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Mars analogue volcano-ice hydrothermal environments at Kverkfjöll and Askja volcanoes, Iceland

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Running title: Volcano – ice environments at Kverkfjöll and Askja, Iceland

Abstract

Hydrothermal environments driven by volcanism are prime astrobiological targets on Mars, due to their ability to support and preserve microbial ecosystems. ~~Volcano – ice interactions on~~ On Earth, volcano – ice interactions produce many hydrothermal habitats available to microbial colonisation, and thus provide an analogue to past environments on Mars~~, where many landforms have been attributed to volcano – cryospheric interaction~~. However, Mars exploration urgently requires a framework for identifying such environments on a range of scales and with a range of geological criteria. In this paper r~~R~~emote sensing data were combined with sub-mm environmental mapping and sample analysis that included ~~(~~X-ray diffraction, Raman spectroscopy, thin section petrography, scanning electron microscopy, electron dispersive spectrometer analysis~~,~~ and dissolved ion water chemistry,~~)~~ to characterise samples from two areas of basaltic volcano – ice interaction: namely Askja and Kverkfjöll volcanoes in Iceland.~~-~~ Askja was erupted subglacially during the Pleistocene~~,~~ and is now exposed within a volcanic desert. Kverkfjöll is a subglacial volcano ~~beneath~~ on the northern margin of Vatnajökull ice cap~~,~~ and hosts active hydrothermal systems. NE-trending fissure swarm ridges extend between these two volcanic systems. Multiple Holocene glacial outburst (jökulhlaup) sedimentary deposits lie to the north of Kverkfjöll. Hydrothermal environments at Kverkfjöll were found to be predominantly acidic, with dissolved sulphate dominating the water chemistry. These hydrothermal environments vary across a small (<100 m) spatial scale, and include hot springs, anoxic pools, meltwater lakes, and sulphur- and iron- depositing fumaroles. Biomats, two in association with individual goethite and pyrite mineral terraces, were common at Kverkfjöll. *In-situ* and laboratory VNIR (440 – 1000 nm) reflectance spectra representative of Mars rover multispectral imaging show spectral profiles to be influenced by $Fe^{2+/3+}$ - bearing minerals. Overall, sediments and lavas display two types of hydrothermal alteration: a low-temperature (<120 °C) assemblage dominated by palagonite, sulfates, and iron oxides; and a high-temperature (>120 °C) assemblage signified by heulandite and quartz. ~~This~~ Overall, this work provides ~~a framework for identifying such environments during future exploration of Mars, given their high astrobiological potential, and~~

~~provides~~ a descriptive reference for ~~the~~ two prominent active hydrothermal environments ~~at Kverkfjöll~~which can be used as analogues for those on Mars.

1. Introduction

Hydrothermal environments on Mars arose from both volcanism and impact cratering (Schulze-Makuch 2007). Both processes have played a major role in shaping the Martian surface (and near-surface) environment, and potentially in providing suitable habitats for life. Hydrothermal environments driven by volcanism are prime targets for astrobiological exploration on Mars, and have well-documented terrestrial analogues (e.g. Yellowstone National Park, USA; REFS). Recently, hydrothermal environments have been proposed as a possible cradle for the emergence of life on Earth (Mulkidjanian *et al.* 2012). A review of hydrothermal areas on Mars is provided by Schulze-Makuch (2007), who highlights a number of astrobiological targets. The key ingredient in the generation of these hydrothermal 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 rift and hot spot volcanism in particular are very analogous to environments on Mars, where the development of early plate tectonics is ambiguous (Nimmo & Tanaka 2005), with no such lithospheric cycling occurring today. Likewise, volcanic systems that have eruptive products of a basaltic to basaltic-andesitic composition (based on total silica and alkali content) are geochemically analogous to the Martian crust (Nimmo & Tanaka 2005). Here, we introduce a new Mars analogue environment that is the result of rift- and hot-spot- basaltic volcanism within a cryospheric environment: volcano – ice interaction at Askja and Kverkfjöll volcanoes in central Iceland.

1.1 Volcano – ice interaction

Terrestrial basaltic volcanoes that interact with ice or permafrost have the potential to reveal much about past environments and life on Mars (for a review see Cousins & Crawford 2011, and references therein). The interaction between volcanism and ice is thought to be widespread on Mars (e.g. Head & Wilson 2002; 2007, Chapman *et al*. 2000), and numerous examples can be found on Earth, both past and present. Basaltic volcanism on Earth, and its interaction with the local cryospheric environment has long provided analogues to surface features and processes on Mars (Cousins & Crawford 2011, and references therein), including those that have interacted with ground ice (e.g. Fagents & Thordarson 2007) and glaciers (e.g. Martinez-Alonso *et al*. 2011). The nature and duration of an eruption, as well as the nature of the local environment sustained in between eruptions, is dependent upon the magma composition, eruption frequency and volume, thickness/volume of ice overlying the volcanic centre, thermal characteristics of the ice, and bedrock topography. One particularly major control is deglaciation, resulting in decreasing lithospheric pressure followed by an increase in volcanism (Carrivick et al. 2009).

