

HYDROGEN PRODUCTION FROM MECHANICALLY-ACTIVATED BASALT UNDER
EXPERIMENTAL CONDITIONS SIMULATING SUBGLACIAL ENVIRONMENTS

by

Kari Rebecca Mitchell

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Earth Science

MONTANA STATE UNIVERSITY
Bozeman, Montana

May 2019

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ACKNOWLEDGEMENTS

Thanks to:

My family, for not having a clue what I'm doing but nodding enthusiastically anyway.

Aubrey Davis, Danette Perez, Dominique Ong, Merissa Strawsine, Taylor Barron, Colleen

Pennington, Jason Gablaski, Mike Gallant, Shannon Mazzei, Richard Frieze, Genne

Nelson, and the whole Death Valley crew, for being simply amazing.

Jacob Gardner, for all the adventures and sloth pictures.

Jordan Allen, for always lending an ear to listen.

Eric Dunham, for his continued good humor throughout this project.

LeaAnne Harbour, for believing in me far more than she should and for being the type of woman who inspires others by simply being herself.

Sandy Underwood, for being an absolute rockstar and for her eternal optimism and good cheer in the face of adversity.

Mary Hubbard, for her strength and wisdom.

My advisor, Mark Skidmore.

My committee members, Jean Dixon and John Dore.

NASA Exobiology grant NNX16AJ64G to PI Skidmore, for funding this project.

And finally,

My cat, Jasper, for ensuring I get up every morning, earlier than I'd like.

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ABSTRACT

Shearing of rocks containing silicate followed by reaction with water has previously been shown to produce hydrogen under experimental conditions relevant to subglacial environments. The abiotic production of hydrogen, carbon dioxide, methane, and other hydrocarbon gases has also been demonstrated in laboratory comminution experiments on rocks from glaciated catchments. Thus, the generation of these biologically useful gases (e.g. hydrogen and methane) beneath glaciers could serve as a source of reductant capable of sustaining microbial ecosystems beneath the ice. Despite the ubiquitous nature of basalt on both Earth and other planetary bodies, production of hydrogen and other gases from basalt through mechanical shearing and reaction with water has not been demonstrated. Basalts were collected from glaciated catchments in Iceland to test whether hydrogen and other gases were produced under laboratory conditions simulating glacial comminution. Rock samples were milled under an inert atmosphere, after which water was added and hydrogen and methane production measured over time. An average of 6.6 nmol hydrogen and 2.6 nmol methane per gram rock were produced after 168 hours from basalt samples tested; additionally, hydrogen peroxide and radicals were produced during grinding. The abiogenic production of hydrogen and methane under these simulated subglacial basaltic environments demonstrated in this study also has implications for supporting subglacial microbial communities during periods of extended glaciation, such as glacial-interglacial cycles in the Pleistocene and during the pervasive low-latitude glaciation of the Cryogenian. This mechanism of hydrogen production also has implications for the potential for life on icy worlds like Mars.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

Introduction

Over the past two decades a significant body of literature has been published on diverse and active subglacial microbial communities in a range of glacial systems worldwide, from small valley glaciers to large ice sheets such as Greenland and Antarctica (Skidmore et al. 2000; Skidmore et al. 2005; Christner et al. 2006; Christner et al. 2008; Hodson et al. 2008; Yde et al. 2009; Lanoil et al. 2009; Boyd et al. 2010; Boyd et al. 2011; Stibal et al. 2012; Hamilton et al. 2013; Boyd et al. 2014a; Christner et al. 2014; Achberger et al. 2016; Michaud et al. 2017; Lamarche-Gagnon et al. 2019). Recently, the abiotic production of hydrogen gas from mechanical activation of silicate rocks under simulated subglacial conditions was demonstrated experimentally; these results suggest that hydrogen production from this mechanism may be sufficient to support hydrogenotrophic subglacial microbial communities (Telling et al. 2015). Hydrogen produced via this mechanism affirms the possibility of subglacial environments acting as reservoirs of biodiversity during periods of increased glacial cover and has implications for the potential for life on icy worlds (Tranter 2015). An abiotic mechanism for hydrogen production provides a potential energy source to sustain these subglacial microbial ecosystems over periods of long-lasting glaciation such as during the Neoproterozoic (635-542 Ma), when the Earth entered a period called “Snowball Earth” when it has been

argued that pervasive low-latitude glaciation existed (Hoffman et al. 1998; MacDonald et al. 2010). Subglacial environments also represent potential microbial habitats on Mars, (Skidmore et al., 2000) that would be protected from the current cold, dry, and oxidizing surface conditions (Cockell et al. 2011). Despite the abundance of basalt on Earth and planetary bodies of astrobiological significance, like Mars, hydrogen production from mechanically activated basalt was not tested by Telling et al. (2015). This thesis fills that knowledge gap by quantifying the production of hydrogen gas from mechanically-activated basalt and basaltic minerals under simulated subglacial conditions in the laboratory. To address this question, basaltic bedrock and sediments were collected from Icelandic glaciated catchments and hydrogen production was experimentally determined by grinding these samples in a mill and then incubating the powders in a cold (2°C) and wet environment. Bedrock and sediments from Icelandic glaciated systems were targeted since these provide good potential analogues for Martian environments capable of supporting life (Cousins and Crawford 2011; Cousins 2015). Further, a parallel research project was also conducted at these field sites characterizing their microbiology, and data from this thesis would be informative for that project.

Literature Review

Glacial Hydrology

The flow of water beneath glaciers affects glacier movement and the occurrence of glacial outburst floods, which strongly affect solute fluxes and impacts weathering

rates (Fountain and Walder 1998; Björnsson and Pálsson 2008). Volcanism beneath ice also affects biogeochemical weathering processes and solute flux, by introducing large quantities of meltwater during eruptions and generating volcanic gases, like carbon dioxide and sulfide dioxide during venting (Kristmannsdóttir et al. 2002). The hydrology of glaciers is thus important to understanding the subglacial environment.

Glaciers form when the rate of snowfall accumulation is greater than the rate of ablation over many years and the weight of the accumulated snow results in the recrystallization of buried layers first into firn and then into glacial ice (Benn and Evans 2010). Most of the ice masses in Iceland are icecaps, as they are unconfined by underlying topography; however, the outlet glaciers are topographically confined (Björnsson and Pálsson 2008; Benn and Evans 2010). The icecap beds exist mostly below the modern-day glaciation limit in Iceland, with only 10-20% of the ice cap beds existing above the limit (Björnsson and Pálsson 2008). The vast majority of the ice masses in Iceland consist of temperate ice (i.e. ice at the pressure melting point) at the glacier bed (Björnsson and Pálsson 2008).

Liquid water moves through icecaps and glaciers through a glacial drainage system (Figure 1.1) (Hodson et al. 2008; Benn and Evans 2010). The hydrologic drainage systems of icecaps likely change from the central portion of the icecap to the outlet glaciers draining the margin (Benn and Evans 2010). Water can flow through supraglacial, englacial, and subglacial pathways and move between the different pathways (Hodson et al. 2008; Benn and Evans 2010). The following review is focused

primarily on subglacial drainage systems. Supraglacial and englacial water can enter the subglacial drainage system through moulins and crevasses in the ice (Hodson et al. 2008; Benn and Evans 2010). In temperate ice masses, such as the Icelandic icecaps, the glacier bed is at the pressure melting point, providing additional liquid water to the subglacial drainage system from melting of basal ice (Björnsson and Pálsson 2008; Hodson et al. 2008). Water flows through the subglacial system either in channelized systems or distributed systems (Fountain and Walder 1998). In a channelized system, channels formed by incision either down into the bedrock or up into the ice serve as the main pathways for basal water movement (Benn and Evans 2010). In contrast, in a distributed system, water exists in water films between ice and rock, in networks of linked cavities or canals, and may move as groundwater flow (Benn and Evans 2010). Both systems may exist within a single icecap (Benn and Evans 2010). At the outlet glaciers relevant to this project, there is at least one main channel through which the subglacial hydrological system ultimately drains.

The Icelandic icecaps, except for Drangajökull, are underlain by areas of geothermal activity which influences the hydrology (Björnsson and Pálsson 2008). Jökulhlaups, or glacial outburst floods, occur periodically from the icecaps from geothermal activity, volcanic eruptions, and ice dam failure of subglacial lakes (Kristmannsdóttir et al. 2002; Björnsson and Pálsson 2008). These catastrophic floods increase river sediment loads and are largely responsible for the deposition of the sandur formations (Björnsson and Pálsson 2008). Geothermal activity and volcanic

activity also alter meltwater chemistry by volcanic out-gassing and magmatic fluid interaction (Kristmannsdóttir et al. 2002). The outlet glaciers of Drangajökull, Kaldalónsjökull and Leirufjarðarjökull are surging glaciers (Brynjólfsson et al. 2014; 2015b; Ingólfsson et al. 2016). To initiate surging, it has been hypothesized that glaciers must have large volume of water at the glacier bed (Walder 1982). Surges can move substantial amounts of ice out of accumulation areas and into ablation areas (Björnsson and Pálsson 2008) and surges increase erosion rates (Humphrey & Raymond 1994). For most Icelandic glaciers, these surges last for several months but at Drangajökull, observed surges have lasted up to five years (Brynjólfsson et al. 2014). Sediment loads from jökulhlaups may move up to five orders of magnitude more sediment than surges and normal load transport (Björnsson and Pálsson 2008).

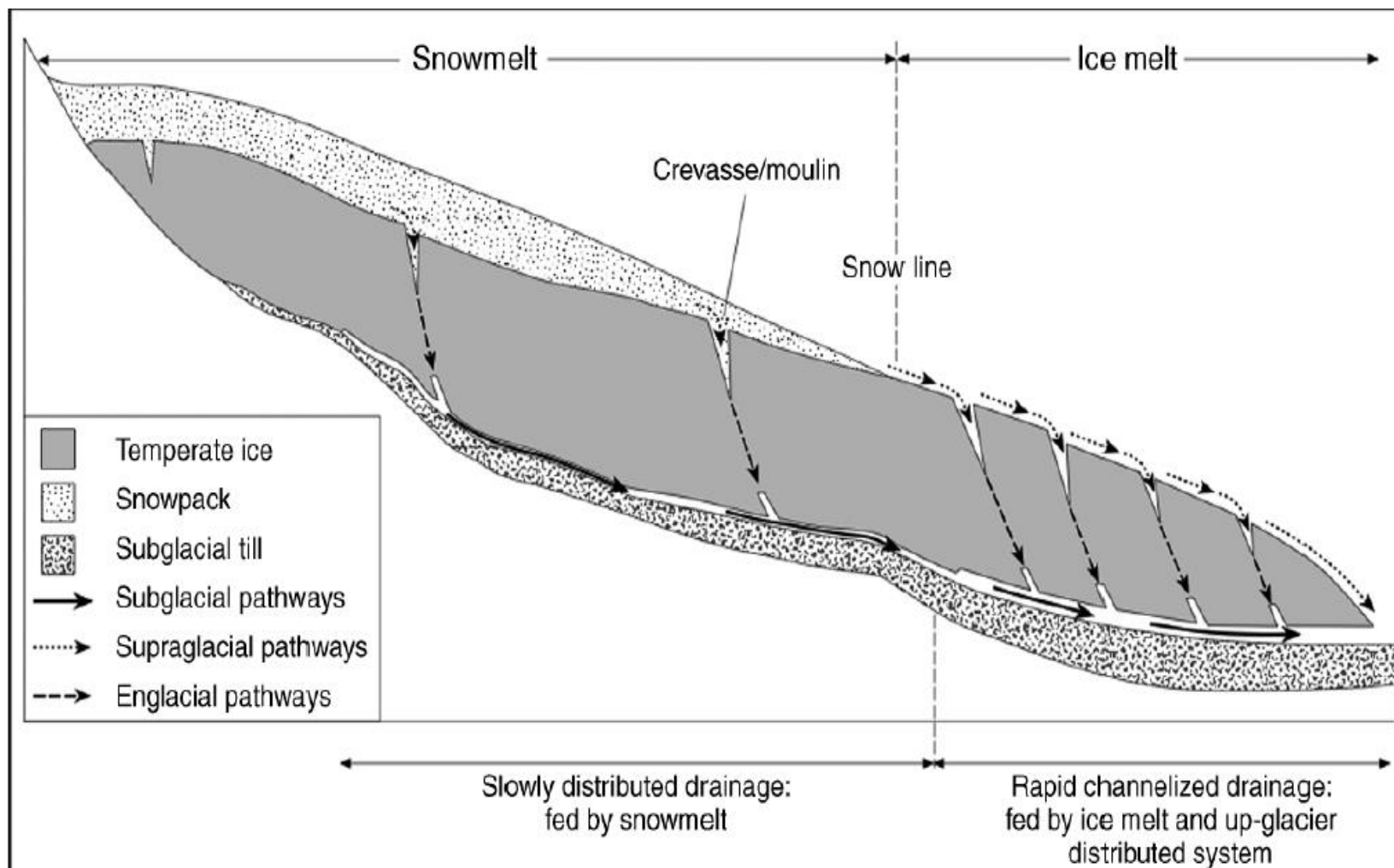


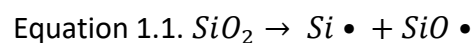
FIGURE 1.1. A generalized glacier drainage system, for a temperate valley glacier (Hodson et al. 2008). © John Wiley and Sons. Reprinted with permission.

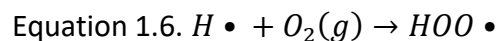
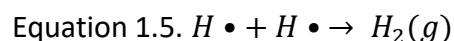
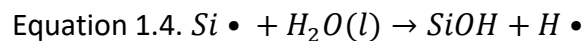
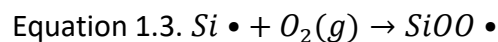
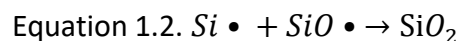
Water-Rock Interactions Produce Hydrogen and Hydrogen Peroxide

Physical erosion at temperate glaciers drives silicate weathering by increasing the available reactive surface area (Anderson 2005). This physical erosion generates biologically-relevant gases and nutrients that can sustain microbial communities (Telling et al 2015; Macdonald et al 2018).

Microbial activity at water-rock interfaces in subglacial systems may be sustained by chemolithotrophic metabolisms such as the oxidation of reduced sulfur and iron present in minerals (Lanoil et al. 2009; Boyd et al. 2014). The abiotic production of hydrogen gas is of interest as this provides an energy source for life in the absence of light, a condition that exists beneath terrestrial glaciers and ice masses (Murray et al. 2012; Stibal et al. 2012) and exists on other planetary bodies (Cockell et al. 2011). Hydrogen can be sourced from: volcanic gas (Cadle 1980), reactions in fault zones (Kameda et al. 2003; Sugisaki et al. 1983), serpentinization (Russell et al. 2010; Stevens & McKinley, 2000), dry crushing of silicate rocks (Macdonald et al. 2018), and shearing of silicate rocks coupled with reaction of anoxic water (Telling et al. 2015).

Shearing of silicates results in the homolytic cleavage of the $\equiv\text{Si-O}$ bonds of silica caused by mechanical activation of the silicate (Equation 1.1) (Narayanasamy & Kubicki 2005; Delogu 2011; Telling et al. 2015). This results in the formation of silyl, $\equiv\text{Si}\bullet$, and siloxyl, $\equiv\text{Si-O}\bullet$, radicals (Delogu 2011).





These radicals can then react with each other to reform the silica bond (Equation 1.2) (Delogu 2011), with oxygen to form peroxides (Equation 1.3) (Damm and Peukert 2009), or with water to form silicon-hydroxyl and hydrogen (Equations 1.4 and 1.5) (Narayanasamy and Kubicki 2005; Delogu 2011; Telling et al. 2015). Reaction of hydrogen radicals with oxygen can also produce hydrogen peroxide (Equation 1.6) (Damm and Peukert 2009). Telling et al. (2015) demonstrated that the reaction of mechanically activated silicates with water produces hydrogen under cold (0°C), simulated subglacial conditions, in the laboratory. Basalt was not one of the rock types tested in the Telling et al. (2015) study, despite having relatively high silica content and being abundant on both Earth and other planetary bodies of interest, such as Mars. Given the proposed reaction mechanism, it seems likely that basalt would produce hydrogen as 2°C after crushing and wetting. Interestingly, the reaction may not be dependent on the silica content of the rock and may be influenced by the specific mineralogy of the sample: Telling et al. (2015) found that a schist (17.7 molar % Si) produced hydrogen at rates greater than the tested quartzite (23.2 molar % Si). This is in

agreement with findings from Macdonald et al. (2018) who found that as the abundance of mica in a sample increased, the production of hydrogen increased. Additionally, Telling et al. (2015) determined that hydrogen production was positively correlated to the reactive surface area. The abrasion of silicates from saltation (Bak et al. 2017) and crushing of basaltic minerals (Hurowitz et al. 2007) under dry conditions also resulted in the production of hydrogen peroxides under laboratory conditions. It has been hypothesized that the production of hydrogen peroxides through mechanical activation may partially explain the oxidizing nature of Martian soil (Bak et al. 2017).

