 *In situ* measurements

For *in-situ* measurements, two regions within the Hveradalur geothermal area were targeted: 1) a dried-up hot spring bed and 2) geothermally altered ground. Ground temperatures for the dried stream bed ranged from 50.6 - 67.2°C for various points along the spring, and 32.2 (± 1.64) °C at the spring source itself (Figure 12A). *In-situ* VNIR (350 – 1000 nm) reflectance spectra of undisturbed surface sediment targets along this dried up stream were measured. Further north along the shore of lake Gengissig, and adjacent to the main geothermal area, is a less-active region of geothermal soils and fumarole mounds, informally termed the “Mars Site”, and this formed the second site at which *in-situ* VNIR reflectance spectra were obtained (Figure 12B-C).

Reflectance spectra of targets along the dried-up stream show chlorophyll *a* (670 nm) and bacteriochlorophyll (865nm) absorption bands (Wakao et al., 1993) within the spectra (Figures 12D + E), either from desiccated microbial mats that may have been present along the hydrothermal stream floor when it was last active, or from microbial communities currently residing within the sediments. In spectral targets 9A-C, a broad Fe³⁺ absorption centred at 900 nm is also present. Sediments and crusts from the “Mars Site” are largely dominated by ferric and ferrous iron absorptions typical of iron oxide minerals and iron sulfates, with absorptions at 500, 650, and 950 nm (Figures 12B and C). XRD analysis indicates these soils are zeolite and sulfate-rich (Table 4), with

few Fe-bearing minerals or oxides identified. The zeolites/sulfate components of the sediments are not represented within the VNIR reflectance spectra due to the lack of spectral features and absorption bands within the 400 - 1100 nm spectral range for these minerals. Therefore, the dominance of Fe-absorptions may come from a fine surface layer, or minor component, that is not represented within the XRD analysis.

4.7.2 Laboratory reflectance spectra

Reflectance spectra of powdered geothermal soils, lavas, and volcaniclastics fall into four spectral categories (Figure 13); 1) broadly featureless basaltic and palagonitic/nano-crystalline ferric oxide spectra; 2) flat sulfur reflectance with a steep absorption edge in the blue; 3) ferric iron absorption features at 500, 650, and 900nm; 4) ferric iron absorption at 900nm and chlorophyll absorptions at 670nm and 830nm. The four types represent the variety and degree of hydrothermal alteration within glaciovolcanic environments at Askja and Kverkfjöll, which are very much dictated by localised conditions.

5. Discussion

5.1 Hydrothermal activity and palaeoenvironments

In this work, hydrothermal environments that are both currently active (e.g. hydrothermal surface environments at Kverkfjöll), and preserved (e.g. secondary hydrothermal mineral deposition in pillow basalts, as at Askja and the fissure swarm) have been explored. The rocks at Askja and Kverkfjöll are young, and therefore have not been buried and exposed to high pressures. As such, hydrothermal alteration mineral assemblages are largely a function of temperature and water activity. This was observed to be the case with the well-documented hydrothermal alteration at Surtsey volcano, Iceland (Jakobsson and Gudmundsson, 2008). Overall, hydrothermal samples at Askja and Kverkfjöll represent two distinct thermal environments. Those dominated by amorphous palagonite, nanocrystalline iron oxides and smectite authigenic secondary phases represent low-

temperature ($<120^{\circ}\text{C}$) aqueous alteration (Stroncik and Schmincke, 2002). This group is populated entirely by the volcanoclastic hyaloclastite and hyalotuff samples from Askja. Basaltic glass easily alters to opal, smectite, zeolites, and clays (Browne, 1978), and this is consistent with geothermal alteration of tephra at Surtsey, which became palagonitized within 2 - 3 years following the eruption under temperatures of $80 - 100^{\circ}\text{C}$ (Jakobsson and Gudmundsson, 2008). Likewise, geothermal temperatures at the subglacial Gjálp 1996 eruption were 240°C at the end of the eruption, cooling to 40°C in 2001 (Jakobsson and Gudmundsson, 2008).