The relevance of these environments to astrobiology and the exploration of life on Mars lie in their generation of liquid water through geothermal and magma interaction with glacial ice and snow. This liquid water ranges in volume from a continual subsurface cycling of hydrothermal fluids throughout the volcanic system, to large volumes of subglacial meltwater, that can either be sustained as a subglacial lake (Gaidos et al. 2008; 2004) or released catastrophically as a glacial outburst flood or "jökulhlaup" (Björnsson 2002). ~~A recently documented example on Mars was described by~~ Hovius et al. (2008~~),~~) have ~~detailing~~ detailed the impacts of an outburst flood~~ing at~~ from the Martian polar cap which occurred as little as 20,000 years ago~~,~~ and which ~~interpreted to be~~ the result of volcano - ice interaction ~~Hovius et al. (2008)~~. Canyons in Iceland have been compared to other terrestrial megafloods (Baker 2) and with outburst floods on Mars (Malin and Eppler, 1981; Baker, ~~2009~~2002; Chapman et al., 2003; Hovius et al., 2008)~~, and have also been used to highlight the association of jökulhlaups with deglaciation (Carrivick 2009)~~. Glacial processes have been widely documented on Mars throughout its history (e.g. Karhel & Strom 1992; Neukum et al. 2004; Dickson et al. 2008), much of which has been in association with volcanic regions (Head &

Wilson 2002; also see Cousins & Crawford and references therein). Such release of subsurface water and subsequent sedimentary deposition can provide a geological record of subsurface environments and potentially biosignatures of any biota that may have been present. Sandur deposits from jökulhlaups in southern Iceland have been previously used as sedimentary analogues for Martian flood deposits (Warner & Farmer 2010), and have been found to be dominated by a low-temperature alteration mineral assemblage of palagonite, smectite, zeolites, and clays (Warner & Farmer 2010). Likewise, it has been recently proposed that large areas of the northern plains of Mars consist of basaltic glass (Horgan & Bell 2012), implying widespread explosive volcanism – such as that found during volcano – ice interaction (Horgan & Bell 2012). One recent example of this process can be seen in the 2010 Ejafjallajokull eruption in southern Iceland, which generated large volumes of ash as fine glass particles (Dellino et al. 2012).

1.2 Searching for 'habitable' palaeoenvironments

Identification of palaeoenvironments that were once "habitable", or those that exhibit evidence of past liquid water activity, is of primary interest for missions such as NASA's Mars Science Laboratory (which landed in Gale Crater in August 2012) and ESA's ExoMars mission (planned for launch in 2018). As such, the lithological and mineralogical deposits representative of these terrains require characterisation, with the aim to improve the detection of similar environments on Mars. Indeed, much Mars analogue work has been conducting focusing on a range of environments, including Hawaiian lava flows (*e.g.* Chemtob et al. 2010), acid hot springs (*e.g.* Szynkiewicz et al. 2012); impact craters (*e.g.* Izawa et al. 2011), and arctic terrains (*e.g.* Pollard et al. 2009). Furthermore, Mars has much geological and palaeoenvironmental diversity, as revealed especially by the instruments HiRiSE and CRISM (e.g. Weitz *et al.* 2011; Ehlmann *et al*. 2011; Carter *et al*. 2010; Bibring et al. 2005). Mineral assemblages identified infer a variety of conditions spanning acidic (ferric oxides, sulfates) to neutral – alkaline (phyllosilicates) environments (Bibring et al. 2006; Chevrier et al. 2007; Ehlmann et al. 2011), with varying levels of water activity, ranging from proposed 'acid fog' aqueous alteration

Comment [JLC1]: The aim of the paper should be clearly stated at the end of the intro…do not hide in in a paragraph…use the phrases in the abstract for this aim and check the wording of the title of the paper to closely reflect the aim; i.e. to be what the paper actually does...

(Schiffman et al. 2006) to subsurface water (Ehlmann et al. 2011) and hydrothermal activity. Many of these proposed environments are based upon terrestrial processes, and as such these environmental analogues provide the means to improve the detection of specific environments and processes thought to have operated at the Martian surface. In particular, the detection of biosignatures is primarily dependent upon the identification of suitable environmental deposits. Target lithofacies and mineralogical assemblages from environments of high astrobiological relevance need to be well-understood in order to ascertain their presence on Mars.

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2. ~~Field~~ Overview of field Area

Field sites at the Kverkfjöll and Askja volcanoes, and the fissure swarm that lies between them represent both past hydrothermal alteration, and currently active hydrothermal environments (**Figure 1**). The landscape and terrain around these volcanoes is dominated by subglacial and subaerial eruptions, jökulhlaup deposits, and aeolian processes (Alho et al. 2005). This region was selected as an ideal astrobiology Mars analogue site for several reasons: (1) the region is dominated by basaltic volcanism and near-surface hydrothermal activity/alteration. (2) the rain shadow cast by the Vatnajökull ice cap means there is little to no vegetation; (3) its geographical isolation has resulted in little disturbance by people, animals, development etc; 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. Taken together, these qualities allow for the characterisation of environmental parameters, and how such environments could be preserved within the rock record for future detection on Mars. A complete list of samples acquired in the field in both 2007 and 2011 is provided in **Table 1**.

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2.1 Askja

Askja (65°3.276'N; 16°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 an explosive 1875 Plinian eruption producing Öskjuvatn (Askja lake) caldera (Hartley & Thordarson 2012). The most recent activity at Askja was an eruption of basaltic lava to the north of the caldera (65° 3' 44.88"N; 16° 36' 58.61" W) in 1961 (Thorarinsson & Sigvaldason 1962). Compositionally, eruptive products at Askja are largely basaltic, with the exception of the rhyolite-producing eruptions at ~10 ka and in 1875 (Sigvaldason 2002).

2.2 Fissure Swarm

A Holocene fissure swarm extends northeast of Kverkfjöll (**Figure 2A**), towards Askja, and intrudes pre-Holocene bedrock (Hjartardottir & Einarsson 2012). Hoskuldsson *et al.* (2006) infer that the pillow lavas within this fissure swarm were erupted under 1.2 to 1.6 km of ice during the last glacial maximum. These fissure swarms have been eroded by catastrophic glacial outburst floods (jökulhlaups) originating from the northern Vatnajökull ice margin (Carrivick and Twigg, 2004; Carrivick *et al.* 2004a). ~~The large volumes of glacial meltwater characteristic of jökulhlaups are caused by a combination of subglacial volcanic activity and rapid failure of ice-dammed lakes (Rushmer 2006; Bjornsson 2002). The last recorded jökulhlaup at Kverkfjöll occurred in January 2002, and was caused by the catastrophic drainage of the geothermal lake "Gengissig" at Hveradalur (Rushmer 2006, **Figure 2B**). These jökulhlaups also produce distinctive depositional and erosional landforms including boulder bars, terraces, gorges, and outwash fans (Carrivick *et al.* 2004a).~~