The potential for other elements, such as iron, to affect the reaction have not been studied in depth; however, discrepancies in hydrogen production between biotite and muscovite indicate that the presence of iron(II) may decrease the amount of hydrogen produced during wet grinding (Kameda et al. 2004). Stevens and McKinley (2000) found the opposite: increasing concentrations of Fe(II) in solution corresponded to increasing hydrogen production from crushed and wetted basalt at 30-60°C.

The hydrogen production from mechanical activation and subsequent wetting of silicates is estimated to be sufficient to support hydrogenotrophic subglacial microbial communities (Telling et al. 2015). Bacteria capable of utilizing hydrogen appear to have evolved early on in Earth's history (Vignais and Billoud 2007; Boyd et al. 2014b) and previous work has demonstrated the likely presence of hydrogen-utilizing bacteria in subglacial environments (e.g. Stibal et al. 2012; Telling et al. 2015). Hydrogenotrophic

bacteria can utilize abiotic hydrogen, carbon monoxide, and carbon dioxide, to produce methane in the process of methanogenesis (Boyd et al. 2014b).

Potential Habitable Zones in Subglacial Systems on Mars

Glaciovolcanism the interaction of volcanoes and ice, has occurred on both Mars and Earth; on Earth, the environments created by glaciovolcanism support life (Cousins et al. 2013). Life beneath glaciers also exists in the absence of volcanism (Skidmore et al. 2000; Skidmore et al. 2005; Christner et al. 2006; Christner et al. 2008; Hodson et al. 2008; Yde et al. 2009; Lanoil et al. 2009; Boyd et al. 2010; Boyd et al. 2011; Stibal et al. 2012; Hamilton et al. 2013; Boyd et al. 2014a; Christner et al. 2014; Achberger et al. 2016; Michaud et al. 2017; Lamarche-Gagnon et al. 2019) suggesting that the subglacial environment of other planetary bodies may be habitable as well (Skidmore et al. 2000; Price 2007). By studying subglacial environments on Earth, we can better understand potential habitable environments on Mars (Price 2007; Cousins et al. 2013). The early climate of Mars was likely warmer and wetter than modern surface conditions (Arvidson 2016; Jakosky et al. 2017). Geomorphological evidence of water-formed features on the Martian surface (Johnsson et al. 2014), mineralogical evidence of hydrated minerals and minerals that form in aqueous environments (Bibring et al. 2006), and evidence for an atmosphere once thick enough for the maintenance of liquid water (Jakosky et al. 2017) indicate that the early Martian surface was potentially similar to early Earth's surface. Additionally, the presence of a near-global cryosphere of permafrost and widespread volcanism throughout much of Martian history indicates volcano-ice interactions were

likely (Carr and Head 2010). Mineralogical evidence has demonstrated the presence of features most likely formed as a result of subglacial volcanism at Sisyphe Montes (Ackiss et al. 2018) and other localities have been identified, based on geomorphology, as possible regions of glaciovolcanism (Allen 1979; Ghatan and Head III 2002; Scanlon et al. 2014), including potential glacial outburst flood deposits (Cousins and Crawford 2011). Subglacial volcanism provides large quantities of liquid water and fresh mineral material, creating potential habitats for life just as subglacial volcanism on Earth does, in particular in Iceland (Gaidos et al. 2004; Gaidos et al. 2009; Cousins and Crawford 2011; Marteinnsson et al. 2013; Ackiss et al. 2018).

Given the possibility of a warmer and wetter Mars during the Noachian and possibly the early Hesperian and likely glaciovolcanism throughout significant portions of Martian history, there exists the possibility that life could have evolved during the late Noachian or early Hesperian (Bibring et al. 2006; Cousins and Crawford 2011), during the same time period when life on Earth first formed (Dodd et al. 2017). It is possible that such microbial life could survive today on Mars, protected in some subglacial reservoir (Price 2007).

Cryospheric environments on Mars, including regions of glaciovolcanism, provide potential microbial habitats (Smith and McKay 2005; Price 2007; McKay 2010; Cockell et al. 2011; Cousins and Crawford 2011; Cousins et al. 2013). Thin films of liquid water can exist at the beds of ice masses (Weertman and Birchfield, 1983) and around entrained rock grains (Price 2007), and substantial volumes of water can exist in subglacial lakes

(Wright and Siegert 2012); these environments all support life presently on Earth (Wadham et al. 2004; Skidmore et al. 2005; Marteinson et al. 2013; Montross et al. 2013; Christner et al. 2014; Achberger et al. 2016; Michaud et al. 2017). Mars has a thick cryosphere with the majority of water frozen at the poles and as a permafrost mantle at mid- to high latitudes (Bibring et al. 2006; Christensen 2006). A potential subglacial lake was recently identified at the south pole of Mars (Orosei et al. 2018) though additional research would be necessary to verify this remotely based inference. It has been hypothesized that subglacial environments on Earth may have generated conditions favorable for microbial communities to survive the period of “snowball Earth” during the Neoproterozoic (Telling et al. 2015). The polar ice caps on Mars, then, could offer potential areas of refuge for life now that the atmosphere is degraded and the surface no longer conducive to life (Lasne et al. 2016; Jakosky et al. 2017).

Iceland’s basaltic bedrock overlain by ice caps and the frequent interaction of volcanism and ice present an opportunity to study how volcano-ice interactions support microbial ecosystems (Gaidos et al. 2004; Gaidos et al. 2009; Cousins et al. 2013) and how subglacial systems can abiogenically produce potential microbial energy sources such as hydrogen (Telling et al. 2015). Iceland’s current subglacial environments produce conditions that have similarities with former environments on Mars, which make these environments reasonable analogues for Martian environments (Cousins et al. 2013).

Research Hypotheses and Approach

Research Question

Will hydrogen be generated from basalt and basaltic sediment during mechanical activation and wetting at 2°C in an anoxic environment?

Hypotheses

1. Mechanically activated basalt will produce hydrogen gas when wetted at 2°C in an anoxic environment.
2. Mechanical activation of basaltic sediment from glaciated catchments produces hydrogen gas when wetted at 2°C in an anoxic environment.
3. The rate of hydrogen production from glaciated sediments is lower than that of basaltic bedrock because the reaction requires fresh mineral surfaces and sediments are weathered.
4. Hydrogen production through silicate mineral shearing is not solely controlled by the amount of silica present in the rocks/sediments.

Approach

Bedrock and subglacially-sourced sediment samples were collected from glaciated catchments underlain by basalt in October 2016 to test for production of hydrogen from the basaltic bedrock and sediments produced from glacial crushing and grinding of the bedrock and sediment. Bedrock and glacial sediment samples were used in weathering experiments to determine the volume of hydrogen

produced from basalt by dry grinding followed by wetting at 2°C under anoxic conditions. The subglacial conditions simulated in the laboratory are the temperature (near 0°C), presence of water (melting at glacier bed), and physical weathering (crushing and scouring action of a moving glacier). Anoxic water was used to prevent competition reactions from dissolved gases. Bedrock of varying composition and pure mineral specimens of common minerals found in basalt were used to test whether the abundance of silica was the sole control on the reaction. Mineral specimens were chosen to represent the minerals determined to present in the basalt samples by bulk mineralogy analyses. Additionally, the concentrations of radicals and hydrogen peroxide produced during grinding were measured in order to study reaction dynamics. This thesis presents new data on hydrogen production from subglacially-sourced basalt, basaltic sediment, and basaltic mineral (clinopyroxene and plagioclase) samples under laboratory conditions that are relevant to subglacial environments.

CHAPTER TWO

METHODS

Field Area

The fieldwork for this thesis was conducted in Iceland as the island is dominated by basaltic bedrock and is extensively glaciated. These Icelandic glacial environments are also considered to be suitable terrestrial analogues to Martian environments (Allen 1979; Ehlmann et al. 2012; Cousins et al. 2013). The specific field sites sampled for this thesis were four outlet glaciers draining two Icelandic icecaps, Kotlujökull and Sólheimajökull, outlets of Mýrdalsjökull, and Kaldalónsjökull and Leirufjarðarjökull, outlets of Drangajökull.

Four outlet glaciers draining two Icelandic icecaps, shown in Figure 2.1, were sampled for meltwater, sediment, and bedrock in October 2016. Kotlujökull and Sólheimajökull, outlets of Mýrdalsjökull, and Kaldalónsjökull and Leirufjarðarjökull, outlets of Drangajökull, were chosen as sample sites due to accessibility. The two ice caps were chosen due to the difference in bedrock ages and geochemical composition; Mýrdalsjökull is located on young bedrock, less than 0.7 Ma, and Drangajökull is located on older bedrock, between 3.3 and 16 Ma (Thordarson and Larsen, 2007). Mýrdalsjökull is also near the zone of active rifting and the region is volcanically active (Saemundsson, 1979). Unaltered Icelandic basalt ranges in composition from olivine tholeiites to porphyritic plagioclase- and pyroxene-rich tholeiites (Saemundsson 1979). Pyroxenes

are predominately augitic, but some rocks approach the Fe-endmember ferrosilite (Ehlmann et al. 2012). Plagioclases are calcium-rich (Ehlmann et al. 2012). Secondary minerals include smectite, hematite, zeolites, celadonite, and cristobalite (Warner and Farmer 2010; Ehlmann et al. 2012).

Field Sampling

Bedrock samples were collected by hammering large sections (~2-3 kg pieces) from outcrops near the subglacial meltwater outlet at each of the four glaciers. Bedrock was collected from both outlets at Kaldalónsjökull. Sediments were collected from the within the meltwater outlet channel at each sampling site using a sterile scoop and stored in 473 ml plastic jars and were frozen within six hours of collection. Samples were collected from meltwater channels as the sediments within the meltwater channel have likely originated beneath the glacier and are thus representative of the sediments underlying the glacier. There were two outlets at Kaldalónsjökull and sediment was collected from each. Samples were stored at -80°C until processing. These samples were used for all experiments.

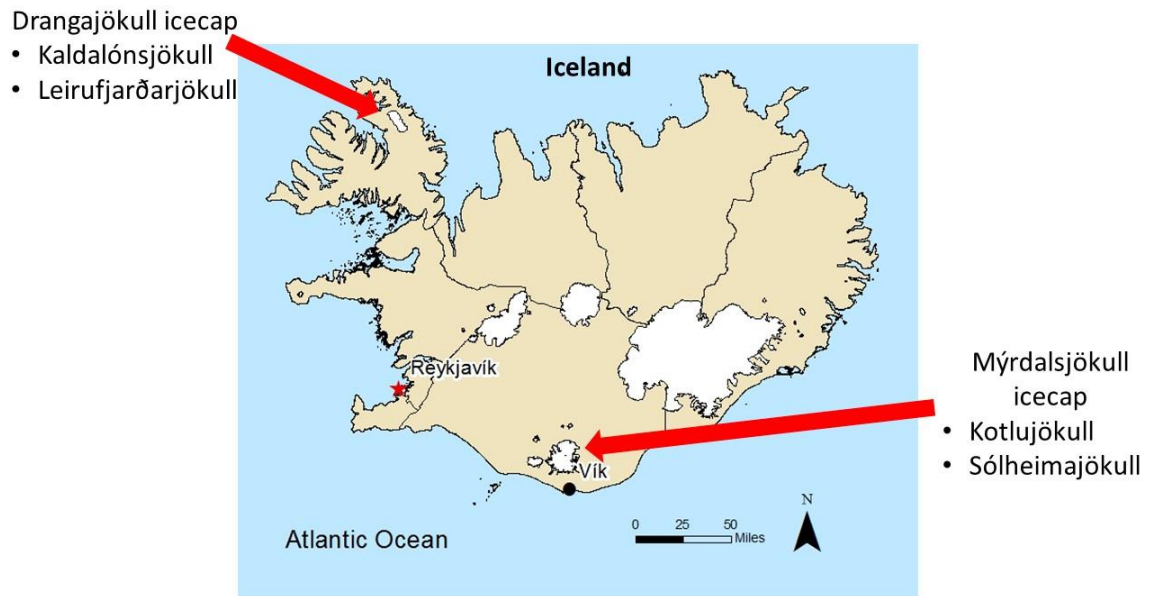


FIGURE 2.1 Map of Iceland showing the two samples ice caps. Created in Esri ArcMap using data from the National Snow and Ice Data Center.

Mýrdalsjökull

The Mýrdalsjökull icecap is located in southern Iceland and covers the active volcano, Katla. Samples were taken from two outlet glaciers, Kotlujökull and Sólheimajökull, both of which drain the southern margin of the Mýrdalsjökull icecap. At Kotlujökull, samples were taken from the southernmost subglacial outlet stream, Múlakvisl, at 150m above sea level. All samples were collected several hundred meters downstream of the glacier terminus as Múlakvisl flows through a steep walled canyon immediately after exiting the glacier. Samples at Sólheimajökull were taken from Jökulsá á Sólheimasandur immediately adjacent to the glacier terminus. Due to heavy rains during the October 2016 sampling expedition, the outlet stream's discharge was

increased and, thus, diluted with respect to baseline conditions. Sample sites are shown in Figure 2.2.

Drangajökull

The Drangajökull ice cap is in the Vestfirðir region of Iceland and is the northernmost Icelandic ice mass. Kaldalónsjökull is a western outlet glacier of Drangajökull, with Leirufjarðarjökull draining the northwestern region of Drangajökull. The termini of Kaldalónsjökull and Leirufjarðarjökull are 62 m and 127 m above sea level, respectively. Kaldalónsjökull had two outlets, which we defined as north and south based on their respective locations. Bedrock, sediment, and water samples were taken directly from the glacial termini. Sample sites are shown in Figure 2.2 and Figure 2.3.



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FIGURE 2.2 Kotlujökull and Sólheimajökull were sampled from the photo location. The red arrows in the top right image are the location of the outlet streams at Kaldalónsjökull. The orange arrows point to locations where the sampled outlet streams are exposed before flowing back under the ice. The two images in the bottom right were taken from the sample locations.



FIGURE 2.3 Photos of outlet sampled at Leirufjarðarjökull. The yellow arrow points to the location of the supraglacial flow sampled.

Meltwater Chemistry Analyses

The following measurements were made in the field at each of the sampling sites: pH, electrical conductivity (EC), dissolved oxygen, and alkalinity; additionally, water samples were filtered (0.2 μm Sterivex filter) and retained for subsequent laboratory analysis of major ion chemistry and dissolved organic carbon concentration. These measurements are not the major focus of the thesis but the methods for their collection and the data generated are tabulated in Appendix B. These measurements provide context for the natural conditions existing beneath the sampled glaciers and may aid future work that more specifically simulates the conditions of these glaciers.

Bulk Mineralogy Measurements

Bedrock samples were milled for 60 minutes at 450rpm in a tungsten-carbide grinding mill and were sent to the GeoAnalytical laboratory at Washington State University for analysis by x-ray fluorescence. X-ray diffraction analysis was performed on chipped bedrock samples that were ground using a mortar and pestle and sieved. The <63 μm size fraction was used for x-ray powder diffraction analysis on a SCINTAG X1 Diffraction System by Dr. David Mogk in the Imaging and Chemical Analysis Laboratory at Montana State University. Thin sections were made by Wagner Petrographics from billets cut from samples using a tile saw.

Weathering Experiments

Sample Processing

Rock samples were cut using a tile saw to remove weathered rinds. Billets of unweathered rock were cleaned with compressed air to remove dust. Billets were triple-wrapped in thick polyethylene bags and hit with a sledgehammer against a concrete floor to chip into smaller pieces. The $<250\mu\text{m}$ size fraction and $>5\text{mm}$ size fractions were removed by dry sieving and the $250\mu\text{m}$ - 5mm size fraction was used for subsequent milling. Chipped samples were dried at 130°C for 24 hours.

Sediments were allowed to thaw for 24 hours at room temperature before drying for 24 hours at 130°C .

Laboratory-sourced Minerals

Pure calcite was used as a non-silica control and pure quartz as an endmember control. Blocks of calcite were purchased from Ward's Science and quartz chips were purchased from Hausen Rock Treasures Wholesale Inc. Augitic clinopyroxene and labradorite plagioclase (purchased from Ward's Science) were used to examine the relative contribution of hydrogen production of individual basaltic minerals. The calcite, clinopyroxene, and plagioclase were treated with a sledgehammer according to the above procedure and the quartz was used as provided.