A higher temperature environment ($>120^{\circ}\text{C}$) is inferred for those samples dominated by heulandite, particularly where quartz is also present (e.g. Sites 11 and 20). These tend to be geothermal samples found at Hveradalur (see Table 4), though many geothermal sediments from Hveradalur and Hveratagl comprise of minerals spanning both thermal environments. This could represent a stage of initial high temperature alteration (Kristmannsdottir and Tomasson, 1978; Franzson, 2000) resulting in extensive alteration of basaltic glass to heulandite and smectite, followed by lower-temperature alteration allowing the formation of sulfates including gypsum and jarosite. This is consistent with the dissolved water chemistry of the low-temperature active springs and hydrothermal pools at Hveradalur (Table 2) which show dissolved sulfate to dominate. Higher temperature minerals such as chlorite ($>230^{\circ}\text{C}$), epidote ($>260^{\circ}\text{C}$), and amphibole ($>280^{\circ}\text{C}$) (Browne, 1978) are not identified. Figure 14 summarises the temperature ranges for these two thermal environments and the associated alteration minerals. Pyrite is present in many sediments from Hveradalur and Hveratagl, and could be associated with either high or low temperature conditions, or alternatively the activity of sulfate reducing bacteria utilising the dissolved sulfate present within the low-temperature hydrothermal fluids.

Finally, pillow basalts ASK09 and KV07 show vesicular hydrothermal deposition of secondary minerals, which based on their elemental composition are likely to be a combination of opaline

silica, jarosite, and iron oxide (see Figure 6), and gypsum (Figure 10) respectively. These suggest subsurface circulation of hydrothermal fluids through the basaltic pillow pile as both these sample sites now exist within a cold volcanic desert, with an annual temperature ranging ~ -8 to $+8$ °C and annual precipitation 400 - 600 mm/year (Einarsson, 1984; Icelandic Met Office data <http://en.vedur.is/climatology/data/>). Therefore this hydrothermal alteration is likely to have occurred while the warm pillows were still within a subglacial environment. Such hydrothermally-driven subsurface environments would have been ideal havens for life within a glaciovolcanic system.

5.2 Detecting glaciovolcanism on Mars

As argued above (also see Schulze-Makuch et al., 2007; Warner and Farmer, 2010; Cousins and Crawford, 2011) regions of volcano – cryosphere interaction on Mars are strong candidates for identifying near-surface evidence for habitable palaeoenvironments. Evidence of glaciovolcanism at Askja and Kverkfjöll occurs on a number of scales, from large-scale topographic and geomorphological features such as fissure swarms (Figure 2A) and flood erosion/deposits (Figure 4), to distinctive lithofacies within the rock record (pillow basalts, volcaniclastics, Figures 2C, 3A+B), and finally hydrothermal alteration minerals and secondary mineral deposits (Figures 6 – 11 and Table 4). A future benefit of Martian topographic data, especially high-resolution data such as the High Resolution Stereo Camera (e.g. Gwinner et al., 2010) and HiRISE (e.g. Li et al., 2011), should be the identification of topographic features such as those identified in Figure 4, and other features including cataracts (dry waterfalls or valley-floor headcuts) and spillways (abraded and plucked topographic edges from a flow over-spilling a topographic divide). Pillow basalt and volcaniclastic lithologies themselves are highly indicative of an eruption into a subglacial aqueous setting, based on both morphological and textural characteristics, and the abundance of volcanic glass either as pillow basalt rims or as individual clasts within volcaniclastic deposits. Similar meter-scale hydrovolcanic features (e.g. rootless cones, entablature-style columnar jointing) have been

successfully identified on Mars using HiRISE image data (Milazzo et al., 2009; Keszthelyi et al., 2010). However, features specifically relating to glaciovolcanism are ambiguous, in part due to features on the < 10 m scale often being reworked or modified by recent aeolian, impact, and cryospheric processes (Keszthelyi et al., 2010). This reworking may limit the detection of these lithological features to future in-situ rover based exploration targeted at terrains likely to have been the result of glaciovolcanism.