2.2 Kverkfjöll

Kverkfjöll lies above the Icelandic mantle plume (Wolfe *et al.* 1997; Sigvaldason *et al.* 1974), and is situated within the northern volcanic zone (NVZ), which marks the mid-Atlantic plate boundary in north Iceland (Hjartardottir & Einarsson 2012). The Kverkfjöll central volcanic system comprises two dormant subglacial calderas, which are both roughly 8 x 5 km across (Hjartardottir & Einarsson

2012), which lie beneathand situated on the northern part margin of Vatnajökull ice cap in central Iceland (64° 38’6.92”N; 16°43’11.84”W) see map in **Figure 1**). Vatnajökull itself is home to seven subglacial volcanic systems, including the highly active Grimsvötn volcano that last erupted in May 2011 (Gudmundsson et al. 2012). Kverkfjöll lies above the Icelandic mantle plume (Wolfe *et al*. 1997; Sigvaldason *et al*. 1974), and is situated within the northern volcanic zone (NVZ), which marks the mid-Atlantic plate boundary in north Iceland (Hjartardottir & Einarsson 2012). Eruptive Kverkfjöll eruptive products are generally basaltic (Oladottir *et al.* 2011), and are typical of volcano – ice interaction, 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 in Ármannsson *et al*. (2000) and Olafsson *et al*. (2000), and comprise high temperature fields around the northern caldera rim (64°40.176’N; 16°41.166’ W), and hydrothermal outflow environments at the glacial front **(Figure 2B)** (Karhunen 1988). 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, b; Carrivick, 2006; 2007a, b). The last recorded jökulhlaup at Kverkfjöll occurred in January 2002, and was caused by the catastrophic drainage of the geothermal lake “Gengissig” at Hveradalur (Rushmer 2006, **Figure 2B**).

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Fieldwork was conducted during summer field campaigns in July 2007 and June 2011, with the aim to characterise examples of these Mars analogue environments in terms of both active environmental parameters, and lithological deposits, with a particular focus on hydrothermal activity. Field sites were characterised *in situ* through a combination of sub-meter scale mapping of hydrothermal environments, field photography, GPS, Visible – Near Infra Red (VNIR) field spectroscopy, pH, temperature, dissolved oxygen, and conductivity measurements. Samples (including rocks, sediments, biomats, and fumarole deposits) were collected from representative sites from Kverkfjöll, Askja, and the fissure swarm, and laboratory analysed using VNIR reflectance

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~~spectra, X-ray diffraction (XRD), Raman spectroscopy, electron microprobe, scanning electron microscope (SEM) imaging, and light microscope petrography. This characterisation provides a framework from which to identify putative volcano-ice interaction environments and deposits on Mars in the future, and also what possible metabolic pathways are available for residing microbial communities.~~

3. Methods

Fieldwork was conducted during summer field campaigns in July 2007 and June 2011, with the aim to characterise examples of these Mars analogue environments in terms of both active environmental parameters, and lithological deposits, with a particular focus on hydrothermal activity. Field sites were characterised *in situ* through a combination of sub-meter scale mapping of hydrothermal environments, field photography, GPS, Visible - Near Infra Red (VNIR) field spectroscopy, pH, temperature, dissolved oxygen, and conductivity measurements. Samples (including rocks, sediments, biomats, and fumarole deposits) were collected from representative sites 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. This characterisation provides a framework from which to identify putative volcano-ice interaction environments and deposits on Mars~~ in the future~~, and also what possible metabolic pathways are available for residing microbial communities.

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3.1 Remote sensing data

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. ~~For further details see~~ [redacted] ~~for which this work was originally conducted.~~

→ What about ASTER? ASTER images are freely available so just state date (need to look at Google Earth which I only have at home so cant check right now) and pixel resolution (15m).

3.2 Sampling and environmental measurements

Hydrothermal environments at Kverkfjöll were ~~preliminary~~ sampled in July 2007~~,~~ and ~~then more extensively~~ in June 2011~~, and these samples and field observations form the bulk of this study~~. Water samples for dissolved ion chemistry were pre-filtered using a Millex-AP prefilter to remove large suspended 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 (30 ml) of dH_2O were taken at the same time as environmental samples. These were kept cold (~4 °C) prior to analysis. Environmental measurements (pH, temperature, dissolved oxygen, conductivity) and field mapping of environments were conducted in situ at the Kverkfjöll geothermal site in 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 resolution of 0.1 mg/l with an accuracy of ± 0.4 mg/l.

Subglacially-erupted lavas were sampled from Askja and the NE-trending fissure swarm in 2007 (see **Figure 1**). Sampling was focused on pillow lava piles, and outcrops of volcaniclastics, the latter of which was often found to be eroded due to their friable nature. We use the term 'volcaniclastic' 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 & Gudmundsson 2008. These samples, and others including unconsolidated geothermal sediments, biomats, hot spring sediment, and fumarole deposits, were collected within Whirlpak sample bags.

3.3 Reflectance spectroscopy

In situ field reflectance spectra were acquired using a GER 1500 portable field spectrometer (loaned from the NERC spectroscopy facility, Edinburgh, UK), which measures wavelengths between 350 – 1100 nm. A spectralon white calibration target was used at the time of measuring. Laboratory visible to near infra-red (400 - 1000nm) reflectance spectra of freeze-dried, powdered samples (using an alumina pestle and mortar; grainsize <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

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 BBK/UCL. Standards were run during analysis, typically every three samples. Cation results were taken as the mean of three repeat measurements, with standard deviations typically between 0.01 – 0.1 mg/l (see **Supplementary Material 1** for blank measurements and errors).

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. SEM imaging of microtextures and mineralogy within Kverkfjöll geothermal sediments and mineral crusts was achieved 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 University College London, calibrated to a pure silica standard prior to sample analysis.