Experimental Protocol

All samples were weighed and placed into an 80mL tungsten-carbide Fritsch grinding bowl. The bowl was sealed using the gas-tight locking mechanism provided by Fritsch and flushed with 5.0 grade Ar for 15 minutes. The bowl was then transferred to a Fritsch Pulverisette 6 Ball Mill where the sample was milled for 60 minutes at 450rpm. Mill setup is shown in Figure 2.4. The sealed bowl was then transferred to a glove box flushed with 5.0 grade Ar. Oxygen concentrations were monitored using a BW Technologies GasAlert Extreme Single Gas Detector. Milled samples were weighed inside the glove box using an A&D EJ-410 scale and subfractions aliquoted into 20mL borosilicate vials (previously cleaned in a 1M HCl bath, rinsed 6x with milliQ water, and furnace at 450°C for 6 hours) using a sterile, plastic scoop. Eight grams of crushed rock material were used for the hydrogen time course experiments. Vials were capped using blue butyl rubber stoppers (previously cleaned by boiling in 1M NaOH for 1 hour and rinsed 6x in milliQ water) and crimp sealed prior to removing them from the glove box. After removal from the glove box, the headspace of the vials were overpressurized with 5.0 grade Ar to a pressure of 103 kPa.

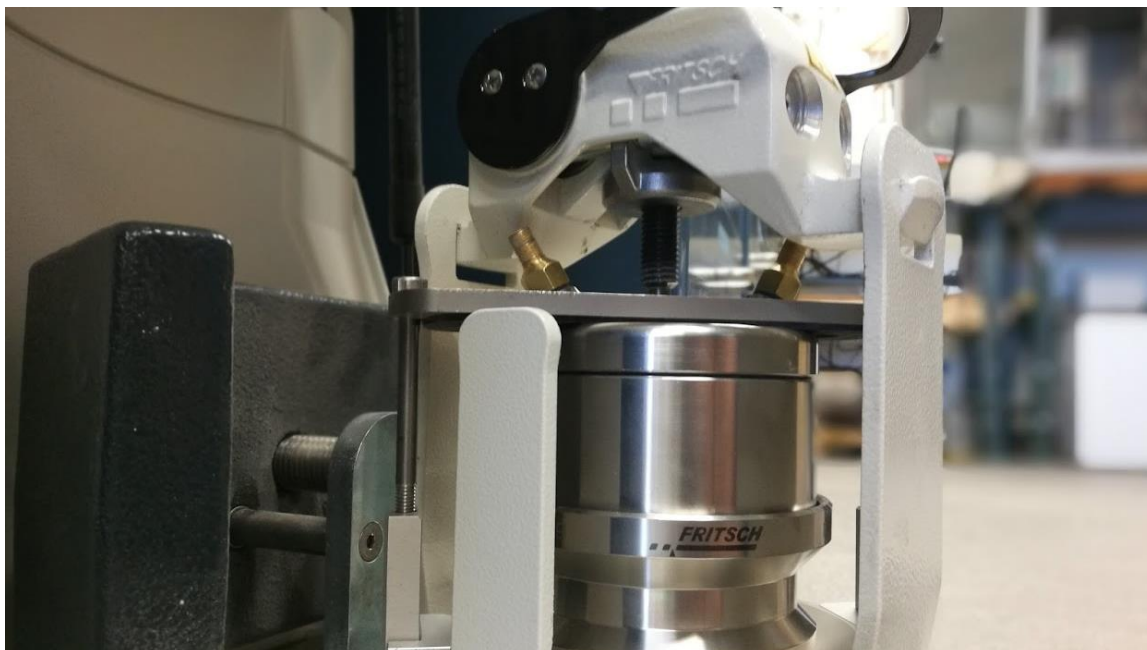


FIGURE 2.4 The grinding apparatus locked into the mill using the gas-tight clamping mechanism.

Hydrogen Measurements

Eight-gram subfractions for gas chromatograph measurements were kept chilled on ice until incubation. Initial headspace measurements were taken by adding 10mL 5.0 grade Ar to the vial using a gas-tight syringe and needle and then removing 10mL headspace for sampling. Four milliliters of chilled water, 0.8-0.9ppm O₂, (sparged with 5.0 grade Ar, 25mL/min for 1 hour, oxygen concentrations measured using a Mettler Toledo dissolved oxygen probe) were added using a syringe and needle. Vials were gently shaken for 1 minute and headspace sampled again by adding 10ml of 5.0 grade Ar to the vials using a gas-tight syringe and then withdrawing 10ml of gas from the vials.

Additional vials containing a water control and a dry control were sampled, and vials were then transferred to an incubator set at 2°C, monitored by a HOBO pendant data logger. Experiment vials are shown in Figure 2.5. The headspace was sampled at 24, 48, 120, and 168 hours and during this sampling time the vials were stored on ice. Headspace was sampled by adding 10ml of 5.0 grade Ar to the vials using a gas-tight syringe and then withdrawing 10ml of gas from the vials. Gas measurements were made on a SRI 8610C gas chromatograph using a Valco Instruments Company Inc. Pulsed



FIGURE 2.5 The experiment vials, filled with calcite in this image. The three vials labeled in green (on the left) are reaction vials with pulverized sample and water. The vial labeled in blue (second from right) is a water-only control. The vial labeled in yellow (right) is a dry sample-only control. Vials are sealed with butyl rubber stoppers and crimp sealed.

Helium Ionization Detector at 100°C for hydrogen quantification with a 2 ml sample loop. Helium was used as the carrier gas at 20 ml/min. Methane was detected using a Flame Ionization Detector at 150°C with a 1 ml sample loop. A set of gas standards (1, 6,

10, 20, 100, and 1000 ppm; $R^2 > 0.99$ for all standard runs) made by performing manual dilution of a 1% standard of H_2 , CH_4 , CO , and CO_2 in ultra-high purity nitrogen were used to calculate gas concentrations in parts per million.

Gas Calculations

Empty vials begin with a total headspace volume of 24.5 ml which is reduced to 21.83 ml after the addition of 8 g milled material (assumed density of 3 g/ml). The initial temperature is assumed to be room temperature (22.5°C, 295.65 K). Initial pressure (2.366 atm) was calculated from an assumed ambient pressure of 84.5 kPa and the initial overpressure of 103 kPa. Before initial sampling, the moles of total vial headspace were calculated using the ideal gas law (Equation 2.1).

Equation 2.1 $n = PV/R/T$

Where,

Pressure, $P = 2.366$ atm

Gas constant, $R = 0.08206$ L*atm/mol/K

Volume, $V = 0.021833$ L

Temperature, $T = 295.65$ K

Total vial headspace before initial sampling is 0.002013 mol. The moles of headspace removed at the initial sampling can be calculated using the initial headspace volume (21.82 ml) and moles (0.002012 mol) and the volume of gas removed (10 ± 0.1 ml). The moles of gas remaining in the vial after sampling are calculated by subtracting the moles of gas removed from the initial moles of gas in the vial. Vial pressure is then

recalculated for the new volume of gas remaining in the vial. This calculation is completed for each time step, accounting for changes in headspace volume due to the addition of water at the first time step and sampling at each time step. The total gas in the vial at each time step is calculated from the concentration of gas in the removed 10 ml sample. The concentration in parts per million is multiplied by the total moles of headspace in the vial to determine the moles of gas (hydrogen or methane) in the vial headspace. To determine the moles of gas in solution, Henry's Law (Equation 2.2) is used.

Equation 2.2 $C = kP$

Where,

C = concentration of gas in solution

P = partial pressure of gas phase

k = solubility constant

The solubility constant of hydrogen used was 0.004 mol/L/atm (Young 1981). The total moles of gas in the vial at each time step is then the sum of the moles in the vial headspace and the moles in solution. Methane concentrations were calculated using the above procedure, using a solubility constant of 0.42 mol/L/atm (Clever and Young 1987). Error for all gas calculations was calculated as a propagating standard error.

Silica Radical Assay

Radical production was quantified using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay following Damm and Peukert (2009). A $\sim 100 \mu\text{M}$ DPPH:ethanol solution was made the morning of each experimental run using 95% DPPH, (Alfa Aesar). Samples were milled according to the procedure described for the weathering experiments and transferred to the glove box. Five milliliters of $\sim 100 \mu\text{M}$ DPPH were added to 50mL conical polypropylene tubes containing 0.5g of milled sample. The vials were shaken by hand for 1 minute, prior to removing samples from the glove box. Samples were then centrifuged for 10 minutes at 10000rpm. The supernatant was transferred to 15mL conical polypropylene tubes and analyzed within one hour. Measurements of the solution absorption at 515nm (extinction coefficient = $11,300 \text{ L mol}^{-1} \text{ cm}^{-1}$) were made using a Horiba Aqualog spectrometer and were used to calculate the concentration of DPPH. A set of five standards ($\sim 0.1 \times 10^{-3} \mu\text{M}$, $\sim 0.075 \times 10^{-3} \mu\text{M}$, $\sim 0.05 \times 10^{-3} \mu\text{M}$, $\sim 0.025 \times 10^{-3} \mu\text{M}$, and $\sim 0.01 \times 10^{-3} \mu\text{M}$; $R^2 > 0.99$ for all standard runs) made from the 0.1mM DPPH stock solution were used to check accuracy of spectrophotometric measurements.

Hydrogen Peroxide Assay

Hydrogen peroxide, 30%, (Fisher Chemical), 2,9-dimethyl-1,10-phenanthroline (DMP), 98%, (Alfa Aesar), copper(II) sulfate (Acros Organics), and 100% ethanol were used as provided. A 0.01M solution of CuSO_4 was prepared using milliQ water and a 1% DMP solution was prepared by adding 1g of DMP to 100mL of 100% ethanol. Peroxide

concentrations were measured following a modified protocol based on the work of Baga et al. (1988).

One gram of milled sample was added to a 50mL conical polypropylene tube within a sealed glove box filled with 5.0 grade Ar. A milliliter of 0.01M CuSO_4 and 1mL of the 1% DMP solution were added to the sample and then brought to a final volume of 10mL using milliQ water. The sample was then shaken for 1 minute to ensure adequate mixing. Samples were centrifuged immediately for 10min at 10000rpm and the supernatant transferred to 15mL conical polypropylene tubes. The change in absorbance at 454nm of the solution was measured on a Horiba Aqualog spectrometer and used to determine hydrogen peroxide concentration in samples by comparison with a standard curve. The standard curve was developed by using the same analytical procedure as the samples on a series of dilutions of the 30% hydrogen peroxide (1, 2.5, 5, 7.5, and 10 μM peroxide; $R^2 > 0.99$ for all standard runs).

Grain Size and Surface Area Analysis

Grain size analysis of the milled samples was performed using a Malvern Mastersizer Laser Particle Size Analyzer. For sediment samples, grain size analyses were completed for samples before and after milling. Excess milled sample material from the weathering experiments was saved and stored in 50mL polypropylene tubes at room temperature until grain size analysis. Twenty milliliters of a 2.5% sodium hexametaphosphate solution prepared using milliQ water were added to 0.1g of milled

sample. Samples were vortexed for 30 seconds to mix and were additionally shaken by hand for 10 seconds immediately before analysis. Samples were sonicated in the Malvern Mastersizer for 15 seconds prior to analysis. Samples were manually pipetted into the Malvern Mastersizer to achieve an obscuration of 4-6%. Particles were assumed to be spherical with an average refractive index of 1.56 (aluminum silicate). Triplicate measurements were run six times each, for a total of 18 measurements per sample. Specific surface area (SSA) was calculated from the particle size distribution (equation 2.3), assuming spherical, non-porous samples with an average density of 3 g/cm³.

Equation 2.3

$$SSA = \frac{6 \sum \frac{V_i}{d_i}}{p \sum V_i}$$

Where,

V_i = relative volume of particle class i

p = particle density

d_i = mean diameter of particle class i

CHAPTER THREE

RESULTS

XRF Data

The minerals used in the weathering experiments had the following weight % SiO_2 : quartz, 99.5, labradorite plagioclase, 54.4, augitic clinopyroxene, 53.9; the calcite contained no measurable SiO_2 as determined via XRF. XRF data for the mineral samples are included in Appendix A.

Bedrock samples from the four glaciated catchments were subalkaline basalts. The bedrock samples can be segregated into two distinct groups on the basis of major (Table 3.1) and trace (Figure 3.1) elemental compositions. Bedrock samples from Drangajökull outlet glaciers (Leirufjarðarjökull and Kaldalónsjökull) were 49.6 – 49.7 %, SiO_2 , in contrast to samples from Mýrdalsjökull outlet glaciers (Kotlujökull and Sólheimajökull) with 46.8 - 47.9 % SiO_2 (Table 3.1). There were also distinct differences in the abundance of the major elemental oxides of titanium, iron, calcium, potassium, and phosphorus, between bedrock samples from Drangajökull and from Mýrdalsjökull (Table 3.1). Marked differences are also evident in the trace element composition of bedrock samples from Drangajökull and Mýrdalsjökull (Figure 3.1); with higher concentrations of nickel, chromium, scandium, and copper in Drangajökull samples relative to those from Mýrdalsjökull, and higher concentrations of barium, rubidium,

strontium, zirconium, niobium, zinc, cesium, and neodymium in Mýrdalsjökull samples relative to those from Drangajökull.

The chemical grouping of the samples corresponds primarily to the age of the basalt. The first group are the older basalts (3.3-16 Ma, Thordarson & Larsen 2007), located in northwest Iceland, under Drangajökull: samples from Kaldalónsjökull and Leirufjarðarjökull. The second group are younger basalts, (<0.8 Ma, Thordarson & Larsen 2007), located in southern Iceland, under Mýrdalsjökull: samples from Kotlujökull and Sólheimajökull.

Major elements, wt% oxide, normalized				
Bedrock samples				
	Leirufjarðarjökull	Kaldalónsjökull north	Kotlujökull	Sólheimajökull
SiO ₂	49.71	49.60	47.91	46.79
TiO ₂	2.42	1.92	4.69	4.85
Al ₂ O ₃	14.30	14.70	12.92	13.03
FeO*	13.24	12.24	15.23	15.56
MnO	0.22	0.21	0.25	0.24
MgO	5.97	7.24	4.84	5.21
CaO	11.24	11.72	9.60	9.98
Na ₂ O	2.47	2.04	3.08	2.95
K ₂ O	0.22	0.18	0.80	0.72
P ₂ O ₅	0.21	0.16	0.68	0.68
Total	100.00	100.00	100.00	100.00

TABLE 3.1. X-ray fluorescence major element oxide analysis for the bedrock samples, all basalt. Differences in the weight % of the oxides of titanium, iron, calcium, potassium, and phosphorus, were used to group the basalt samples into two groups on the basis of their chemical composition. Group 1, samples from Drangajökull outlet glaciers (Leirufjarðarjökull and Kaldalónsjökull) were chemically similar, highlighted in blue, and Group 2 samples from Mýrdalsjökull outlet glaciers (Kotlujökull and Sólheimajökull) highlighted in red, were chemical similar, but distinct from the Group 1 samples.

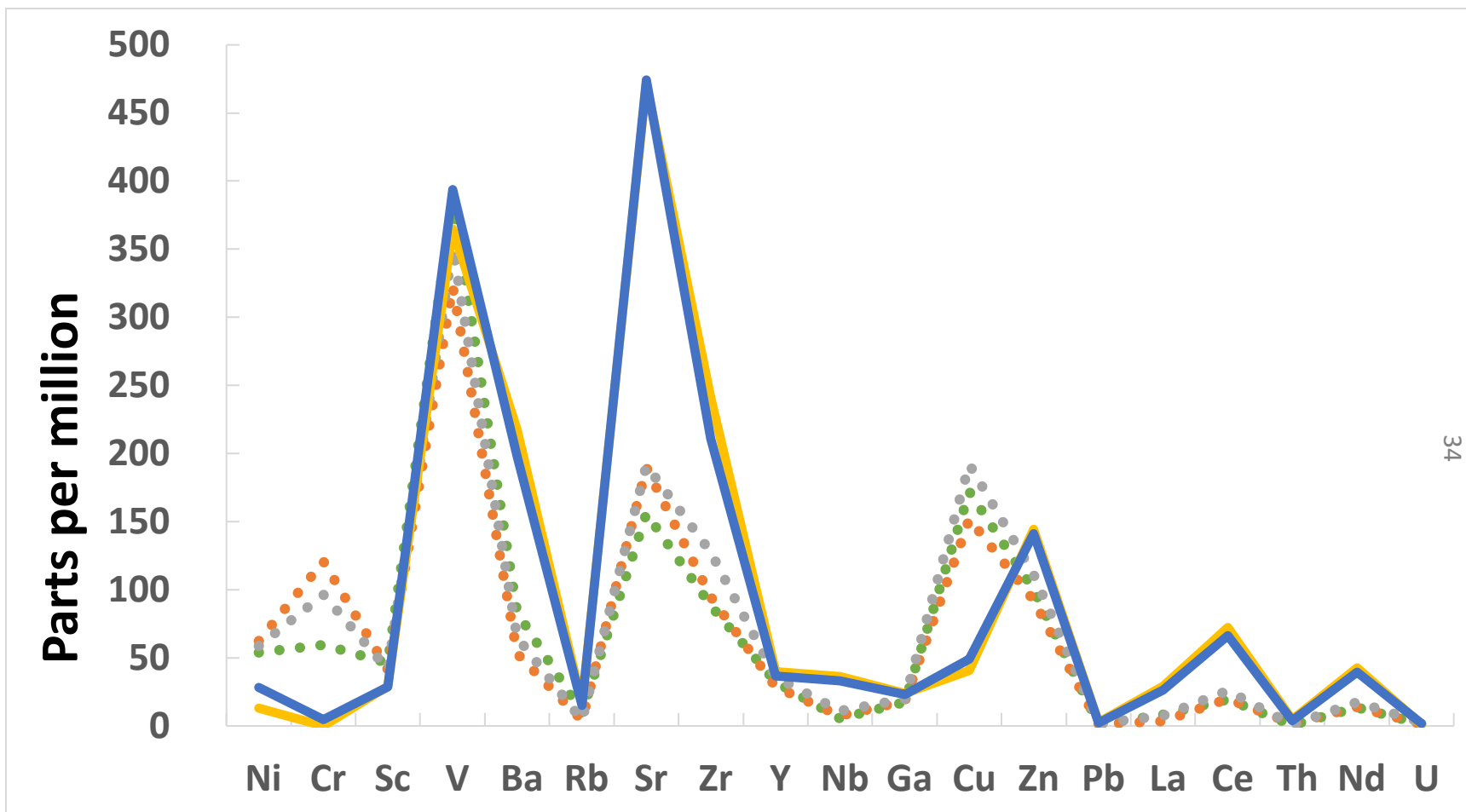


FIGURE 3.1. Trace element concentrations (by weight) in bedrock samples. The solid lines represent samples from Mýrdalsjökull outlet glaciers, and the dotted lines samples from Drangajökull outlet glaciers.