Whilst capable of detecting small-scale, in situ features at the Martian surface, a robotic rover will only be able to deploy a sub-set of analytical techniques in a given area. Moreover, it will do so sequentially, with VNIR multispectral imaging currently used to identify promising outcrops for analysis with other remote and contact/analytical instruments. The ability to make rapid and appropriate decisions regarding traverse planning and prioritisation of sample analysis will be crucial to the success of such missions. The best way to ensure this prior to flight is through the testing of instruments and operational procedures at analogue sites that exhibit a comparable range of mineralogical complexity to that likely to be encountered on Mars (e.g. Steele et al., 2006; Stern et al., In Press). For example, the discrepancies between VNIR reflectance spectra (which were strongly influenced by ferric iron-bearing phases), XRD patterns, and Raman spectra of heterogeneous samples at Askja and Kverkfjöll demonstrate the necessity for a multi-instrument approach. In the specific case of identifying regions of past glaciovolcanism, the Kverkfjöll – Askja region of Iceland is one such locality where lithological analogues can be used for testing rover instrumentation and their subsequent data products in their ability to detect evidence of liquid water and potentially “habitable” environments (summarised in Table 5). The unconsolidated sedimentary deposits at Kverkfjöll that are comprised of proglacial jökulhlaup deposits, and geothermal sediments at Hveradalur and Hveratagl are ideal for this purpose. For example, an exposure of a 3 km incision into the Kverkfjöll sandur allows sedimentary sections up to 15 m in height to be characterised (Marren

et al., 2009), providing a sedimentological framework from which to recognise similar deposits on Mars.

Mineralogy can provide a valuable insight into the subsurface hydrothermal environment within a glaciovolcanic system, and should be incorporated into future orbital and rover exploration strategies attempting to detect past volcano – ice interaction. Hydrated minerals including heulandite (zeolite), smectite, and sulfates, are a common component of the samples studied (see Table 4). Such minerals have the capacity to be identified on Mars with orbital instruments such as CRISM (Wray et al., 2009; Michalski et al., 2010), and the specific mineral assemblages identified at Kverkfjöll and Askja provide a starting point in the search for glaciovolcanic environments. This mineral ‘fingerprint’ includes a common alteration assemblage of nanophase iron oxides, smectite, and zeolite, supplemented with additional alteration minerals including jarosite, gypsum, opal, quartz, sulfur, pyrite, goethite/ferrihydrite, hematite, and carbonate. These alteration assemblages already share similarities with those identified at proposed localities of hydrovolcanism or volcanogenic hydrothermal alteration on Mars. This includes acid sulfate alteration at Gusev Crater (Morris et al., 2008) and neutral to alkaline alteration at Nili Fossae (Brown et al., 2010). Fe-bearing phases at Gusev Crater in particular are comparable to those identified at Kverkfjöll, including pyroxene, nanophase iron oxide, Fe-sulfate (jarosite), hematite, goethite, and pyrite. Finally, active hot spring environments were found to cover a broad range of acidic to neutral pH conditions (Figure 5), incorporating acidic sulfate-depositing environments (e.g. Hveradalur and Hveratagl geothermal fields, Figure 3D-F) and neutral carbonate-depositing environments (e.g. Hveragil, Figure 3C) within a single volcanic system covering <100 km². As such, areas of glaciovolcanism appear to be environmentally-diverse, and this is reflected in their mineral deposits.

5.3 Astrobiological Implications

Aside from understanding past surface processes on Mars, this study highlights two areas that warrant further investigation with regard to the search for life on Mars. Firstly, the physicochemical variety of hydrothermal environments characterised at Kverkfjöll suggests this system to be inhabited by a well-adapted microbial community that may serve as model organisms for astrobiological research. Sulfur cycling is potentially an important biogeochemical process within the hydrothermal environments at Kverkfjöll, based on the dominance of dissolved SO_4^{2-} in hydrothermal fluids and identification of FeS_2 (pyrite) within hydrothermal sediments. Given the temperature and pH range of the hydrothermal environments at Hveradalur and Hveratagl sites at Kverkfjöll (Figure 5), mesophilic (20 - 40 °C), moderate thermophilic (40 - 60 °C), and thermophilic (>60 °C) acidophiles are likely to be active. Future studies should address the microbiology of this site to establish whether sulfur-driven metabolism would be a feasible mechanism for sustaining microbial life within glacial hydrothermal environments.

Despite the widespread occurrence of bioalteration textures in oceanic basaltic lavas (e.g. Furnes et al., 2007), none were identified in pillow basalts or volcanoclastics from Askja and Kverkfjöll. All palagonite-glass alteration boundaries were smooth and consistently banded, typical of abiotic aqueous alteration (Staudigel et al., 2008). This is similar to previous textural studies of hyaloclastites from southern Iceland where only granular and 'pitted' bioweathering textures were identified (Thorseth et al., 1992; Cockell et al., 2009). Likewise, Cousins et al. (2009) showed bioalteration textures to occur preferentially within marine altered hyaloclastite, but not fresh-water (i.e. glacial) altered hyaloclastite. This suggests alternative biosignatures should be explored when considering glaciovolcanic terrains as a suitable target for life exploration on Mars.