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. Major element analysis of glass compositions from hyaloclastite and pillow lavas was achieved 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.

4. Results

4.1 Field observations at Askja and the fissure swarm

The terrain around Askja, Kverkfjöll, and along the fissure swarm is dominated by prominent pillow lava edifices and palagonite mounds, typical of the 'inverse topography' of exposed subglacial volcanic landscapes (**Figures 2A and 2C**). The subglacial terrain around Askja itself is dominated by hyaloclastite and hyalotuff deposits produced by explosive magma-water interaction, in addition to occasional pillow lava exposures (Sigvaldason 2002). Some hyaloclastite outcrops display depositional bedding features (**Figure 3A**), likely from deposition of volcaniclastic material within meltwater that typically forms during a subglacial eruption (Jakobsson & Gudmundsson 2008). All hyaloclastite outcrops are heavily palagonitized throughout, all exhibiting buff-colouration (**Figure 3B**), contrasting to the darker, unaltered basaltic terrain of the surrounding subaerial lava flows.

Along the fissure swarm, pillow lava mounds dominate the subglacial lithology, following the strike of the rift towards the Kverkfjöll subglacial caldera (**Figures 2A and 2C**), with which the fissure swarm is associated with (Hjartardottir & Einarsson 2012). Pillow mounds are typically comprised of unconsolidated scree slopes at the base, with the best-preserved pillows near the top of the mounds (**Figure 2C)**. The pillow mounds themselves are surrounded by dry, loose basaltic sand, and individual pillows range from ~30 cm diameter at site ASK09 to up to 1m Site KV02 (**Figures 3D and E)**. Surface oxidation of iron can be seen on individual pillows at site KV07 producing a thin (< 1mm) orange crust on the top surface of pillows (**Figure 3C**). Columnar jointing, indicative of rapid cooling, can also be identified along the fissure swarm (**Figure 2D)**.

4.2. Field observations at Kverkfjoll

Hydrothermal activity at Kverkfjöll is primarily controlled by fractures, faults, and the underlying lithology (Hjartardottir & Einarsson 2012). Fumarole gas measured by Olafsson *et al.* (2000) between 1992 - 1998 show CO_2 to be the dominant species (80 – 97% of the gas emitted), with both H and H_2S accounting for 1 – 12% each. As such, pH measurements from the hydrothermal environments investigated at the summit of Kverkfjöll (Hveradalur and Hveratagl - **Figure 2B**) show them to be acidic - neutral, depending on the extent of dilution by melting ice and snow. Conversely, at the forefront of the glacier, the geothermal outflow stream in Hveragil gorge (**Figure 2B)** precipitates calcite from near-neutral CO_2-rich waters (Olafsson *et al.* (2000), and the outflow river Volga has a circum-neutral pH due to extensive dilution of subglacial hydrothermal fluids with glacial meltwater. The temperature and pH range of all geothermal environments investigated at Kverkfjöll is shown in **Figure 4**, and given in **Supplimentary Material 2**. Generally, geothermal environments at Kverkfjöll range from pH 2 - 7.5, across a wide range of temperatures from near 0°C to 94.4°C (boiling point at the 1750m elevation). The geothermal field Hveratagl (64° 41.117' N; 16° 40.550' W), and the ice cave at the glacier front (64°43.326'N; 16°39.445'W) with its outflow river (Volga), were investigated in 2007. Following this initial investigation, Hveradalur (64° 40.173' N; 16° 41.100' W) was mapped and sampled extensively in 2011. These geothermal regions and their environments are detailed in the following sections, with Hveradalur (sampled 2011) forming the main focus of this study.

4.2.1 Hveradalur

The Hveradalur geothermal area (64°40.176'N; 16°41.166' W; **Figure 2B)** is dominated by two large glacier-dammed meltwater lakes, which sit high up on the edge of the caldera's western rim (**Figure 5**). Lake "Gengissig" was formed during a geothermal steam explosion event in 1959 (Gudmundsson & Hognadottir 2009). By 1970 the lake level was established to a similar level as seen today, and is approximately 350 - 450 m in diameter (Gudmundsson & Hognadottir 2009). The geothermally-heated ground both beneath and around this lake maintains a relatively warm lake temperature, which ranges between ~10 – 20 °C, as measured in June 2011 (see **Figure 4**). 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 & Hognadottir 2009). The nearby lake, "Galtarlón" lies to the northwest, and is thought to be more stable (Gudmundsson & Hognadottir 2009). In June 2011, this lake was ice-covered (**Figure 6A**), however in July 2007 it was observed to be ice-free (**Figure 6F**). The geothermal lake "Gengissig" was the focus of our investigation into this region. This lake is bounded by steep, 30 - 50 m tall ice walls, with steep mountain slopes on the north-western edge (Gudmundsson & Hognadottir 2009). Adjacent to the NW shore of the lake is a geothermal field across, leading down to the lake edge (**Figure 5A**). The geothermal field is entirely enclosed on all sides by ice and snow, which is gradually receding due to bottom-up geothermal heating, and top-down solar melting as the air temperatures increase during spring and summer. **Figure 6** gives examples of the environments at this geothermal site. This geothermal field is ~100 m across and is characterised by a number of small and large boiling (or near-boiling) hydrothermal pools, sulphurous fumaroles, snow-fed warm meltwater streams, and hydrothermally altered ground. These environments were mapped in detail to reveal a wide diversity of interconnected hydrothermal environments and deposits (**Figure 7**). There are two distinct areas within the area mapped: a larger (~ 60 m), highly active geothermal field with a variety of fumaroles, hydrothermal pools, and streams, and a smaller (~ 30 m) area dominated by geothermal sediments and mounds of altered rocks and fumaroles.