Sediment samples from three of the outlet glaciers were also analyzed via XRF (Table 3.2). These three samples can also be grouped on the basis of their major elemental composition, as they also exhibit similar distributions of magnesium, calcium, sodium, potassium, and phosphorus as for their parent bedrock (Tables 3.1, 3.2). The trace element composition of the sediments from each catchment closely resembles the bedrock composition, with a couple of exceptions. The sediments from Drangajökull outlet glaciers, show elevated chromium concentrations with respect to the bedrock samples (Figure 3.2) whereas the single sediment sample from Mýrdalsjökull has lower vanadium and strontium concentrations than the bedrock samples (Figure 3.3). The sediments from Kaldalónsjökull and Leirufjarðarjökull have increased iron oxides (>1%) relative to bedrock from the same location, while sediment from Kotlujökull shows decreased iron oxides (>1%) with respect to the bedrock sample. The bedrock collected from the two outlets of Drangajökull (Leirufjarðarjökull and Kaldalónsjökull) are chemically similar and the bedrock collected from the two outlets of (Kotlujökull and Sólheimajökull) are similar.

Major elements, wt% oxide, normalized			
Sediment samples			
	Leirufjarðarjökull	Kaldalónsjökull north	Kotlujökull
SiO ₂	47.71	48.38	51.16
TiO ₂	2.71	2.03	3.90
Al ₂ O ₃	13.04	14.23	13.18
FeO*	14.88	13.58	14.24
MnO	0.23	0.22	0.23
MgO	7.84	8.13	3.89
CaO	11.39	11.35	8.47
Na ₂ O	1.89	1.82	3.27
K ₂ O	0.17	0.18	1.13
P ₂ O ₅	0.13	0.10	0.52
Total	100.00	100.00	100.00

TABLE 3.2. Major element oxide composition of the sediment samples. Differences in the weight % of the oxides of titanium, magnesium, calcium, potassium, and phosphorus were used to group the basalt samples into two groups on the basis of their chemical composition. Group 1, samples from Drangajökull outlet glaciers (Leirufjarðarjökull and Kaldalónsjökull) highlighted in blue, were chemically similar, but distinct from the Mýrdalsjökull outlet glacier sample from Kotlujökull highlighted in red.

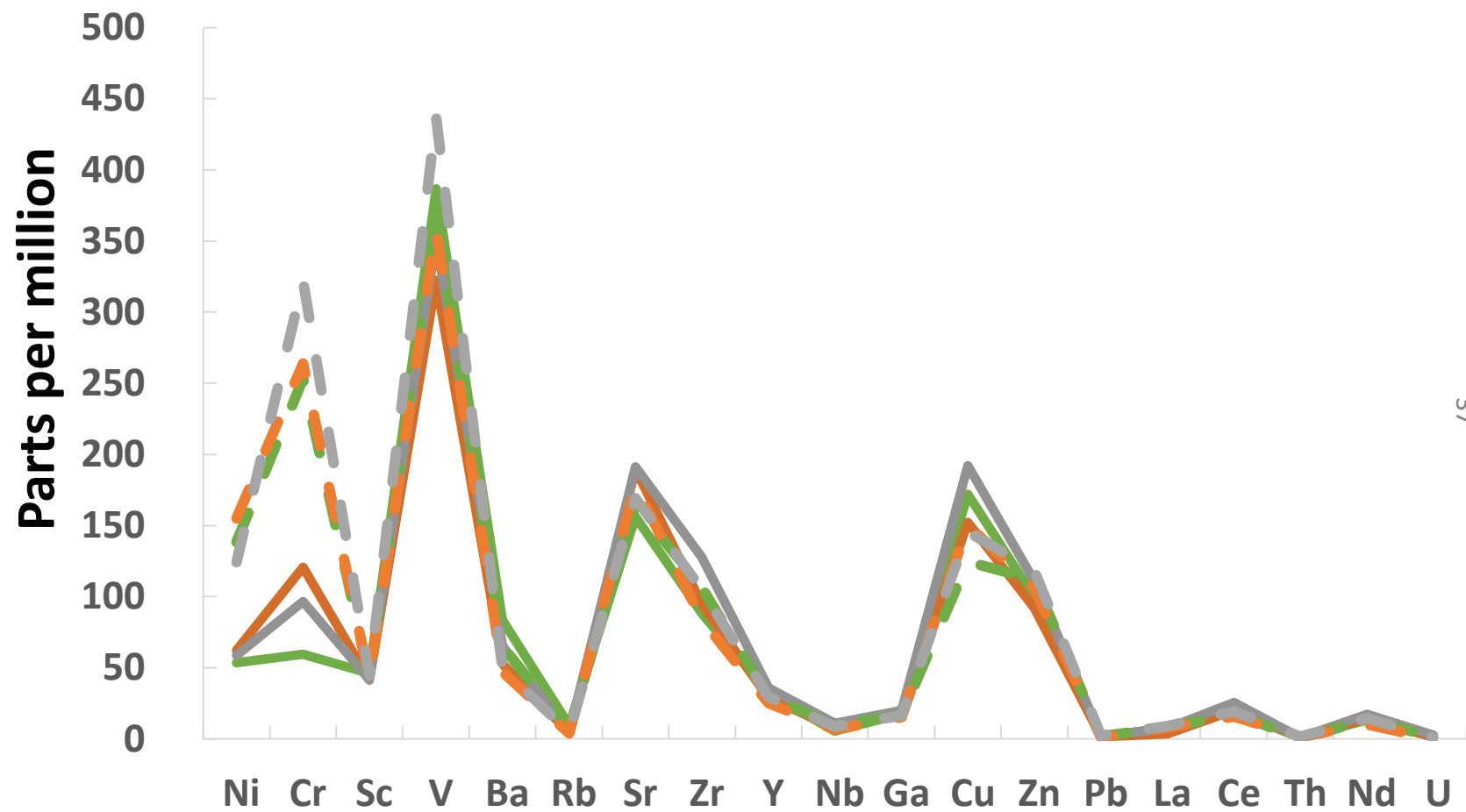


FIGURE 3.2. Trace element composition (by weight) of the bedrock and glacial sediment samples from Drangajökull. Solid lines represent bedrock samples, dashed lines represent, sediment samples.

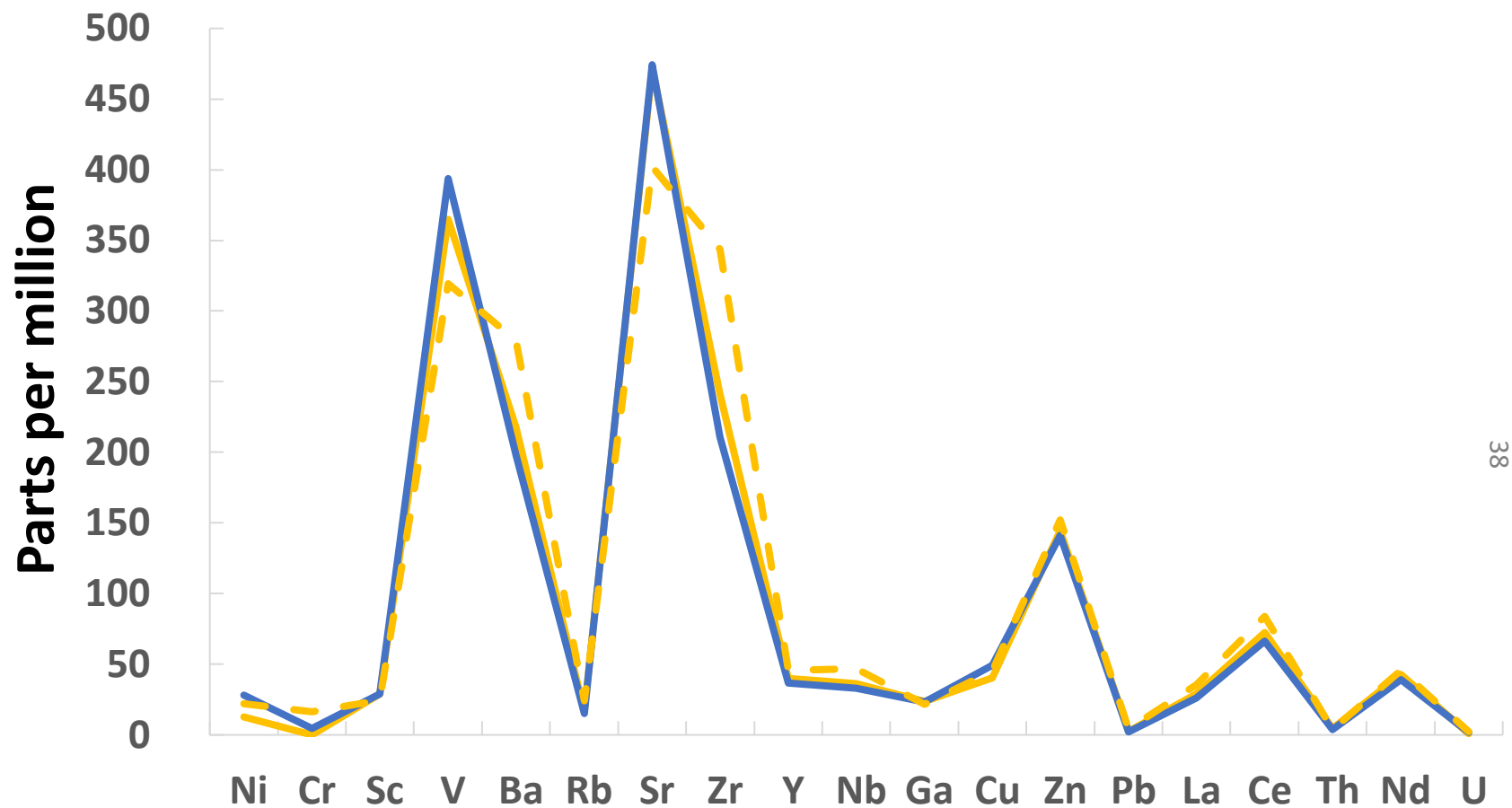
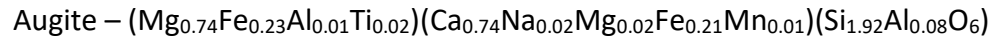
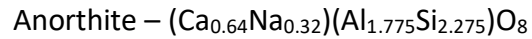
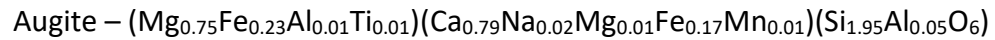
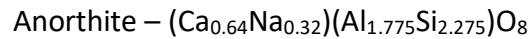
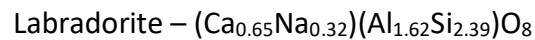
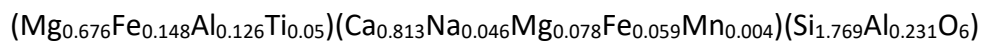


FIGURE 3.3. Trace element composition (by weight) of the bedrock and glacial sediment samples from Mýrdalsjökull. Solid lines represent bedrock samples and the dashed line a sediment sample.

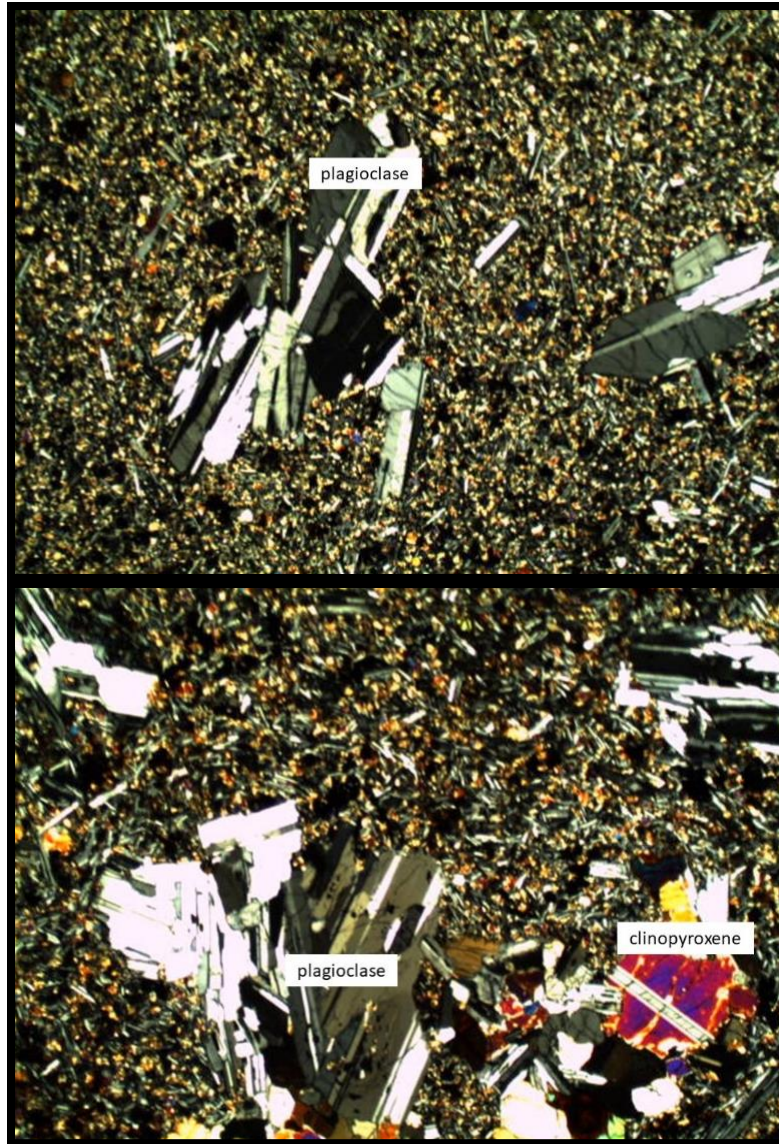
XRD Data

The bedrock samples from Mýrdalsjökull outlet glaciers (Kotlujökull and Sólheimajökull) contain anorthite plagioclase and augitic clinopyroxene, whereas bedrock samples from Drangajökull outlet glaciers (Leirufjarðarjökull and Kaldalónsjökull) contain labradorite plagioclase and augitic clinopyroxene. The following are the compositions of the two primary rock-forming minerals in each sample as determined via XRD.

Kotlujökull bedrockSólheimajökull bedrockLeirufjarðarjökull bedrockKaldalónsjökull north bedrock

Petrography

Samples from Drangajökull, (Kaldalónsjökull North and Leirufjarðarjökull) are both porphyritic basalt (Figure 3.4). The Kaldalónsjökull North sample has an aphanitic groundmass that is composed of plagioclase feldspar, clinopyroxene, and iron oxides. Phenocrysts of plagioclase are generally 2mm or less and grains are subhedral, displaying irregular cracks. Trace amounts of olivine displaying characteristic irregular cracking have been partially altered to a reddish-brown oxide. The Leirufjarðarjökull sample has an aphanitic groundmass composed of plagioclase laths, 0.1mm-0.5mm in length, clinopyroxene, and iron oxides. Phenocrysts are composed of intergrown plagioclase feldspar and clinopyroxene, likely augite. Trace amounts of altered olivine are present in association with phenocrysts. Samples from Mýrdalsjökull (Sólheimajökull and Kotlujökull) are both aphanitic basalt, with groundmasses composed of plagioclase feldspar and clinopyroxene and plagioclase laths generally less than 0.25mm in length, (Figure 3.5).