Finally, regarding the detection of biosignatures preserved within the rock record, glaciovolcanic systems offer a variety of preservation environments for past microbial life (Cousins and Crawford, 2011). Biomolecules could be preserved within subsurface sulfate deposits such as those identified

in pillow basalts ASK09 and KV07. These would be protected from surface radiation and oxidation, potentially preserving organic biosignatures over long timescales. As another example, jökulhlaups provide a high-volume sedimentary deposit that could bury and preserve subglacial organic matter, much in the same way proposed for delta deposits on Mars (Ehlmann et al., 2008).

6. Conclusions

The Kverkfjöll and Askja volcanic systems and their associated hydrothermal environments and deposits provide a wealth of understudied mineralogical and palaeoenvironmental Mars analogues, which have been described collectively within this paper for the first time. Environments at the active Kverkfjöll geothermal areas range from acid to neutral pH, low to high temperature, and anoxic to oxic. Associated mineralogical alteration assemblages that are analogous to those present on Mars include zeolites (heulandite), sulfates (gypsum, jarosite, alunogen), crystalline iron oxides (goethite, hematite), smectite clays (montmorillonite, saponite), and nanophase ferric oxides. Future work should address whether or not such assemblages correspond to putative glaciovolcanic terrains identified on Mars by geomorphology alone. The wide diversity of hydrothermal environments at Kverkfjöll in particular provide a valuable, and as yet not fully-explored, range of glaciovolcanic environments that may be used to test instruments and operational strategies for searching for similar past environments on Mars. Moreover, the microbiology of these environments may reveal much about the metabolic and survival strategies adopted by life in order to thrive within these geological systems on both Earth and Mars.

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Figure Captions

Figure 1. Google Earth SPOT-5 2011 image of Askja and Kverkfjöll fieldsites. All maps are orientated north, unless otherwise stated. A) Overview of the three field areas, which from north - south are the Askja volcano, NE-trending fissure swarm (encompassing samples KV02 and KV07), and the Kverkfjöll volcano (approximate subglacial caldera position indicated by dashed line): geothermal sites at Kverkfjöll are shown in blue, and more detail is given in Figure 2. B) Map of Iceland, showing the location of Askja – Kverkfjöll (area shown in (A) is cross-hatched). C) Google Earth SPOT-5 2011 image of sampling localities ASK03, ASK04, and ASK09; the volcanoclastic outcrops are covered in a layer of pale rhyolitic pumice, which itself is overlain by a subaerial basaltic lava flow in the northern part of the image.

Figure 2. Fissure swarm features (A, C-D) and geothermal localities at Kverkfjöll (B). All maps are orientated north unless otherwise stated. A) hill-shaded digital elevation model (DEM) highlighting the NE-trending subglacially-formed ridges that delineate the Kverkfjöll fissure swarm, dominantly composed of weathered pillow lava mounds (shown in C); B) ASTER image draped over a DEM of Kverkfjöll, looking south. Four geothermal areas investigated at Kverkfjöll are shown: Hveradalur, Hveratagl, Hveragil, and the proglacial ice cave; C) Google Earth SPOT 5 2011 image of a pillow mound ridge within the fissure swarm (A), orange box indicates sampling area KV07; D) Columnar jointed basalt surrounded by basaltic sand within the fissure swarm zone.

Figure 3. Field examples of glaciovolcanic lithologies and hydrothermalism. A) Banded welded hyalotuff intercollated with friable volcanoclastic material at Askja; B) Pillow basalt morphology within pillow mounds at site KV07; C) Carbonate terraces at the geothermal stream in Hveragil gorge, Kverkfjöll; D) Active ice-fed hydrothermal pools (“Site 4”, each ~ 10 m across) at the Hveradalur geothermal field, Kverkfjöll; E) Shallow hydrothermal ice-fed meltwater pool (~2 m across) at Hveratagl, Kverkfjöll; F) Lake Gengissig and the adjacent ice-bound hydrothermal field at Hveradalur, Kverkfjöll.