4.2.2. Hveratagl

Hveratagl (64° 41.122'N; 16° 40.562'W) lies ~ 2 km north of Hveradalur and comprises of a high temperature geothermal field, but has no lakes like those at Hveradalur. The geothermal field sits at the top of a north-south trending ridge, and is surrounded by high temperature fumaroles that cover the flanks of the ridge on the western side (**Figure 8C**). Like Hveradalur, the geothermal field is characterised by several meltwater pools, and fed by glacial and snow melt during spring and summer months. Over winter, the site becomes covered in thick snow (**Figure 8D**), which melts away variably every summer, depending on annual climatic conditions. Pools here typically lie within shallow surface depressions (**Figures 8E and 8F**), with an underlying layer of fine, soft sediment, suggesting these pools very likely form in the same location annually. Additionally, a collapsed ice-cave was also found at Hveratagl in 2007 (**Figure 8A**), out of which a subglacial outflow stream emerged (**Figure 8B**). Temperature and pH measurements taken in 2007 are shown in **Figure 4**, and again show aqueous environments to be acidic (pH 3 - 4).

4.1.3 Kverkfjöll proglacial environments

The proglacial region at Kverkfjöll; 'Kvaerkfjallarani', is dominated by extensive sedimentological deposits and geomorphological features from jökulhlaups originating from Kverkfjöll (Carrivick et al. ~~2009~~2004a, b), as well as glacial moraine deposits (Carrivick and Twigg, 2004). The Kverkfjökull sandur comprises ~~of~~ multiple jökulhlaup sedimentary successions (Marren *et al.* 2009)~~, with distinctive erosional and depositional features~~. Erosional ~~features~~ landforms in Kverkfjallarani include 'streamlining' of the pillow lava and hyaloclastite ridges that run northeast of Kverkfjöll volcano, gorges, smoothing of lava flows, and scours and potholes on basalt surfaces (Carrivick *et al.* 2004a). Depositional features are similarly extensive, and include outwash fans, depositional terraces, boulder clusters~~,~~ and fragmented hyaloclastite (Carrivick *et al*. 2004b). The 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), and so provides a sedimentological framework from which to recognise similar deposits on Mars. ~~Such~~ Specifically, these proglacial glaciofluvial deposits exhibit a wide variety in glacifluvial sedimentary facies, ranging from (i) coarse-grained matrix-supported boulder facies indicative of jökulhlaups , and (ii) ~~to~~ fine-grained clast-supported gravel facies with multi-directional clast orientations indicative of varying flow energy ~~together with directional flow and erosional surface features~~and an ablation-fed braided river flow regime.

To the NE of Kverkfjöll, Hveragil gorge (**Figure 2)** contains a hydrothermal stream. This stream deposits carbonate (Olafsson *et al*. 2000), and has previously been found to have temperatures of up to 62 °C, with an average temperature of 50 °C (Olafsson *et al*. 2000). Hveragil~~The~~ ~~gorge itself originally formed~~probably formed subglacially during the last glacial maximum (~~Carrivik~~Carrivick ~~et al. 2008~~2005). To the west~~ along the glacier front~~, the river Volga emerges from the Kverk~~ár~~jökull glacier and runs northwards, and is believed to be, at least initially, of subglacial origin (Olafsson *et al.* 2000; Friedman et al. (1972). Along the western edge of the ~~Kverkfjokull~~Kverkjökull glacier tongue, the river Volga has carved out a large ice cave (**Figure 9**). Ice caves such as these are unstable, and this particular cave has collapsed in summer 2010.

4.2 Petrology of Askja and fissure swarm pillow lava and hyaloclastite

Askja hyaloclastite samples ASK03, ASK04, and ASK07 are heavily palagonitized, with randomly orientated angular glass fragments surrounded by an amorphous palagonite matrix plus nano-crystalline oxide phases (**Figure 10**). Many glass fragments have alteration rims where the glass has begun breaking down along clast boundaries. In sample ASK04, larger glass clasts are typically highly vesicular (**Figure 11A**). Secondary mineral alteration in all three hyaloclastites does not extend beyond palagonitisation. Zeolites and any other secondary phases are not seen. Pillow lava KV02 is typified by large (2 -4 mm) plagioclase phenocrysts, surrounded by a fine-grained groundmass of fine plagioclase laths (**Figure 11B**). However there are no signs of aqueous or hydrothermal alteration within this lava. Finally, pillow lava ASK09 is dominated by a fine-grained groundmass primarily made up of small (approx. 10 x 100 µm) plagioclase laths, typical of rapidly-cooled lava. This lava is vesicular (**Figure 11C**), with vesicles entirely or partially in-filled with secondary alteration minerals (**Figure 11D**), including iron oxides, silica, and sulphates (**Figures 11E, F, & G**), representing subglacial hydrothermal alteration of the lava following emplacement beneath the ice.

Despite the widespread occurrence of bioalteration textures in oceanic basaltic lavas (Furnes *et al*., 2007; McLoughlin *et al*., 2009), none were identified in either of these pillow basalts. 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, and the samples from Askja and Kverkfjöll are consistent with this.

Major element composition of glass fragments and rims within the hyaloclastite and pillow lava samples (**Table 3)** show compositions to be typically basaltic, with SiO_2 content ranging from 48.60 (KV02) to 52.33 wt. % (ASK07). On a Total Alkali – Silica (TAS) classification plot (**Figure 12**) these samples plot alongside martian surface measurements and rocks, lying between basaltic and basaltic andesite in composition.

Table 3. Major element analysis of glass clasts and glass rims of volcaniclastics and pillow lavas from Askja and the fissure swarm. Values are given as means with 1σ standard deviation.