A

B

FIGURE 3.4. Micrographs of bedrock thin sections displayed under cross-polarized light, collected from: a) Kaldalónsjökull; subhedral plagioclase phenocrysts are surrounded by a groundmass of clinopyroxene, plagioclase, and iron oxides, b) Leirufjarðarjökull; phenocrysts of plagioclase and clinopyroxene in a groundmass of plagioclase, clinopyroxene, and iron oxides. Field of view is 2mm in both images.



A



B

FIGURE 3.5. Micrographs of bedrock thin sections displayed under cross-polarized light, collected from: a) Sólheimajökull, and b) Kotlujökull. Both show an aphanitic texture, composed of plagioclase and clinopyroxene. Field of view is 2mm in both images.

Weathering Experiments

The crushed, wetted basalts produced, on average, 75% less hydrogen gas than pure quartz; 6.6 ± 1.2 nmol H₂ per gram basalt compared to 26.6 ± 2.0 nmol H₂ per gram quartz, when reacted with deoxygenated deionized water in 7-day experiments at 2°C (Table 3.3; Figure 3.6). Normalizing the hydrogen gas production to silica (SiO₂) content results in the basalt values increasing relative to quartz by a factor of ~ 2 , due to the lower silica content in the basalt (46-50%, Table 3.1) (Figure 3.7). In comparison, the crushed glacial sediments produced an average of only 1.1 ± 0.3 nmol H₂ per gram sediment under the same experimental conditions as for the crushed bedrock (Figure 3.8). Interestingly, no systematic difference was observed in hydrogen production from either the crushed bedrock or crushed glacial sediment samples from Drangajökull relative to those from Mýrdalsjökull. Individual mineral components of basalt such as labradorite plagioclase and augitic clinopyroxene were crushed and reacted with deoxygenated deionized water to determine mineral specific hydrogen production in comparison with the basalt, glacial sediments and quartz. The labradorite plagioclase and augitic clinopyroxene produced 9.0 ± 1.4 , and 173.8 ± 9.7 nmol H₂ per gram respectively (Figure 3.9), with no measurable hydrogen production in a parallel calcite control. These results suggest that (i) other components within basalt, and (ii) the structural type of silicate mineral, may affect hydrogen production, given the range of hydrogen production from the pure mineral samples.

Measurement of hydrogen production was the primary goal of these weathering experiments, however, (minor) methane production was also measured in many of the experiments (Figures 3.10, 3.11, 3.12). The bedrock samples produced methane during the experiment, at an average of 2.6 ± 1.8 nmol CH₄ per gram rock. This is greater than the 0.6 ± 0.1 nmol CH₄ per gram sample produced from pure quartz. Sólheimajökull bedrock produced the most, at 5.6 ± 0.6 nmol CH₄ per gram rock and Kotlujökull and Leirufjarðarjökull bedrock the least at 1.4 ± 0.3 nmol CH₄ per gram rock. Plagioclase and clinopyroxene released methane, 12.9 ± 2.2 nmol and 4.2 ± 0.8 nmol CH₄ per gram sample, respectively. Sediments on average produced 5.8 ± 0.1 nmol CH₄ per gram sample. Leirufjarðarjökull sediment produced 14.7 ± 0.2 nmol CH₄ per gram sample, while sediments from Kaldalónsjökull and Kotlujökull produced 0.1 ± 0.02 and 2.7 ± 0.2 nmol CH₄ per gram sample. For several experiments, headspace samples were taken directly from the grinding bowl and two of the bedrock samples produced hydrogen and methane after dry grinding (Table 3.4).

	Cumulative nmol H ₂ per gram sample	Cumulative nmol CH ₄ per gram sample
Bedrock and Mineral Samples		
Kaldalónsjökull	7.1 ± 1.8	2.1 ± 0.8
Leirufjarðarjökull	5.0 ± 0.8	1.4 ± 0.3
Kotlujökull	3.2 ± 0.2	1.4 ± 0.1
Sólheimajökull	11.9 ± 1.9	5.6 ± 0.6
Average basalt	6.6 ± 1.2	2.6 ± 1.8
Quartz	26.6 ± 2.0	0.6 ± 0.1
Clinopyroxene	173.8 ± 9.7	4.2 ± 0.8
Plagioclase	9.0 ± 1.4	12.9 ± 2.2
Calcite	Below detection limit	Below detection limit
Sediment Samples		
Kaldalónsjökull North	1.4 ± 0.4	0.1 ± 0.02
Leirufjarðarjökull	1.2 ± 0.4	14.7 ± 0.2
Kotlujökull	0.6 ± 0.3	2.7 ± 0.2
Average sediment	1.1 ± 0.3	5.8 ± 0.1

TABLE 3.3 Cumulative gas production from bedrock, mineral, and sediment samples, crushed and wetted, and incubated at 2°C for 168 hours (7 days). Error is standard error calculated from triplicate samples.

	nmol H ₂ per gram sample	nmol CH ₄ per gram sample
Kaldalónsjökull	0.08	0.07
Leirufjarðarjökull	0.63	0.44
Sólheimajökull	0	0

TABLE 3.4. Gas production from dry crushing of bedrock samples.

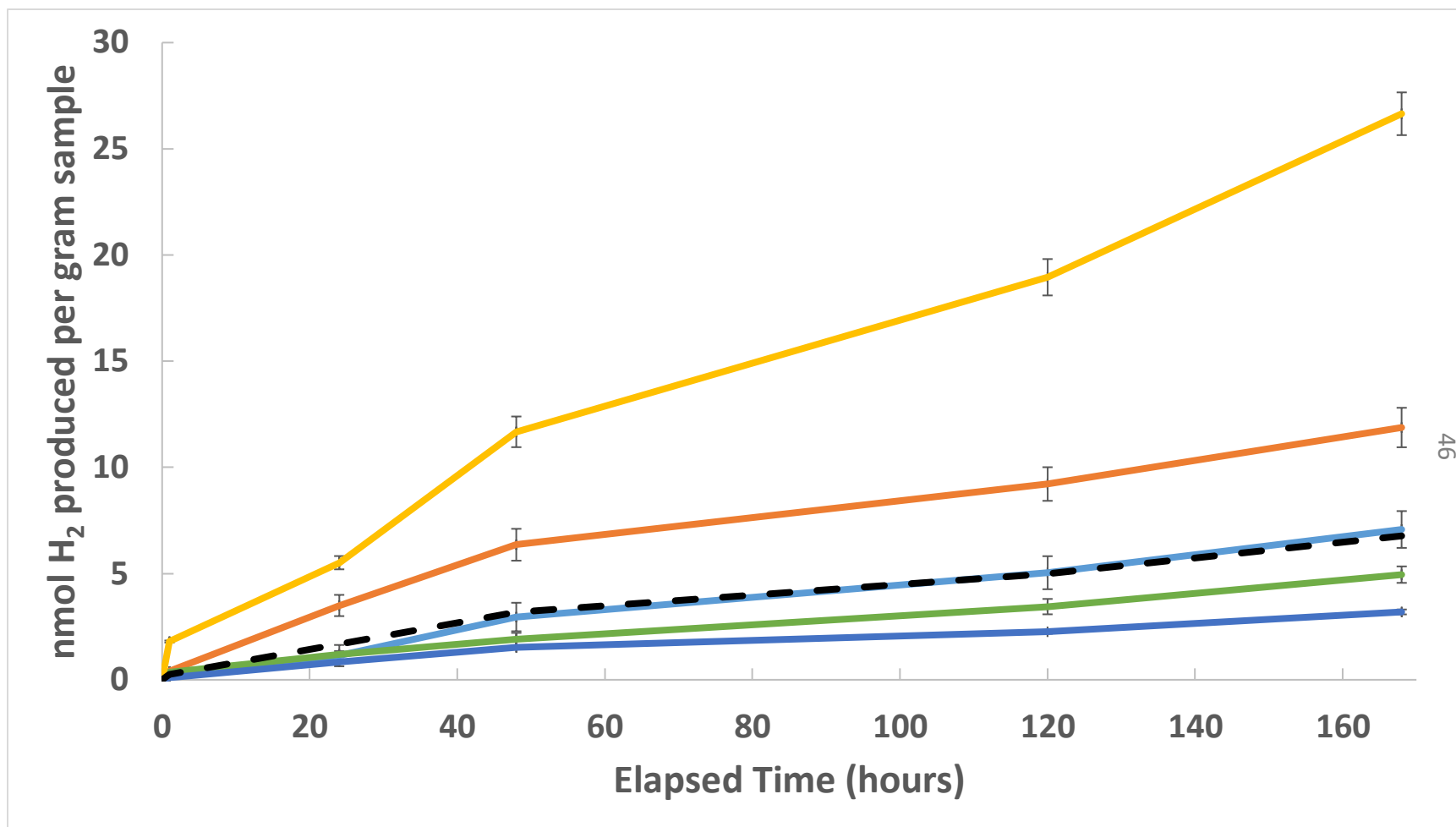


FIGURE 3.6. Production of hydrogen from mechanically-activated Icelandic basalt and quartz incubated with Ar-sparged deionized water under and Ar headspace at 2°C . The dashed line is the average hydrogen production from basalt. The error bars represent the standard error of triplicate experiments.

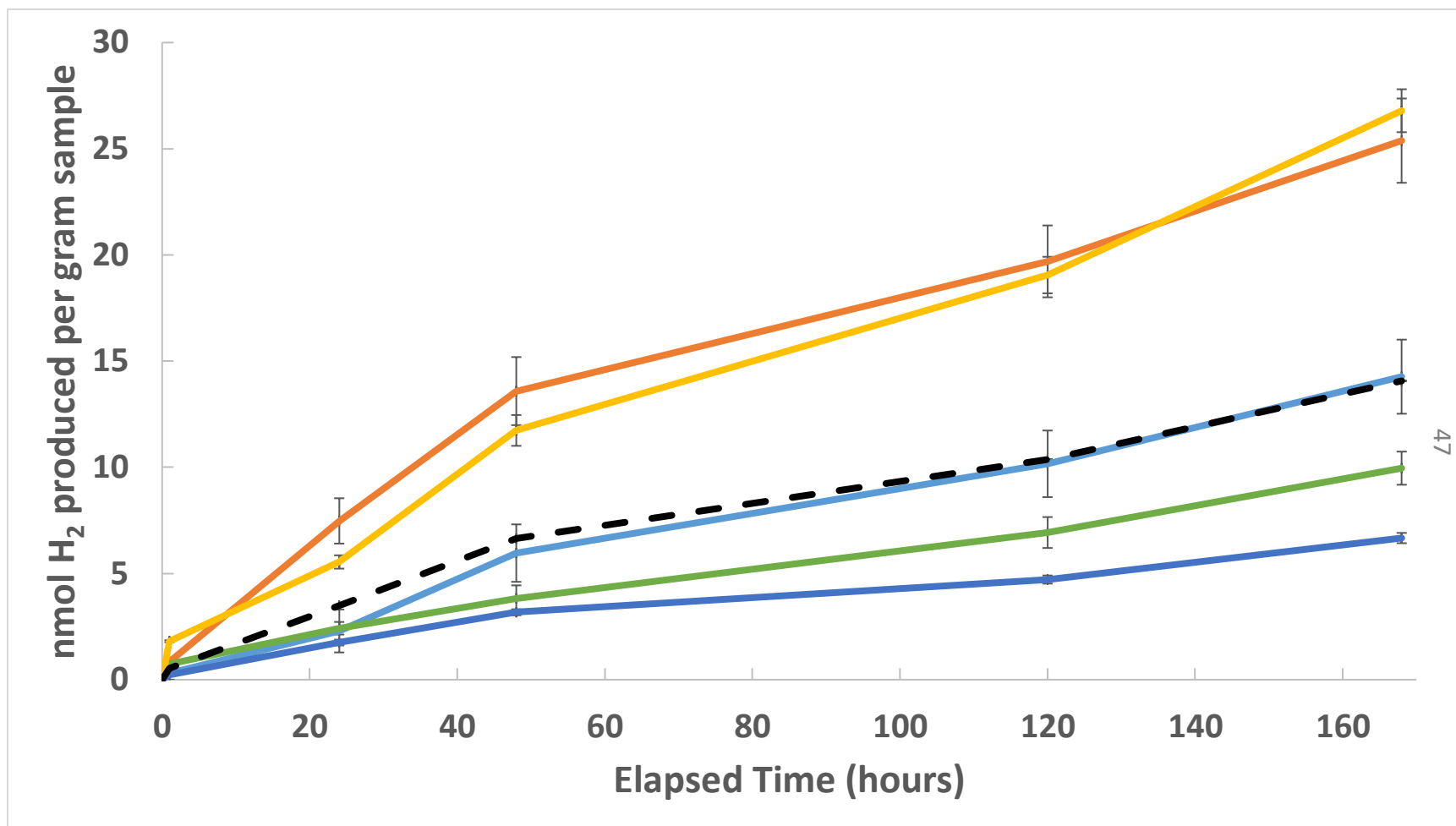


FIGURE 3.7. Production of hydrogen from mechanically-activated Icelandic basalt and quartz incubated with Ar-sparged deionized water under and Ar headspace at 2°C, normalized to weight percent silica. The dashed line is the average hydrogen production from basalt, normalized to the average silica content. The error bars represent the standard error of triplicate experiments.

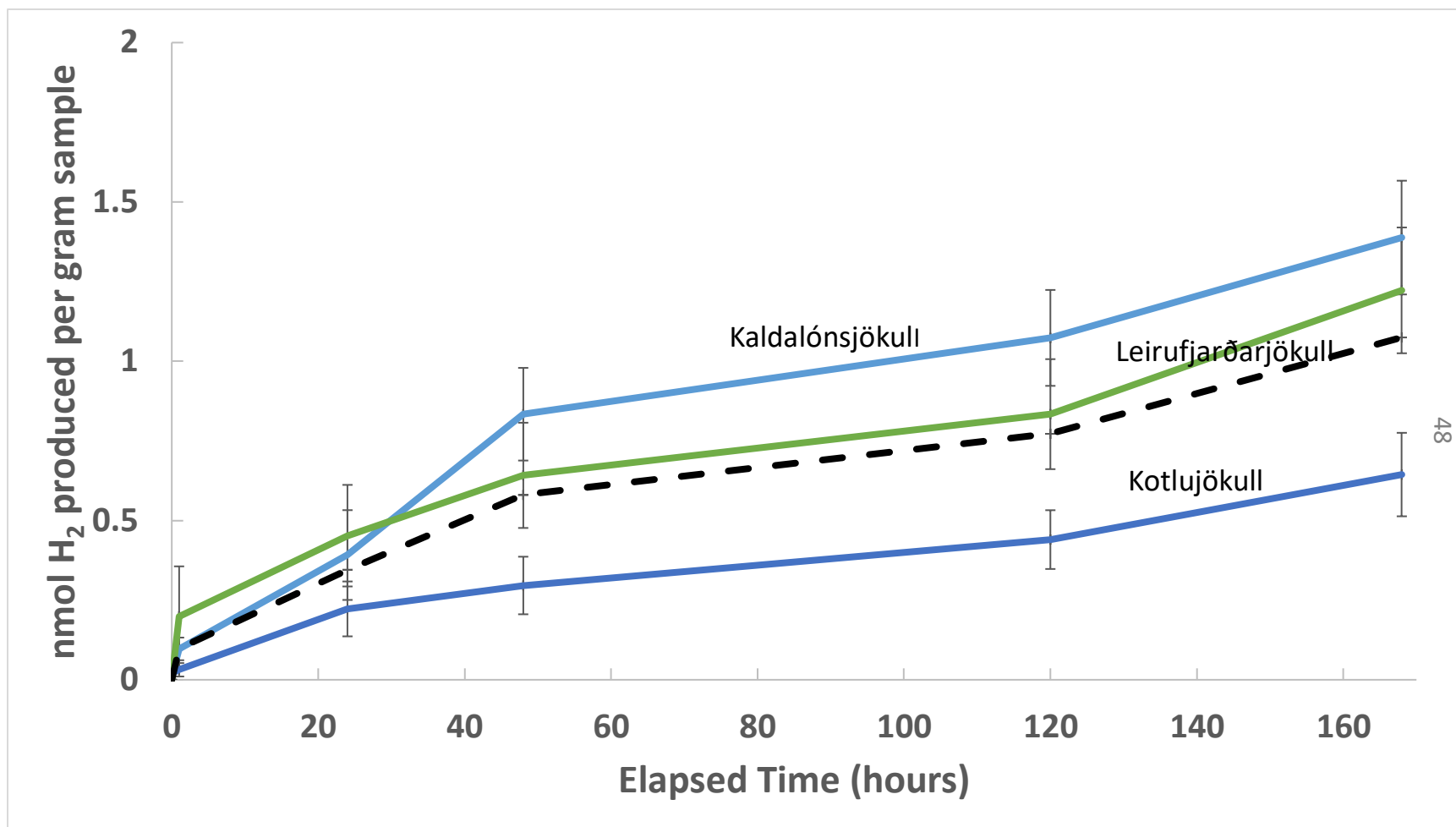


FIGURE 3.8. Production of hydrogen from mechanically-activated Icelandic sediments incubated with Ar-sparged deionized water under and Ar headspace at 2°C. The dashed line represents the average hydrogen production from sediments. The error bars represent the standard error of triplicate experiments.