Figure 4. Large-scale (<100 m) jokulhlaup influenced topography and sedimentary deposits within the Kverkfjöll proglacial area, identified within the Google Earth SPOT 5 2011 2.5 m image. A) streamlined ridges overlain with depositional sediments; B) depositional fan with palaeoflow direction preserved as micro-terraces and ridges; C) valley-fill sediments deposited during ponding.

Figure 5. pH and temperature range of aqueous environments at Kverkfjöll. *Data from Ólafsson et al. (2000); †Data measured in July 2007. All other data were measured in June 2011. For a list of pH and temperature data see Supplementary Material.

Figure 6. Thin section light micrographs and BSE image of hyaloclastite and pillow lavas: A) Vesicular sideromelane clast in hyaloclastite ASK04, also containing nano-crystalline phases (C); B) Sub-angular welded sideromelane fragments in ASK07; C) Nanocrystalline oxides within a sideromelane fragment in ASK04; D) BSE image of the vesicle shown in (C), with associated EDS element plots for the red spot (G) and blue spot (H); E) Vesicle in pillow lava ASK09 with secondary hydrothermal mineral deposition; F) Fine-grained plagioclase-rich groundmass in pillow lava ASK09, with some vesicles partially or completely in-filled with secondary hydrothermal minerals; G + H) EDS element peak plots for spot measurements in (D).

Figure 7. XRD patterns for A) Geothermal sediments at Hveratagl; and B) Basaltic pillow lava assemblages from the fissure swarm and Askja, and Hveradalur tuff sample KS03. Sm = smectite; A = anorthite; Q = quartz; H = heulandite; P = pyrite; G = gypsum; D = diopside.

Figure 8. XRD patterns for hot spring sediments (Sites 1,2,3,4,12,15), fumarole sediments (Sites 11 and 20), and sediment from lake Gengissig (Sites 7 and 21) at Hveradalur. . Sm = smectite; A = anorthite; Q = quartz; H = heulandite; Py = pyrite; G = gypsum; J = jarosite; S = sulfur.

Figure 9. XRD patterns for sediments used for VNIR spectral targets, both in the field (sample ID prefixed with an "I_") and laboratory-only VNIR measurements. . Sm = smectite; A = anorthite; Q = quartz; H = heulandite; Py = pyrite; G = gypsum; D = diopside

Figure 10. Raman spectra for I_9C (for XRD plot see Figure 9), Site 6 red crust, KS03 alteration surface, and white mineral deposits within the vesicles of pillow basalt KV07. Diamonds indicate peaks for jarosite (blue), gypsum (grey), goethite (black), and hematite (red), as identified using the RRUFF spectral database.

Figure 11. SEM secondary electron images (SEI) of geothermal sediments and terrace crusts from Hveradalur: A) Cubic pyrite embedded within smectite (Site 1); B) Site 2 vesicular basaltic clast with hydrothermal alteration rims and infilling within the larger vesicles; C) Heulandite from Site 21; D) Pitted and etched cubic pyrite crystals in Site 8 crust; E) Small (1 μm) goethite crystals in Site 6 crust; F) Smectite in Site 1 sediment.

Figure 12. GER 1500 in-situ reflectance measurements taken at the Hveradalur geothermal field at Kverkfjöll. A) Dried-up spring and stream, showing the estimated extent and flow of the stream down towards the lake (yellow dashed line). (B-E) Reflectance spectra of targets; B) I6A-E; C) I_Red, I17, and I18; D+E) reflectance spectra measurements from dried-up stream targets I9A-F. Solid lines depict Fe absorptions, dashed lines depict chlorophyll a absorption line.

Figure 13. VNIR (400 - 1000 nm) reflectance spectra for powdered (<500 μm) samples from Askja, the fissure swarm, and the Hveradalur geothermal area at Kverkfjöll. A) Basaltic and palagonite-bearing samples; B) Hydrothermal samples dominated by flat pyrite and/or sulfur reflectance; C) Iron oxide/oxyhydroxide-bearing samples with $\text{Fe}^{2+/3+}$ absorptions (grey lines); D) Samples from the dried-up stream at Hveradalur (see Figure 12A), some exhibiting a strong chlorophyll a absorption (grey line).

Figure 14. Formation temperature ranges for mineral species identified in Kverkfjöll and Askja samples. Note: temperatures are approximate as they are affected by other factors such as solution chemistry. Figure adapted from Warner and Farmer (2010).