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	ASK03	ASK04	ASK07	ASK09	KV02	KV07
	n= 27	n= 33	n= 20	n= 10	n= 23	n= 26
SiO_2	50.0 (±2.2)	50.6 (±0.9)	52.3 (±0.5)	51.8 (±1.1)	49.1 (±0.8)	50.0 (±0.8)
TiO_2	2.7 (±0.2)	2.4 (±0.2)	3.6 (±0.2)	2.6 (±0.2)	3.1 (±0.2)	2.9 (±0.2)
Al_2O_3	13.6 (±0.6)	13.4 (±0.7)	13.3 (±0.2)	13.6 (±0.8)	13.0 (±0.3)	12.8 (±0.6)
FeO	14.4 (±0.6)	14.1 (±0.3)	15.0 (±0.5)	14.8 (±1.5)	14.4 (±0.7)	14.7 (±1.3)
MnO	0.2 (±0.1)	0.2 (±0.1)	0.2 (±0.1)	0.2 (±0.1)	0.25 (±0.1)	0.2 (±0.1)
MgO	5.6 (±0.5)	5.3 (±0.2)	4.3 (±0.1)	5.4 (±0.6)	4.5 (±0.4)	4.9 (±0.7)
CaO	10.2 (±0.6)	9.5 (±0.2)	8.5 (±0.3)	9.9 (±0.3)	9.5 (±0.5)	9.8 (±1.0)
Na_2O	2.7 (±0.2)	2.6 (±0.2)	3.0 (±0.2)	2.9 (±0.3)	3.1 (±0.2)	2.9 (±0.3)
K_2O	0.4 (±0.1)	0.6 (±0.1)	0.8 (±0.1)	0.5 (±0.1)	0.7 (±0.1)	0.6 (±0.2)
SO_3	0.4 (±0.1)	0.4 (±0.1)	0.3 (±0.1)	0.3 (±0.1)	0.5 (±0.1)	0.3 (±0.1)
Total	*100.6 (±1.7)*	*99.3 (±1.3)*	*101.4 (±0.8)*	*102.1 (±0.7)*	*98.3 (±1.1)*	*99.2 (±1.2)*

4.3 Water chemistry at Hverdalur, Kverkfjöll

Environmental parameters measured in situ and dissolved ion chemistry of aqueous environments at the Hverdalur geothermal field are given in **Table 2**. Aqueous chemistry and *in-situ* measurements of hot spring pools and steams, and the lake itself, show the system to be dominated by dissolved sulfate (up to 227.3 mg/l), with gradients of dissolved oxygen (<1 - 10.4 mg/l DO), and temperature (3.0 - 53.2 °C along a stream gradient). 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 4**). Despite the basaltic composition of the host rocks and geothermal activity, aqueous environments were typically low in dissolved Fe^{2+}, due to the low temperatures (< 50 °C) of many of the environments (see **Table 2**). Typically highly mobile cations such as Si, Na, Ca, Mg, and K make up the remaining bulk of the dissolved load after sulfate, sourced from the underlying local basaltic bedrock, buffering pH.

4.4 Mineralogy

Mineralogical compositions of the lavas and geothermal sediments from Kverkfjöll and the fissure swarm were determined by XRD and/or Raman spectroscopy, and SEM imagery, and are given in **Table 4**. **Figures 13 - 15** show XRD patterns of bulk, homogenised sediments from Hveratagl, Hveradalur (including VNIR spectral targets), and the fissure swarm lavas. Crystalline pillow lava samples from sites KV02 and KV07 are dominated by peaks for primary basaltic minerals pyroxene and plagioclase (**Table 3**), as is the bulk unaltered component of sample KS03 (a tuff, see **Table 1**) from Hveradalur. **Figure 16** shows Raman spectra of white mineral deposits within the vesicles of pillow lava KV07, which are identified as gypsum. The surface alteration of KS03 and the biomat 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 samples, and it's possible other mineral species are also present. **Figure 16** 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.

Overall sample alteration and hot spring sediment samples divide into two groups. Those dominated by amorphous palagonite, nanocrystalline oxides and smectite authigenic secondary phases represent low-temperature (<120 °C) aqueous alteration (Stroncik & Schmincke 2002), which typically would have occurred beneath the ice prior to glacial retreat. This group is populated entirely by the volcaniclastic hyaloclastite and hyalotuff samples from Askja. These amorphous phases are difficult to detect using standard XRD techniques (Bishop *et al*. 2002), and their presence is identified from thin section (**Figure 11**). The second group comprises of higher-temperature (>120

°C) alteration and secondary minerals, predominantly zeolites, sulphates, and pyrite. Geothermal sediments, fumarole deposits, and hot spring sediments from Hveradalur and Hveratagl all fall within this group, and vary in their individual mineralogical composition (see **Table 4**). Heulandite (Ca/Na zeolite), smectite (Fe/Mg phyllosilicates), and alunogen (Al sulfate) are especially prevalent in sediments from fumarole mounds, geothermally altered soil, and hot spring sediment. Other alteration minerals identified include gypsum, quartz, sulfur, jarosite, and pyrite. Pyrite is limited to environments that presumably are, or were, anoxic at the time of its precipitation. Certainly this is true of samples from Site 4 and Site 8 (see **Table 2**) where the dissolved oxygen was <2 mg/l.

4.5 VNIR reflectance spectra

Within the context of martian rover exploration, Vis-NIR reflectance spectroscopy often provides the first putative composition and mineralogy of a nearby outcrop or target region, via VNIR multispectral imaging. Panoramic cameras on the NASA Mars Exploration Rovers, NASA Mars Science Laboratory, and ESA ExoMars 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).

4.5.1 *In situ* measurements

For *in-situ* measurements, two regions at the Kverkfjöll Hveradalur geothermal field were targeted: 1) a dried-up hot spring stream bed and 2) an area of geothermal altered ground. The first lies within the mapped geothermal area (**Figure 7)**, and was originally sourced by an overflowing spring (**Figure 18A+B**). Current ground temperatures for this dried stream bed ranged from 50.6 - 67.2°C for various points around the site, and 32.2 (±1.64) °C at the spring source itself. In-situ VNIR (350 – 1000nm) 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 (see **Figure 7**), informally termed the "Mars Site", and this formed the second site at which in-situ VNIR reflectance spectra were obtained (**Figure 18A**).