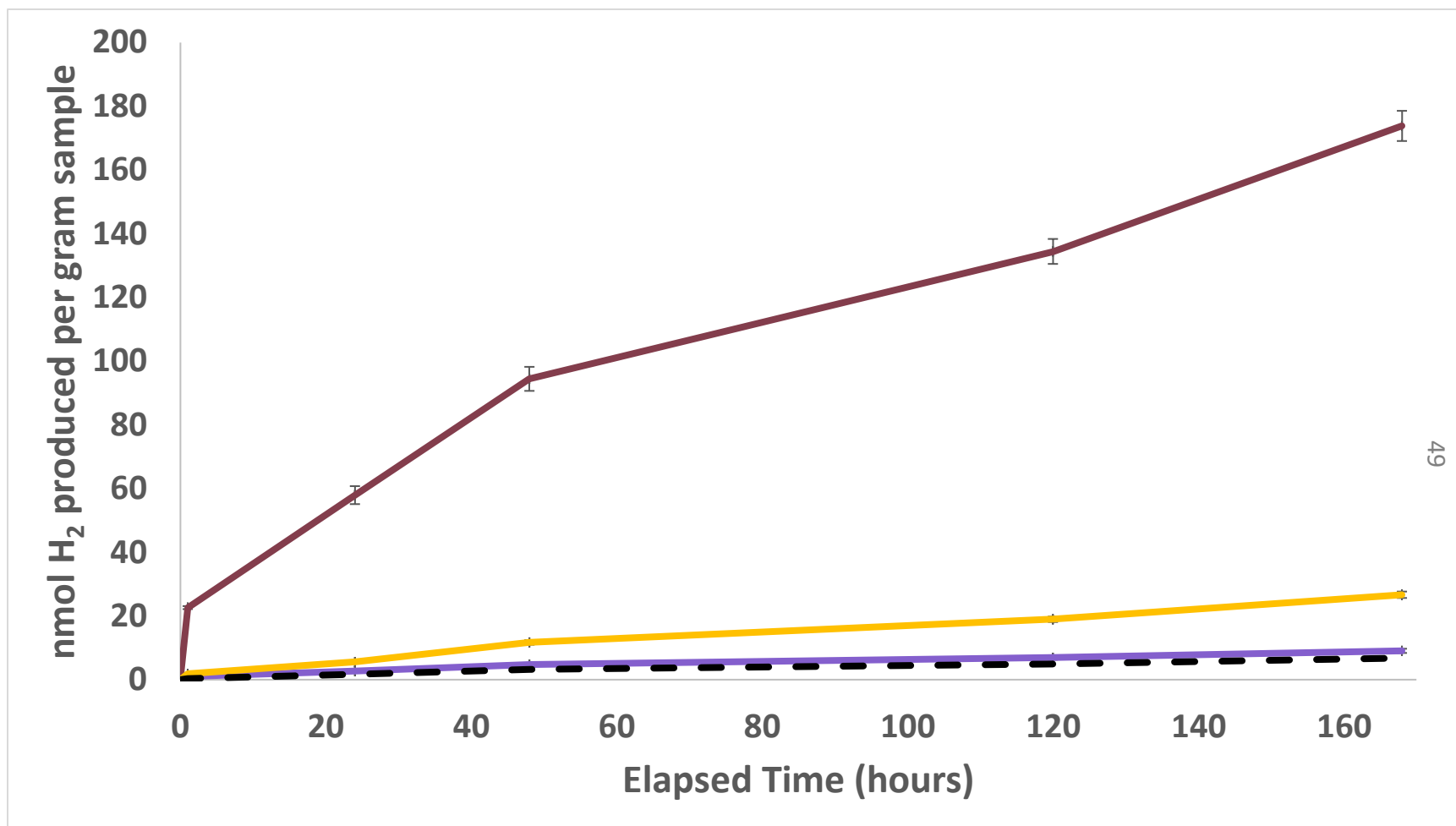


FIGURE 3.9. Production of hydrogen from mechanically-activated silicate minerals incubated with Ar-sparged deionized water under and Ar headspace at 2°C. The dashed line is the average hydrogen production from basalt. The error bars represent the standard error of triplicate experiments.

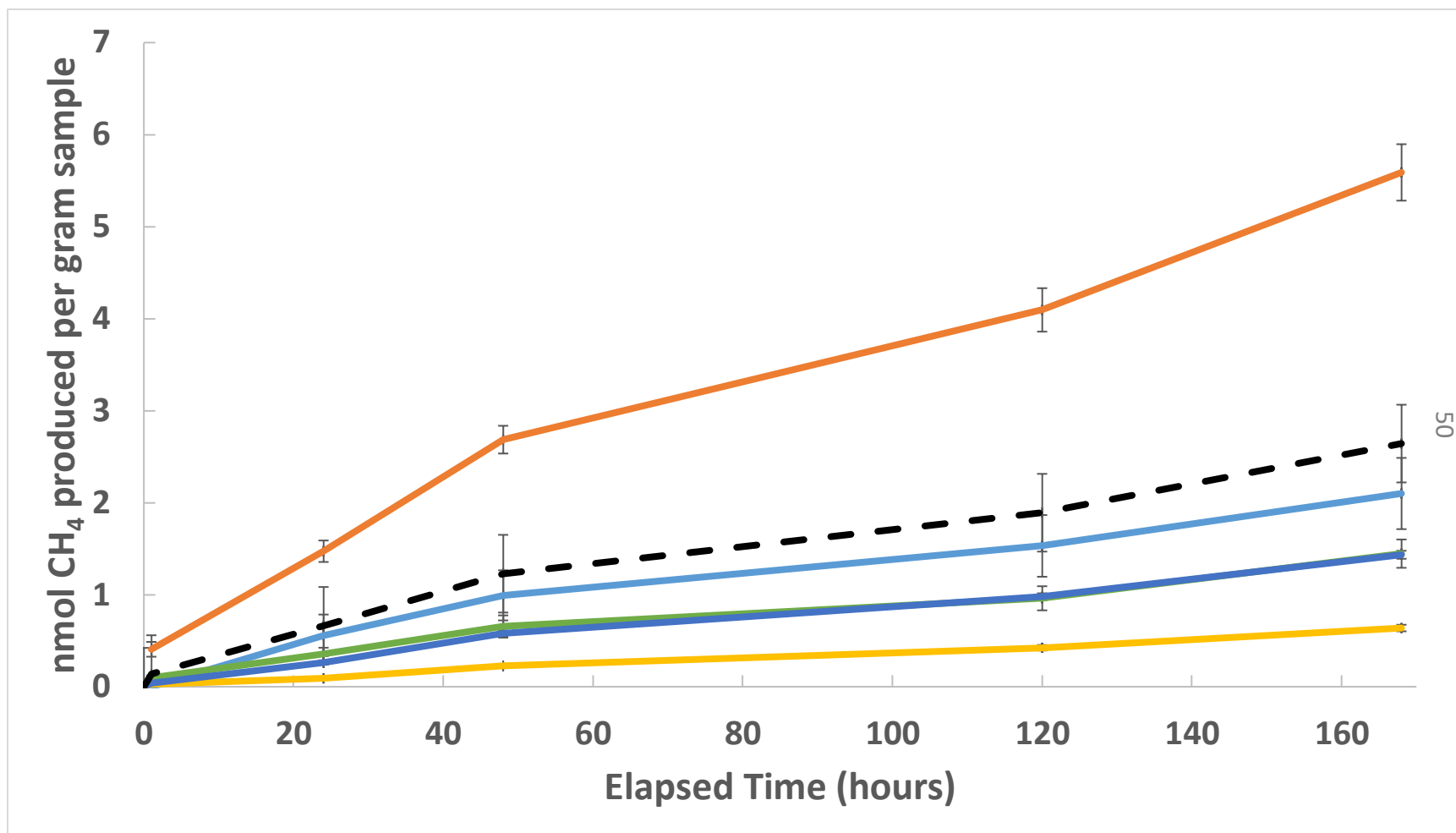


FIGURE 3.10. Methane production from mechanically-activated Icelandic basalt incubated with Ar-sparged deionized water under and Ar headspace at 2°C. The dashed line is the average methane production from basalt. The error bars represent the standard error of triplicate experiments.

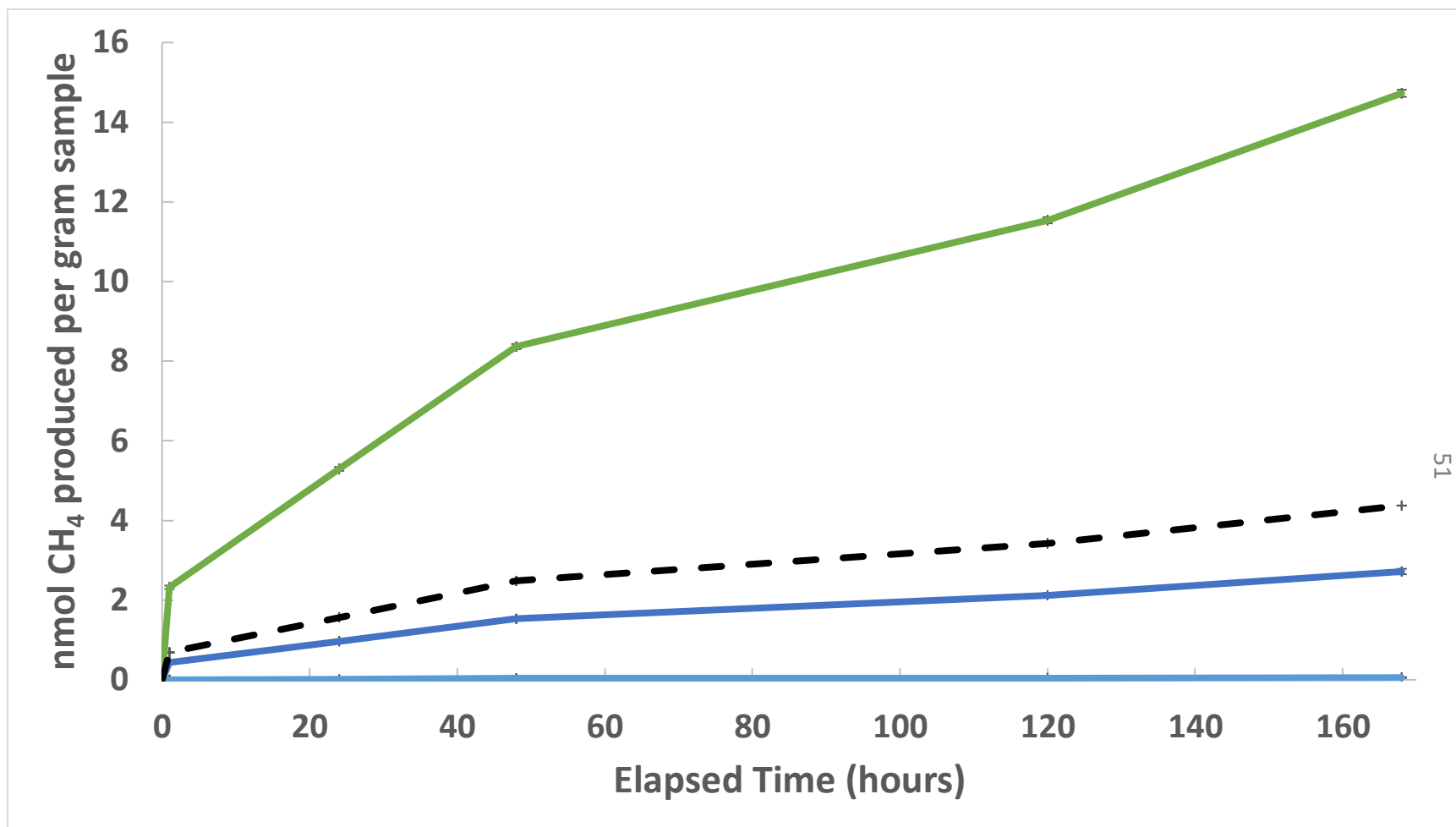


FIGURE 3.11. Methane production from mechanically-activated Icelandic sediment incubated with Ar-sparged deionized water under and Ar headspace at 2°C. The dashed line is the average methane production from sediments. The error bars represent the standard error of triplicate experiments.

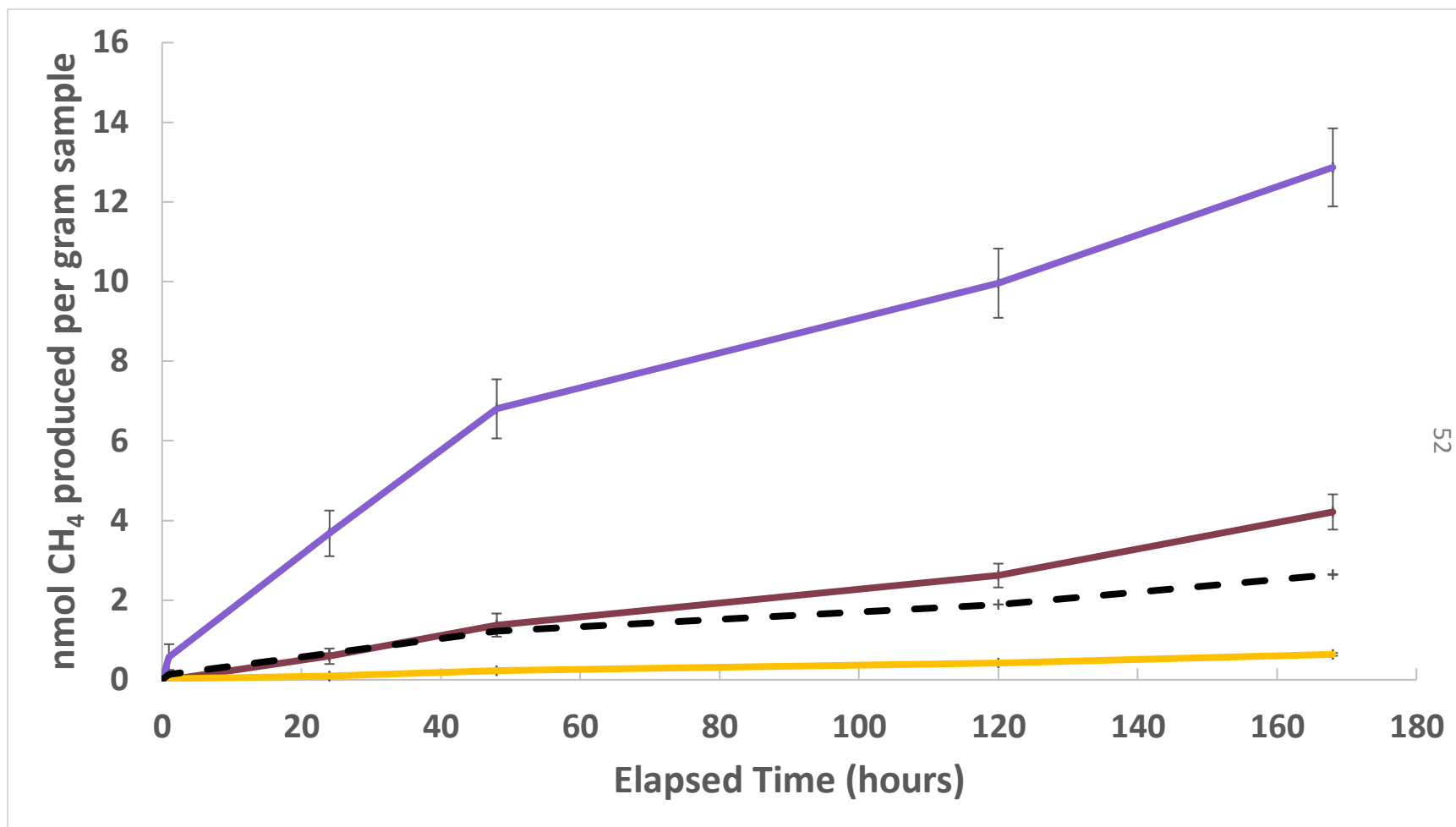


FIGURE 3.12. Methane production from mechanically-activated mineral samples incubated with Ar-sparged deionized water under and Ar headspace at 2°C. The error bars represent the standard error of triplicate experiments.