Table 1. Samples from Askja, fissure swarm, and hydrothermal fields Hveradalur and Hveratagl at Kverkfjöll. Sample ID's marked with an asterisk are from outcrops and targets used for in-situ Vis-NIR reflectance spectroscopy.

Location	GPS	Sample	Sample description
Askja	65°3.276'N 16°30.480'W	ASK03	Finely banded hyaloclastite
		ASK04	Hyaloclastite
		ASK07	Hyaloclastite
		ASK09	Pillow basalt
Fissure swarm	64° 44.525'N 16° 37.304'W	KV02	Pillow basalt
		KV07	Pillow basalt with gypsum deposits
Kverkfjöll - Hveradalur	64°40.176'N 16°41.166' W	I_6A*	Red – orange coloured hydrothermally altered mound at the “Mars Site”.
		I_6B*	
		I_6C*	
		I_6D*	
		I_6E*	
		I_17*	Sulfur mound sediment at the “Mars Site”
		I_18*	
		I_Red*	Red ground sediment at the “Mars Site”
		KS03	Welded tuff with iron oxide surface crust
		Site 1	Unconsolidated sediment and fluid from an active hot spring
		Site 2	
		Site 3	
		Site 4	
		Site 6	Red mineral terrace crust from an active hot spring
		Site 7	Unconsolidated lake sediment and lake water
		Site 8	Orange mineral terrace crust from an active hot spring
		Site 9A*	Dried-up inactive hot spring stream surface sediment
		Site 9B*	
		Site 9C*	
		Site 9D*	
		Site 9E*	
		Site 9F*	
		Site 10	Active fumarole sediment/precipitates
		Site 11	
		Site 12	Active hot spring unconsolidated sediment and fluid
		Site 15	
		Site 20	Active fumarole sediment and precipitates
Kverkfjöll – Hveratagl	64° 41.122'N 16° 40.562'W	KV04	Unconsolidated sediment from hydrothermal pools
		KV06b	
		KV06d	

Table 2. Physicochemical characteristics and dissolved ion chemistry of selected aqueous environments at Hveradalur. BD = below detection. DO = Dissolved Oxygen, Cond. = conductivity. Instrumental errors are given in brackets and based on repeat measurements. Cation results are the mean of three repeat measurements (standard deviation between 0.01 – 3.5 mg/l depending on the cation and sample). Anion results are ± 0.2 mg/l for sulphate and $\pm <0.05$ mg/l for nitrate, chloride, and fluoride based on repeat measurements of standards.

Environment		In situ environmental parameters				Dissolved ions (mg/l)											
ID	Type	pH (± 0.1)	Temp ($^{\circ}\text{C}$) (± 0.5)	DO (mg/l) (± 0.4 mg/l)	Cond. (μS) (± 30)	Fe	P	Si	Na	Ca	Mg	Mn	K	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	F ⁻
Site 1	Stream	4.2	34.7	5.9	700	1.59	0.59	119.89	100.32	37.24	5.50	0.70	19.74	227.33	6.15	8.69	3.32
Site 2	Stream	3.8	37.1	5.1	720	1.40	0.52	108.54	89.28	33.36	4.80	0.63	18.34	223.89	BD	7.29	1.57
Site 3	Stream	3.6	40.2	4.0	700	1.27	0.53	90.78	76.58	26.99	3.99	0.53	15.93	220.55	2.80	8.61	1.73
Site 4	Pool	4.8	53.2	~0-2	688	1.26	0.54	91.66	80.51	26.79	3.94	0.53	17.31	218.64	BD	6.54	1.76
Site 7	Lake	6.0	11.4	3.9	320	0.03	0.04	27.61	27.93	57.61	6.40	0.89	3.79	157.79	3.28	6.21	2.07
Site 12	Stream	4.6	3.0	10.4	12	B	B	1.92	BD	0.92	B	0.03	0.21	1.052	1.72	6.55	0.88
Site 15	Stream	4.5	18.4	9.0	12	B	B	1.74	BD	0.17	B	0.01	0.18	1.110	2.10	5.60	0.67
Site 21	Lake	5.0	10.4	0.8	220	0.25	0.05	23.81	23.41	39.88	3.42	0.60	2.04	123.46	BD	7.34	6.15

Table 3. Major element analysis of glass clasts and glass rims of volcanoclastics and pillow lavas from Askja and the fissure swarm. Values are given as means (n= number of analyses) with 1 σ standard deviation.