Reflectance spectra of targets along the dried-up stream show chlorophyll *a* (670nm) and bacteriochlorophyll (865nm) absorption bands within the spectra (**Figures 19C + D**), either from desiccated biomats that would have been present along the hydrothermal stream floor when it was last active, or any microbial population currently present. In spectral targets 9A-C, a broad iron absorption centred at 900nm 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 sulphates, with absorptions at 500, 650, and 950 nm (**Figures 19A and B**). XRD analysis indicates these soils are zeolite and sulphate-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 - 1100nm 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. As operational decisions for rovers on Mars will be initially dependent upon multispectral imaging, it is important to understand the discrepancies between these two techniques.

4.5.2 Laboratory reflectance spectra

Reflectance spectra in the 400 - 1000nm range were acquired in-situ from surface targets, and in the laboratory of crushed, homogonized samples. Reflectance spectra of powdered geothermal soils, lavas, and volcaniclastics fall into 4 spectral categories (**Figure 20**); those with a broadly featureless basaltic and palagonitic/nano-crystalline ferric oxide spectrum, those dominated by a bright, flat, sulphur reflectance with a steep absorption edge in the blue, those with ferric iron absorption features at 500, 650, and 900nm, and lastly those with a ferric iron absorption at 900nm and chlorophyll absorptions at 670nm and 830nm. The four types represent the variety and degree of hydrothermal alteration within volcano – ice environments at Askja and Kverkfjoll, which are very much dictated by localised conditions.

5. Discussion

5.1 Fingerprint for environmental conditions

Sediments, lavas, and volcaniclastics at Kverkfjöll and Askja can be used to infer palaeoenvironmental conditions. They therefore provide lithological analogues for testing both rover instrumentation and their subsequent data products in their ability to detect evidence of liquid water and potentially "habitable" environments (summarised in **Table 5**). Similarly, the mineralogical composition of these sediments can provide an insight into the subsurface hydrothermal environment within the subglacial volcanic system. Pillow lavas from Askja (ASK09) and the fissure swarm (KV02, KV07) provide evidence of subsurface liquid water by their distinctive pillow morphology, indicative of rapid quenching of erupting basaltic lava. Pillow lava ASK09 shows extensive hydrothermal deposition of secondary minerals within vesicles, which based on their elemental composition are likely to be a combination of opaline silica, jarosite, and iron oxide (see **Figure 11**). Similarly, gypsum deposits within the vesicles of pillow lava KV07 indicate subsurface circulation of hydrothermal fluids in and around the pillow pile (Storrie-Lombardi *et al*. 2010). Both these sample sites currently exist within a cold volcanic desert, and this hydrothermal alteration therefore is likely to have occurred whilst the warm pillows were still beneath the glacier or meltwater they had erupted into. Such hydrothermally-driven subsurface environments would be ideal havens for life within a subglacial volcanic system. Conversely, pillow lava KV02 shows no such hydrothermal activity or alteration. Aside from the initial eruption into ice or a subsurface meltwater lens, there is no evidence for sustained liquid water activity. Volcaniclastic deposits at Askja (ASK03, ASK04, ASK07) were found to be dominated by palagonite alteration products, which result from low-temperature (<120 °C) aqueous alteration of basaltic glass (Stroncik & Schmincke 2002). As with the pillow lavas, this alteration is likely to have occurred when these deposits were still beneath the ice, being altered by cooler circulating hydrothermal fluids and/or meltwater. However, basaltic glass easily breaks down in the presence of water, and it's also possible that this alteration is a continual process occurring today through the action of meteoric water.

Unconsolidated sedimentary deposits at Kverkfjöll are comprised of proglacial jökulhlaup deposits, and geothermal sediments deposited in-situ at the hydrothermal fields around the Kverkfjöll summit. Jökulhlaups produce distinctive depositional and erosional features (Marren et al. 2009) and are analogous to flood deposits identified on Mars (Warner & Farmer 2010). They are of astrobiological interest due to the release of subsurface material and water to the surface (Cousins & Crawford 2011), and the evidence for hydrothermal activity they contain through alteration mineral assemblages (Warner & Farmer 2010). Bodies of water produced both during, and between, volcanic eruptions can be either released after a short period of time, such as was seen at Grimsvötn following the Gjálp eruption in 1996 (Gudmundsson et al. 1997), or maintained as a relatively stable lake (Björnsson 2002). The latter is of significant astrobiological interest, as a stable, hydrothermally-sourced body of liquid water can provide a unique environment for microorganisms. Indeed this is observed to be the case for two such subglacial caldera lakes in Iceland (Gaidos et al. 2008; Gaidos et al. 2004). The geothermal sediments at Hveradalur and Hveratagl, Kverkfjöll are largely indicative of acidic-neutral hydrothermal alteration of basaltic material. Hydrated alteration minerals including heulandite (zeolite) and smectite form a common component to the samples studied (see **Table 4**), as do the sulphates jarosite and gypsum. Such minerals have been widely identified on Mars, with sulfate and phyllosilicate terrains highlighted as suitable astrobiological targets (Wray et al. 2009; Michalski et al. 2010). The palaeoenvironments of some of these terrains are difficult to ascertain from orbital data alone, but analogues on Earth (such as Kverkfjöll) can provide a means to establish the suitability of volcano – ice environments to support life. Fumarole environments such as those at Sites 10, 11, and 20 for example represent some of the more 'extreme' environments within volcano - ice systems, yet similar fumarole environments are commonly inhabited by a specialised population of thermophillic and/or acidophilic bacteria and archaea (*e.g*. Dopson & Johnson 2012; Benson et al. 2011).

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, and indeed this was observed to be the case with the well-documented hydrothermal alteration at Surtsey, Iceland (Jakobsson & Gudmundsson 2008). Overall, hydrothermal environments at Askja and Kverkfjöll represent two distinct thermal environments. A low-temperature environment (<120 °C), is characterised by those samples dominated by palagonite alteration, as well as sulphate, iron oxide, and smectite secondary alteration products (Stroncik & Schmincke 2002). This is typical as basaltic glass easily alters to opal, smecitite, zeolites, and clays (Browne 1978). Askja samples ASK03, ASK04, ASK07, ASK09, and fissure swarm sample KV07 fall within this range. 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°C (Jakobsson & 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 & Gudmundsson 2008).