Consumption of DPPH

The sample groupings seen in the geochemical data do not appear to control the consumption of DPPH by the mechanically-activated samples. Despite quartz and clinopyroxene being the highest hydrogen producers, plagioclase, sediment samples, and Kotlujökull bedrock consume equivalent or greater concentrations of DPPH (Figures 3.13, 3.14, 3.15). Milled sediments from Kaldalónsjökull, Kotlujökull, and Leirufjarðarjökull each consumed $160 \pm 9 \mu\text{M}$, $160 \pm 2 \mu\text{M}$, and $230 \pm 7 \mu\text{M}$ DPPH per gram sample respectively (Figure 3.13). The crushed bedrock sample from Kotlujökull consumed the most DPPH of the bedrock samples, at $160 \pm 2 \mu\text{M}$ DPPH per gram sample followed in decreasing order by Leirufjarðarjökull, $67 \pm 10 \mu\text{M}$, Sólheimajökull $37 \pm 4 \mu\text{M}$ and Kaldalónsjökull north $19 \pm 4 \mu\text{M}$ DPPH per gram sample, respectively (Figure 3.14). Crushed clinopyroxene consumed the greatest amount of DPPH per gram sample of the minerals tested, $130 \pm 20 \mu\text{M}$ followed by plagioclase, $455 \pm 30 \mu\text{M}$, and quartz $40 \pm 0.3 \mu\text{M}$ (Figure 3.15). Calcite did not consume a measurable amount of DPPH.

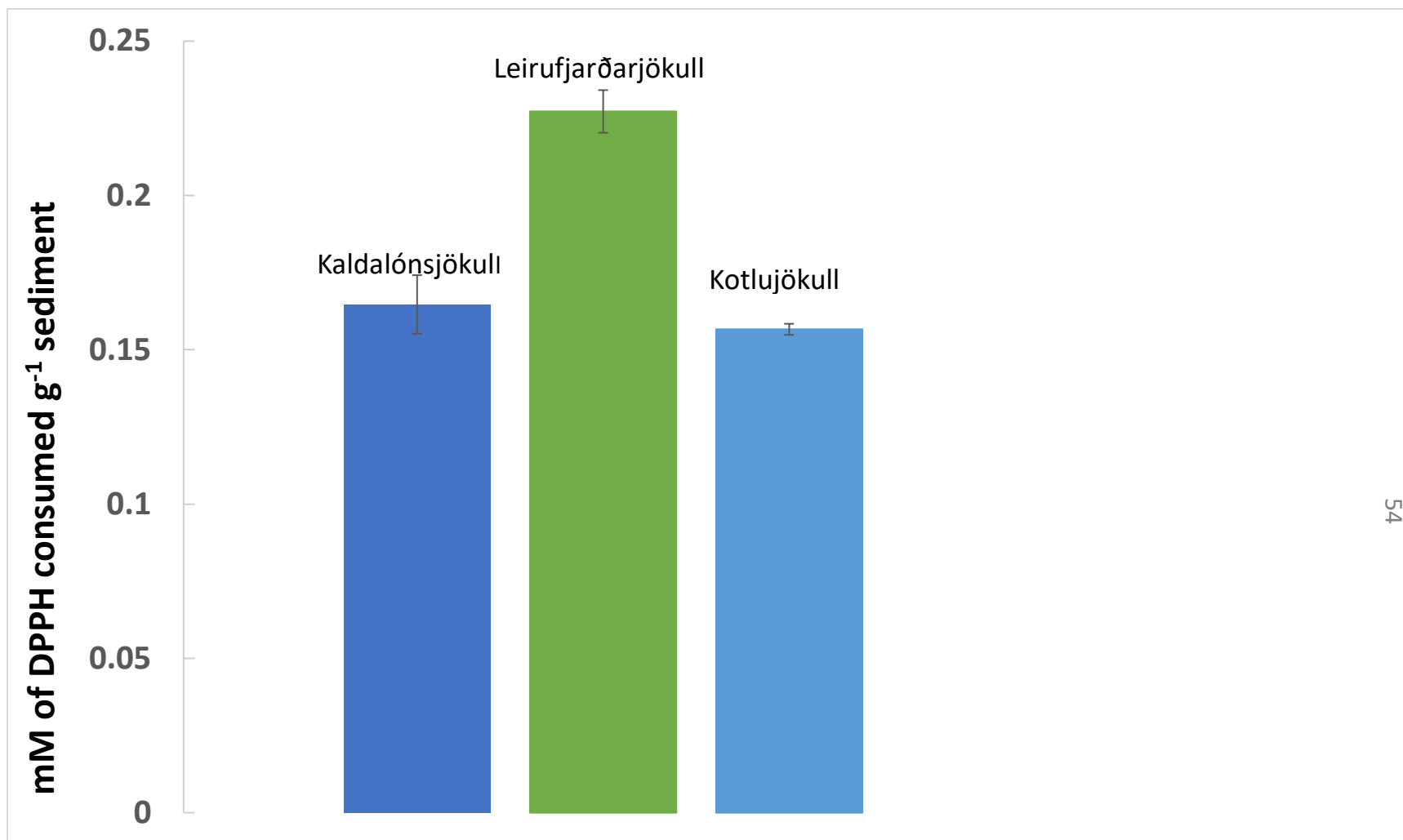


FIGURE 3.13. Consumption of DPPH from mechanically-activated Icelandic glacial sediments. Error bars represent the standard error of triplicate experiments.

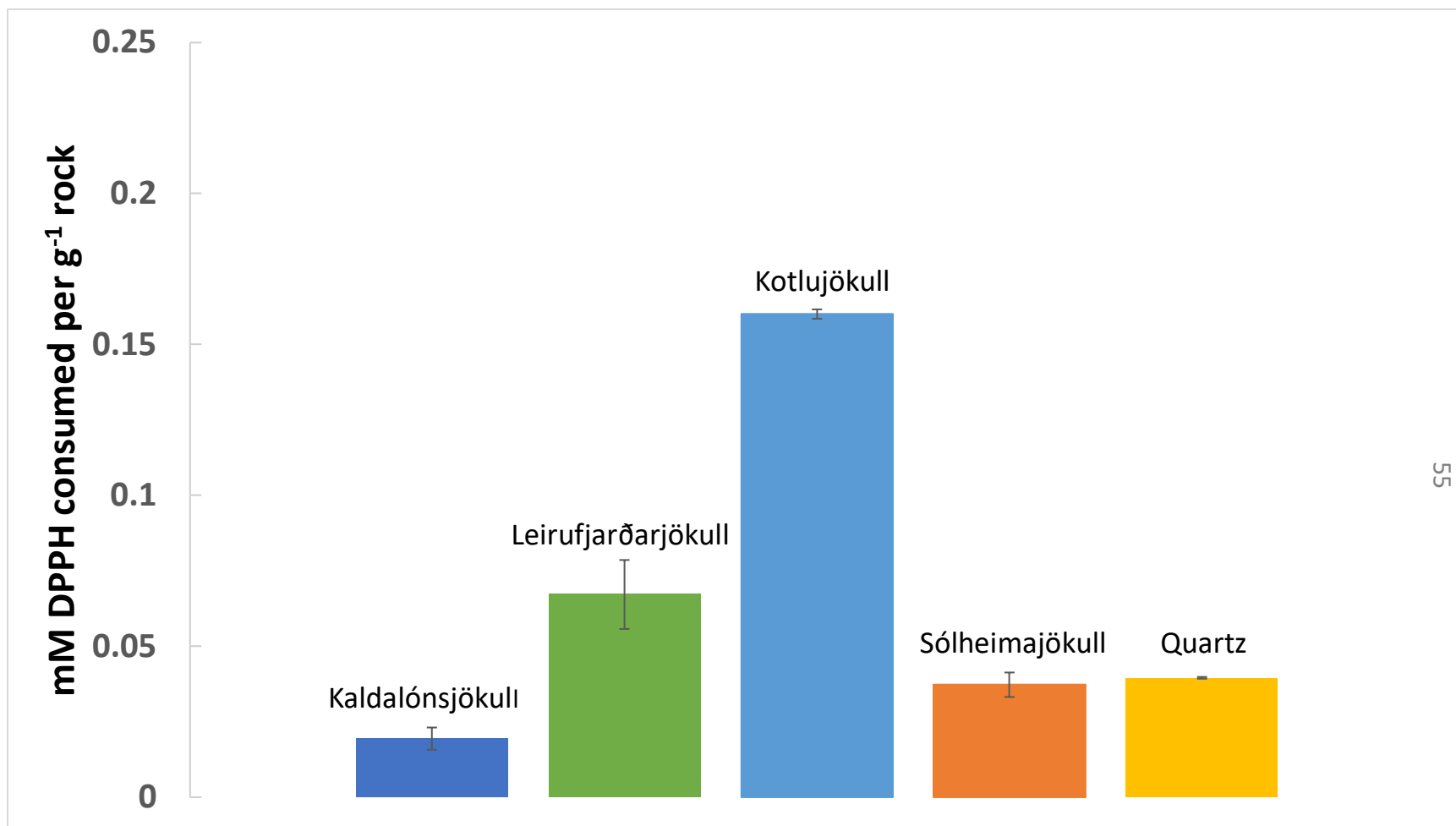


FIGURE 3.14. Consumption of DPPH from mechanically-activated Icelandic basalt and quartz. Error bars represent the standard error of triplicate experiments.

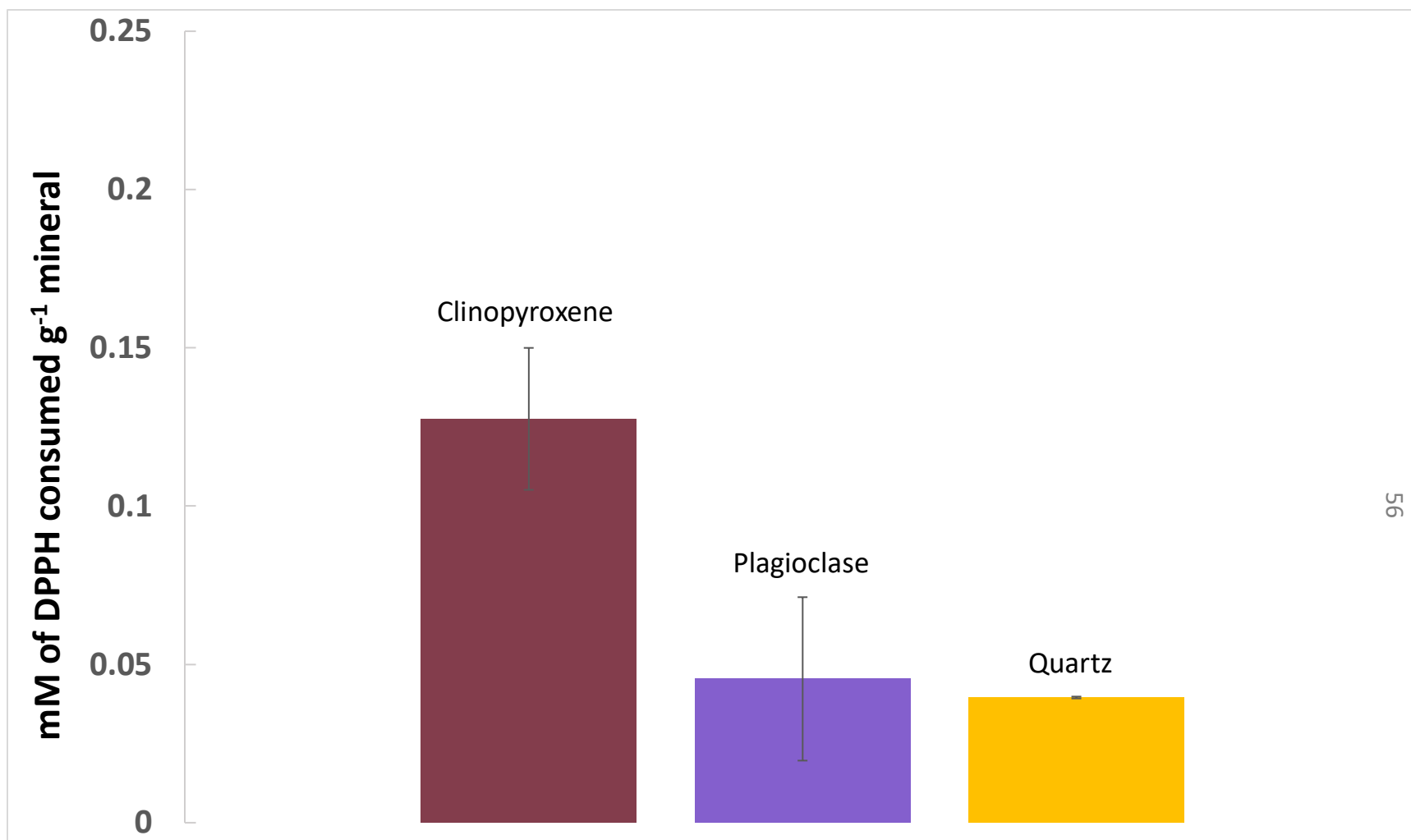


FIGURE 3.15. DPPH consumption from mechanically-activated silicate minerals. Error bars represent the standard error of triplicate experiments.

Hydrogen Peroxide Production

Peroxide production shows a clear grouping ($P = 1.5 \cdot 10^{-7}$) of the samples based on the age of the basalts. The younger basalt samples from Mýrdalsjökull (Sólheimajökull and Kotlujökull), produced on average more than twice the amount of peroxide relative to those from Drangajökull, (Kaldalónsjökull north and Leirufjarðarjökull), $82 \pm 5 \mu\text{M}$ compared to $30 \pm 7 \mu\text{M}$ per gram sample, respectively (Figure 3.16). The milled quartz produced a peroxide value intermediate to the two sets of basalt bedrock at $42 \pm 1 \mu\text{M}$ per gram sample.

Peroxide production from the glacial sediments follows a similar pattern to that of the bedrock samples, with greater production from the Mýrdalsjökull sample, relative to samples from Drangajökull, but in this case the difference is an order of magnitude, $23 \pm 1 \mu\text{M}$ compared to $1.6 \pm 0.1 \mu\text{M}$ per gram sample, respectively (Figure 3.17). Hydrogen peroxide production from the clinopyroxene and labradorite is roughly equivalent to peroxide production from the sediments and about half that of the bedrock samples. Clinopyroxene produced $15 \pm 0.5 \mu\text{M}$ per gram sample and labradorite produced $18 \pm 1.8 \mu\text{M}$ per gram sample (Figure 3.18). Calcite produced low levels of hydrogen peroxide as well at $7 \pm 0.7 \mu\text{M}$, four times lower than the lowest bedrock concentration.

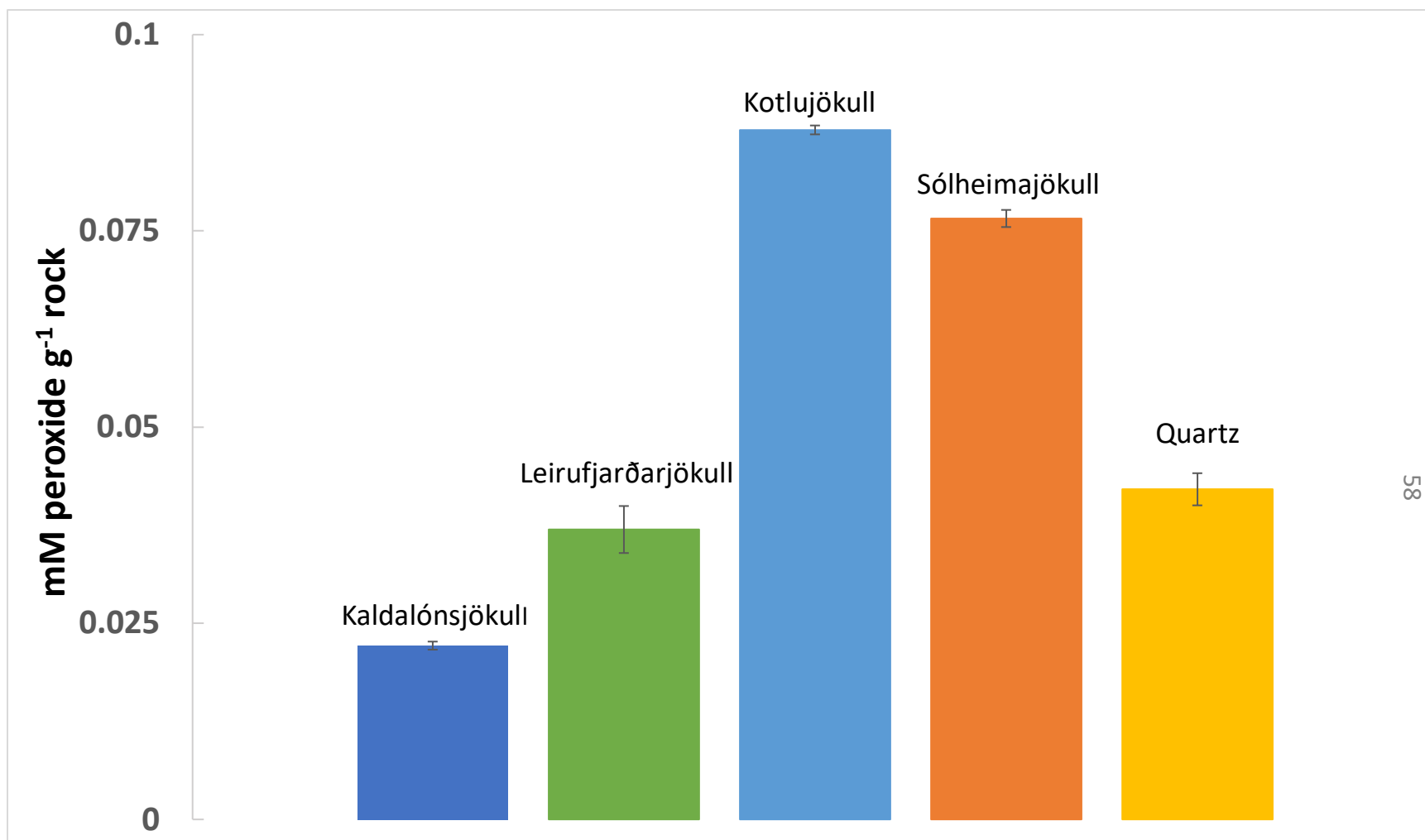


FIGURE 3.16. Hydrogen peroxide production from mechanically-activated Icelandic basalt and quartz. Error bars represent the standard error of triplicate experiments.