	ASK03	ASK04	ASK07	ASK09	KV02	KV07
	n= 27	n= 33	n= 20	n= 10	n= 23	n= 26
SiO ₂	50.0 ($\pm$ 2.2)	50.6 ($\pm$ 0.9)	52.3 ($\pm$ 0.5)	51.8 ($\pm$ 1.1)	49.1 ($\pm$ 0.8)	50.0 ($\pm$ 0.8)
TiO ₂	2.7 ($\pm$ 0.2)	2.4 ($\pm$ 0.2)	3.6 ($\pm$ 0.2)	2.6 ($\pm$ 0.2)	3.1 ($\pm$ 0.2)	2.9 ($\pm$ 0.2)
Al ₂ O ₃	13.6 ($\pm$ 0.6)	13.4 ($\pm$ 0.7)	13.3 ($\pm$ 0.2)	13.6 ($\pm$ 0.8)	13.0 ($\pm$ 0.3)	12.8 ($\pm$ 0.6)
FeO	14.4 ($\pm$ 0.6)	14.1 ($\pm$ 0.3)	15.0 ($\pm$ 0.5)	14.8 ($\pm$ 1.5)	14.4 ($\pm$ 0.7)	14.7 ($\pm$ 1.3)
MnO	0.2 ($\pm$ 0.1)	0.2 ($\pm$ 0.1)	0.2 ($\pm$ 0.1)	0.2 ($\pm$ 0.1)	0.25 ($\pm$ 0.1)	0.2 ($\pm$ 0.1)
MgO	5.6 ($\pm$ 0.5)	5.3 ($\pm$ 0.2)	4.3 ($\pm$ 0.1)	5.4 ($\pm$ 0.6)	4.5 ($\pm$ 0.4)	4.9 ($\pm$ 0.7)
CaO	10.2 ($\pm$ 0.6)	9.5 ($\pm$ 0.2)	8.5 ($\pm$ 0.3)	9.9 ($\pm$ 0.3)	9.5 ($\pm$ 0.5)	9.8 ($\pm$ 1.0)
Na ₂ O	2.7 ($\pm$ 0.2)	2.6 ($\pm$ 0.2)	3.0 ($\pm$ 0.2)	2.9 ($\pm$ 0.3)	3.1 ($\pm$ 0.2)	2.9 ($\pm$ 0.3)
K ₂ O	0.4 ($\pm$ 0.1)	0.6 ($\pm$ 0.1)	0.8 ($\pm$ 0.1)	0.5 ($\pm$ 0.1)	0.7 ($\pm$ 0.1)	0.6 ($\pm$ 0.2)
SO ₃	0.4 ($\pm$ 0.1)	0.4 ($\pm$ 0.1)	0.3 ($\pm$ 0.1)	0.3 ($\pm$ 0.1)	0.5 ($\pm$ 0.1)	0.3 ($\pm$ 0.1)
<i>Total</i>	<i>100.6 ($\pm$1.7)</i>	<i>99.3 ($\pm$1.3)</i>	<i>101.4 ($\pm$0.8)</i>	<i>102.1 ($\pm$0.7)</i>	<i>98.3 ($\pm$1.1)</i>	<i>99.2 ($\pm$1.2)</i>

Table 4. Summary of mineral species identified in samples, primarily with XRD, but also with Raman spectroscopy and SEM imaging. (X) indicates inferred minerals based on EDS chemistry and BSE images. Pa = palagonite; An = anorthite; D = diopside; H = heulandite; G = gypsum; Q = quartz; S = sulfur; J = jarosite; Sm = smectite; P = pyrite; Hm = hematite; G = goethite

Sample	Type	Pa	An	D	H	G	Q	S	J	Sm	P	He	G
ASK09	Lava		X	X		(X)	(X)		(X)			(X)	
KV02	Lava		X	X									
KV07	Lava		X	X		X							
KS03	Volcaniclastic		X	X								X	
ASK03, ASK04, ASK07	Volcaniclastic	X											
I_6A, I_6B, I_6C, I_6D, I_6E	Sediment				X	X		X		X			
I_17, I_18	Sediment				X	X		X		X	X		
Site 1, Site 2, Site 3, Site 7, Site 21	Sediment		X		X		X			X			
Site 4	Sediment										X		
Site 8	Crust										X		
Site 6	Crust												X
Site 9A,B,C,D,E,F	Sediment				X				X	X	X		
Site 11, Site 20	Sediment				X	X	X	X	X	X			
Site 12, Site 15	Sediment				X		X			X			
KV04	Sediment			X	X		X			X			
KV06b, KV06d	Sediment					X				X	X		

Table 5. Summary of environments and their deposits at Kverkfjöll, Askja, and the fissure swarm, along with postulations as to their ability to preserve biosignatures within the rock record, and their comparable localities on Mars.