A higher temperature environment (>120 °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 & 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 such as gypsum and jarosite. Higher temperature minerals such as chlorite (>230°C), epidote (>260°C), and amphibole (>280 °C) (Browne 1978) are not identified. **Figure 21** 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. However, the formation of pyrite may be primarily controlled by biogeochemical sulphur cycling, as discussed in the following section.

5.2 Biogeochemical pathways at Hverdalur and Hveratagl, Kverkfjoll

Sulfur cycling is likely to be a significant biogeochemical process within the hydrothermal environments at Kverkfjöll, and potentially may form the basis of many metabolic reactions amongst the residing biota. Abiogenic S is delivered to these environments primarily via elemental S^0 condensed from SO_2 and H_2S, and H_2S and SO_2 gas input into aqueous environments (pools and lakes). Given the temperature and pH range of the hydrothermal environments at Kverkfjöll (**Figure 4**), mesophilic (20 - 40 °C), moderate thermophilic (40 - 60 °C), and thermophilic (<60 °C) acidophiles are expected to be active at Kverkfjöll. Nearly all sulfur-metabolizing thermophiles are crenarchaeotes, whilst sulfur-metabolizing mesophiles are exclusively bacteria (Dopson & Johnson 2012). Sulfur metabolizers also vary in terms of carbon assimilation, including obligate autotrophs, heterotrophs, and facultative autotrophs/heterotrophs (Dopson & Johnson 2012). Therefore there is the potential for a wide range of sulfur -metabolising bacteria and archaea to be supported by the volcanic environments found at Kverkfjöll. Indeed, well-developed biomats were observed (**Figure 22)**, two of which were associated with a thin crust of pyrite (Site 8, also see **Figure 17D**) and goethite (Site 6, also see **Figure 17E**) respectively, suggesting the importance of S- and Fe-biogeochemical cycling and subsequent biomineralization. Photosynthetic green and pink biomats were also observed (**Figure 22**), presumably exploiting the long daylight hours (~20 hours in June) present at Kverkfjöll during the summer.

Pyrite is also common to many geothermal soils and anoxic pool sediments, and is likely a product of both the biological reduction of dissolved sulphate (which dominates dissolved water chemistry) and abiotic reaction of H_2S with dissolved Fe^{2+}. This H_2S can also be subject to oxidation by sulphur oxidizing bacteria. Such oxidation of reduced sulfur species typically leads to the acidification of the local environment due to the production of sulphuric acid (e.g. $S^0 + H_2O + 1.5\ O_2 \rightarrow H_2SO_4$; Dopson & Johnson 2012). Sulfate present in aqueous environments can be utilised by sulfate reducing bacteria, although probably not in the most acidic environments (pH <3; Dopson & Johnson 2012). In-depth metagenomic analysis of these environments would reveal the extent that sulphur has a metabolic control on the residing biota within the environments at Kverkfjöll. It appears that sulphur-driven metabolism would be a feasible mechanism for sustaining microbial life within glacial hydrothermal environments, should similar processes have existed on Mars in the past. As such, biosignatures relating to sulphur metabolism (*e.g.* sulphur stable isotope signatures, biomineral morphologies) could be a particular target when exploring these environments.

5.3 Detection of volcano – ice environments on Mars

As argued above (see also Cousins & Crawford 2011; Warner & Farmer 2010; Schulze-Makuch et al. 2007) regions of volcano – cryosphere interaction on Mars are strong candidates for identifying near-surface evidence for past life. Evidence of volcano – ice interaction specifically occurs on a number of scales, from large-scale topographic and geomorphological features such as fissure swarms and flood erosion/deposits, to distinctive lithofacies within the rock record (pillow basalts, volcaniclastics), and finally hydrothermal alteration minerals and secondary mineral deposits. In this work, hydrothermal environments that are both currently active (*e.g*. geothermal environments at Kverkfjöll), and preserved (*e.g*. secondary hydrothermal mineral deposition in subsurface pillow basalts, as at Askja and the fissure swarm) have been explored. The combination of a variety of instrumental techniques (XRD, Vis-NIR spectroscopy, thin section petrology, Raman spectroscopy, SEM, EDS) together with field observations has been used to characterise the geology and habitability of these environments. However, in the context of Mars exploration, a robotic rover will only be able to deploy a sub-set of these techniques in a given area. Moreover, it will do so sequentially, with multispectral imaging being used to identify promising outcrops for analysis with remote and contact/analytical instruments such as Raman, XRD, Laser-Induced Breakdown Spectroscopy, and X-ray fluorescence spectroscopy. 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*. Stern et al. In Press; Steele et al. 2006). In the specific case of identifying regions of past volcano – ice interaction, the Kverkfjöll – Askja region of Iceland is one such locality.

6. Conclusions

The Kverkfjöll and Askja volcanic systems and their associated geothermal environments and sedimentary deposits provide a wealth of understudied geological 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 - neutral pH, low - high temperature, and anoxic - oxic. Associated mineralogical alteration assemblages that are analogous to those present on Mars include zeolites (heulandite/clinoptilolite, ferrierite), sulphates (gypsum, jarosite, alunogen), iron oxides (goethite), and smectite clays (montmorillonite, saponite). Likewise, the basaltic rock units (hyaloclastite, hyalotuffs, pillow lavas) and jökulhlaup sedimentary deposits provide a lithological fingerprint that is highly characteristic of a basaltic volcano - ice interaction environment. Previous work investigating the microbiology of subglacial volcanic environments beneath Vatnajökull has shown these volcanic systems to support specialised microbial communities (Gaidos et al. 2004, 2008). The wide diversity of hydrothermal environments at Kverkfjöll provide a valuable, and as yet not fully-explored, range of volcano - ice interaction 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 will potentially 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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8. References

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