Environment	Physiochemical properties	Lithological features	Biosignature preservation?	Comparable localities on Mars
Subglacially-erupted pillow basalts and volcanoclastics (Askja, fissure swarm)	PAST: Eruption into ice and liquid water; hydrothermal circulation; low-temperature (<120 °C) alteration PRESENT: dry, exposed, and weathered	Pillow piles and volcanoclastic ridges where confining ice prevented the lateral spread of lava and explosive material; aqueous alteration of sideromelane to palagonite; deposition of secondary mineral species including sulphates, silica, and iron oxides	Possible – only within hydrothermal mineral deposits such as vesicular gypsum deposits in sample KV07. Basaltic glass shows no evidence of bioalteration features.	Similar lithologies may be found at proposed subglacial constructs at Chryse/Acidalia Planitia, (Martinez-Alonso et al., 2011) and proposed moberg ridge constructs at Pavonis Mons (Head and Wilson, 2007).
Active geothermal fields (Hveradalur, Hveratagl, Hveragil)	Pools, springs, and lakes are acidic-neutral pH, ranging from 0 to 97 °C. Sulphate-dominated water chemistry. Water sourced primarily from surrounding snow/ice melt and rain/snowfall.	Unconsolidated sediments at Hveradalur and Hveratagl dominated by zeolites, sulfates, smectite, and pyrite. Mineral terraces at Hveragil dominated by thick carbonate deposits.	Yes – biological activity could be recorded within minerals such as pyrite (e.g. $\delta^{34}\text{S}$ isotope signatures), as preserved organic compounds trapped within the sediment, or as microfossils and organic matter within carbonate terraces.	Past volcanogenic hydrothermal systems, particularly those with similar mineral terrains, e.g. hydrovolcanic features and Fe-bearing alteration minerals Gusev Crater/ Home Plate (Morris et al., 2008).
Jökulhlaup-dominated sandurs (Kverkfjöll)	Unconsolidated and semi-consolidated sediment within a dry volcanic desert, continually modified by glacial meltwater, jökulhlaups, and surface weathering.	A wide variety in glaci-fluvial sedimentary facies, ranging from (i) coarse-grained matrix-supported boulder facies indicative of jökulhlaups, and (ii) fine-grained clast-supported gravel facies with multi-directional clast orientations indicative of varying flow energy and an ablation-fed braided river flow regime.	Yes – catastrophic drainage of subglacial and supraglacial lakes (e.g. Gengissig) will deposit the residing microbial community along with sediments forming jökulhlaup deposits. Also, minerals (e.g. pyrite – see above) within sedimentary deposits may record isotopic fingerprints of microbial activity.	Outburst flood deposits at Aromatum Chaos (Leask et al., 2006); Athabasca Valles (Burr et al., 2002); and depositional fans at Ceraunius Tholus and Hecates Tholus (Fasset and Head, 2006; 2007).
Ice cave (Kverkfjöll)	Cold, subsurface glacial environment maintained by continual drainage of warm subglacial hydrothermal fluids supplemented with glacial meltwater.	Sediments and moraine forming the ice-cave floor, but nothing definitive of ice-caves themselves.	Possibly – within the sediments and glacial moraine, and potentially through any microbial communities transported via the drainage of subglacial	Regions of past glaciation that are spatially and temporally associated with volcanism; e.g. Cavi Angusti, South polar region (Dickson and Head,

			hydrothermal fluids.	2006).
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ACCEPTED MANUSCRIPT

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Highlights

- Hydrothermal volcano - ice environments are proposed as a Mars analogue
- Askja and Kverkfjöll volcanoes in Iceland used as a model for Mars
- Hot spring environments are acidic and sulphate dominated
- Mineralogy comprises of zeolites, smectites, iron oxides, sulphates and pyrite