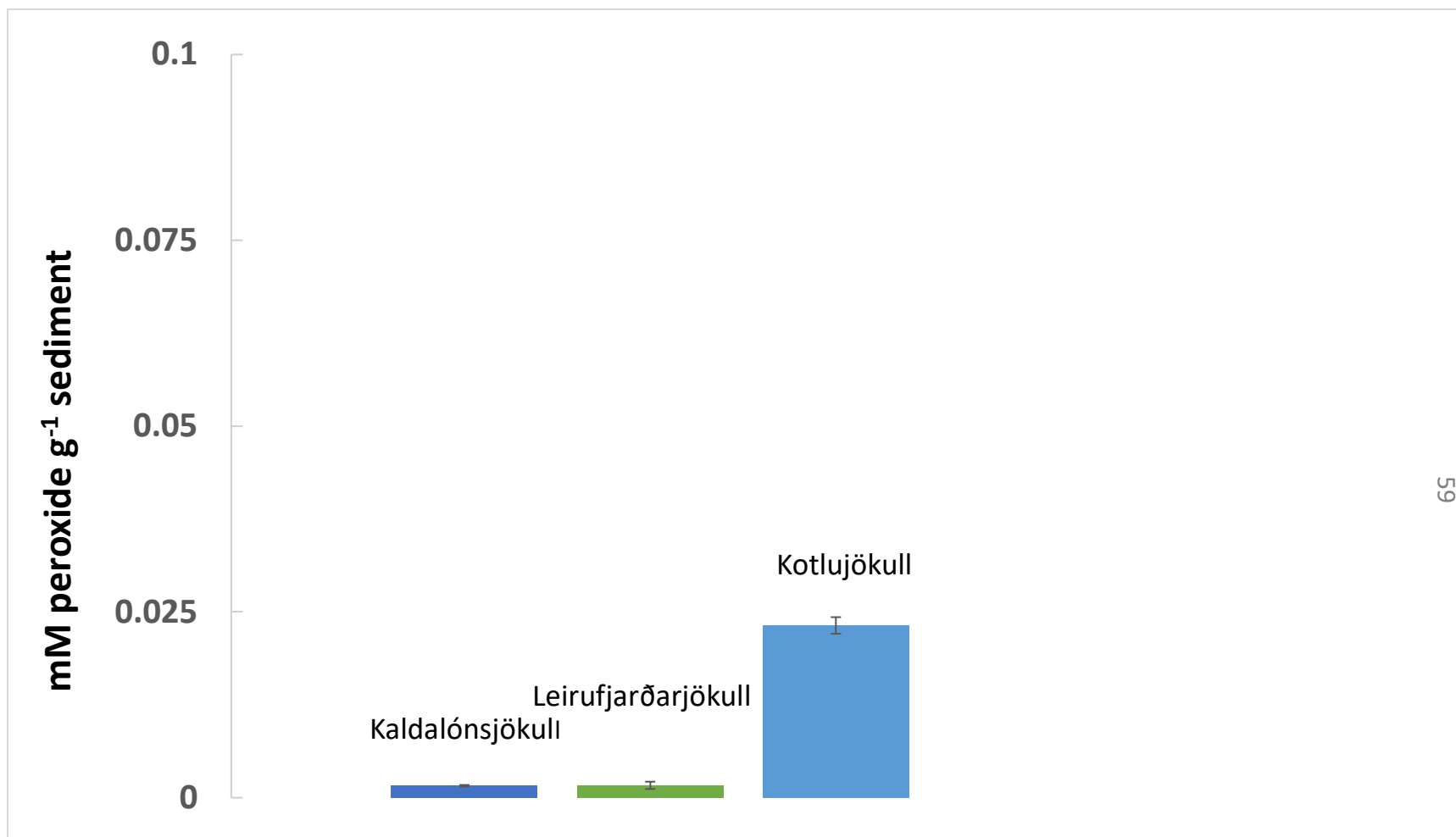


FIGURE 3.17. Hydrogen peroxide production from mechanically-activated Icelandic glacial sediments. Error bars represent the standard error of triplicate experiments.

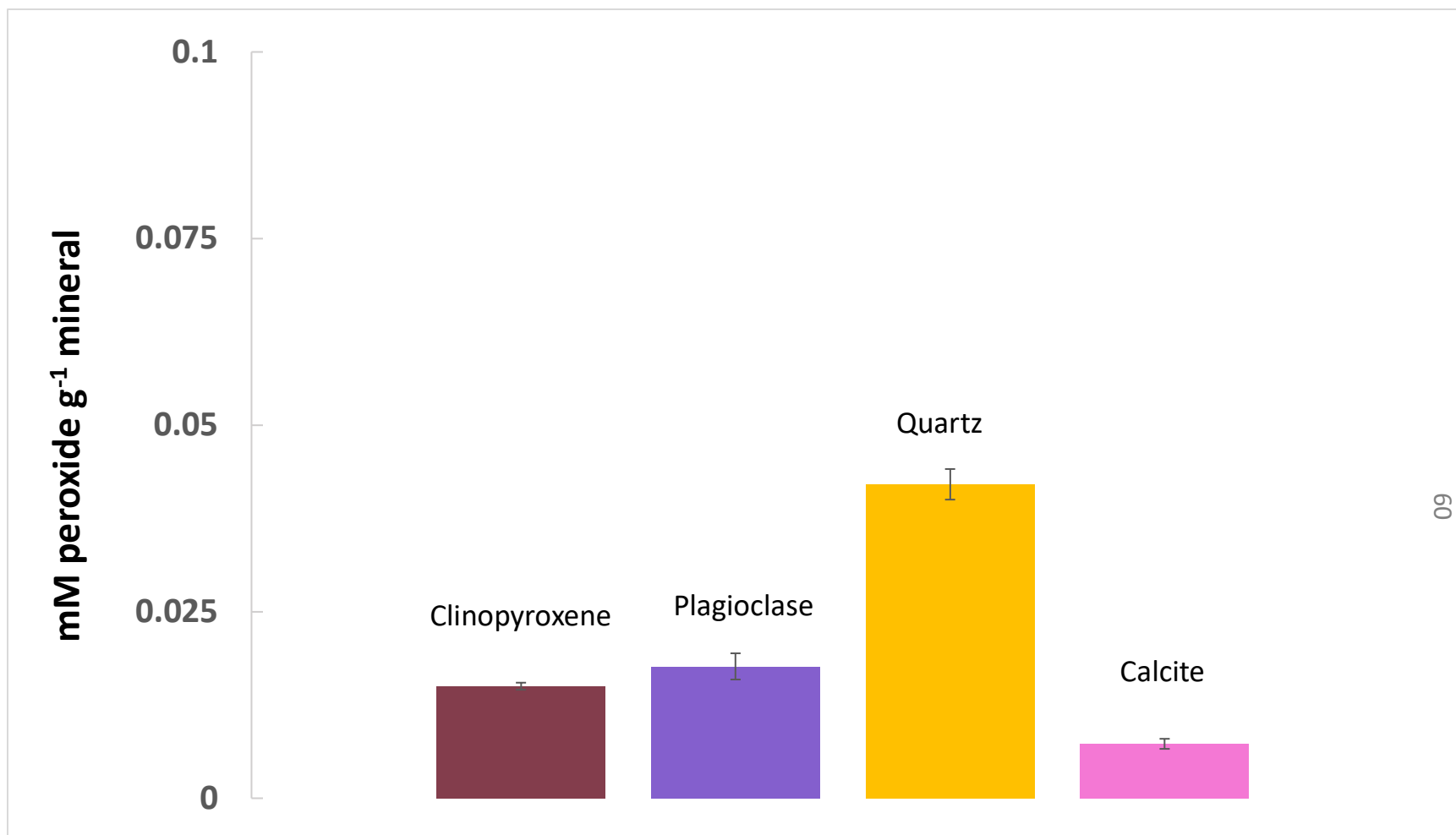


FIGURE 3.18. Hydrogen peroxide production from mechanically-activated silicate minerals and calcite. Error bars represent the standard error of triplicate experiments.

Grain Size and Surface Area

The median grain size of the bedrock samples after an hour of milling was 4.5 microns, compared to 9.0 microns for quartz. The average median grain size of the sediments was 186 microns prior to grinding, which was reduced to 18 microns after ten minutes of grinding. The median grain size of milled clinopyroxene and plagioclase was 31 and 34 microns respectively after 60 minutes of grinding. Table 3.5 shows the 10th (Dx(10)), 50th (Dx(50)), and 90th (Dx(90)) percentiles for grain size distributions.

Average specific surface area (SSA) of bedrock samples after grinding was $1545 \pm 6.38 \mu\text{m}^2$. Average SSA of sediments before grinding was $24.64 \pm 0.18 \mu\text{m}^2$ and after grinding was $573.5 \pm 0.06 \mu\text{m}^2$. Table 3.6 shows the calculated SSA for all samples.

	D_x (10), μm	D_x (50), μm	D_x (90), μm
Kaldalónsjökull	0.43 ± 0.003	1.83 ± 0.04	26.96 ± 0.73
Leirufjarðarjökull	0.44 ± 0.002	2.67 ± 0.22	62.56 ± 12.65
Sólheimajökull	0.53 ± 0.007	7.74 ± 0.47	109.54 ± 17.30
Kotlujökull	0.51 ± 0.01	5.67 ± 0.52	74.22 ± 13.18
Kaldalónsjökull sediment, before grind	41.53 ± 10.93	163.83 ± 11.01	457.67 ± 41.13
Kaldalónsjökull sediment, after grind	1.03 ± 0.37	13.70 ± 0.55	64.06 ± 3.89
Leirufjarðarjökull sediment, before grind	53.34 ± 8.34	192.42 ± 19.49	501.42 ± 72.86
Leirufjarðarjökull sediment, after grind	0.81 ± 0.06	17.23 ± 3.54	102.56 ± 53.15
Kotlujökull sediment, before grind	68.32 ± 5.47	201.72 ± 7.07	469.61 ± 20.04
Kotlujökull sediment, after grind	2.27 ± 1.73	22.32 ± 17.22	157.99 ± 82.36
Quartz, 60 minute grind	0.72 ± 0.02	8.97 ± 0.17	59.05 ± 3.42
Quartz, 10 minute grind	1.04 ± 0.08	18.88 ± 2.87	99.69 ± 26.37
Plagioclase	0.91 ± 0.24	33.58 ± 23.29	238.72 ± 104.12
Clinopyroxene	0.56 ± 0.04	31.23 ± 6.96	201.11 ± 38.15
Calcite	0.57 ± 0.02	9.80 ± 1.24	183.16 ± 56.87

TABLE 3.5. Measured grain size distributions for bedrock and mineral samples after grinding and sediment samples before and after grind.

	Specific Surface Area, μm^2	Standard error
Kaldalónsjökull	1835	0.14
Leirufjarðarjökull	1712	2.67
Sólheimajökull	1185	3.62
Kotlujökull	1447	2.83
Kaldalónsjökull sediment, before grind	37	2.41
Kaldalónsjökull sediment, after grind	612	5.34
Leirufjarðarjökull sediment, before grind	21	1.19
Leirufjarðarjökull sediment, after grind	665	2.43
Kotlujökull sediment, before grind	15	0.29
Kotlujökull sediment, after grind	442	5.98
Quartz, 60 minute grind	811	0.74
Quartz, 10 minute grind	528	1.80
Plagioclase	621	5.40
Clinopyroxene	962	3.44
Calcite	1080	2.84

TABLE 3.6 Specific surface area of bedrock and minerals samples after grindings and sediment samples before and after grind. Surface area was calculated from particle size distribution.

CHAPTER FOUR

DISCUSSION and CONCLUSION

The data presented in this thesis demonstrate that 1) mechanically activated basalt and basaltic sediments produce hydrogen when wetted under anoxic conditions at 2°C, 2) grinding and wetting of basaltic sediments from glaciated catchments produces less hydrogen than basaltic bedrock from the same catchments and 3) the production of hydrogen from sheared and wetted silicate rocks is not solely controlled by the silica content or surface area. Telling et al. (2015) demonstrated that weathering of silicate rocks in laboratory experiments simulating subglacial environmental conditions produced hydrogen, and estimated that the experimental rates of hydrogen production were sufficient to support subglacial hydrogenotrophic microbial communities at Robertson Glacier in the Canadian Rockies, and Leverett Glacier in west Greenland. During mechanical activation, breakage of silicon-oxygen bonds results in the formation of silyl radicals which react with water to form hydrogen gas (Equations 1.1, 1.4 and 1.5) (Narayanasamy and Kubicki 2005; Delogu 2011; Telling et al. 2015). Telling et al. (2015) argued that the reaction rate was primarily controlled by temperature, surface area, and silica content.

Telling et al. (2015) showed correlation between hydrogen production and surface area ($R^2 = 0.53$), with an improved correlation when surface area was normalized to silica content ($R^2 = 0.70$). The results of this study do not show correlation

between hydrogen production and surface area ($R^2 = 0.0012$), even when surface area is normalized to silica content ($R^2 = 0.0073$). Since not all the silica will become mechanically activated to make silica radicals during artificial weathering of silicate rocks and minerals, the production of hydrogen from pure quartz was used as a control since quartz is nearly pure SiO_2 . Hydrogen production from pure quartz was more than four times greater than that from basalt. A lower volume of hydrogen produced from basalt relative to pure quartz was expected given its lower silica content; however, after normalizing the cumulative hydrogen production to each sample's weight percent silica, quartz still produced twice the amount of hydrogen relative to the basalt.

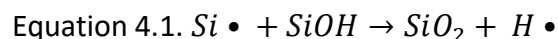
There are several possible explanations as to why hydrogen production was greater for quartz than basalt even after normalizing to silica content. First, the availability of silica at the reactive surface differs between pure quartz and basalt (Damm and Peukert 2009). The other components of basalt reduce the amount of silica available at the reaction surface. Second, there are likely competition reactions from the other components, like oxides, in the basalt that reduced the amount of hydrogen produced. The presence of iron(II) appears to be able to decrease hydrogen production (Kameda et al. 2004), providing a possible explanation for the decrease in hydrogen produced from the basalt samples versus the pure silicate minerals. However, Stevens and McKinley (2000) found that hydrogen production occurred simultaneously with an increasing dissolved iron(II) concentration when basalts were crushed and wetted. This discrepancy is likely due to minerals within the basalt (olivine and pyroxenes) that may

be undergoing serpentinization reactions to generate hydrogen, a reaction dependent on the concentration of Fe(II) (Klein et al. 2013). Third, the proposed reaction implies that it is the total silica surface area controlling the reaction and hydrogen production; however, prior research (Kameda et al. 2004; MacDonald et al. 2018) has demonstrated that the structure of the silicate mineral can impact hydrogen production. The silica in basalt is largely in the form of the silicate minerals plagioclase and clinopyroxene which are a tectosilicate and a single-chain inosilicate respectively, whereas, quartz is pure silica in the form of SiO_2 as a tectosilicate.

Weathering experiments conducted on the individual minerals, plagioclase and clinopyroxene using the same conditions as for the basalt and quartz demonstrated significant differences in hydrogen production, which are most likely related to the mineral structure, given that the rates of hydrogen generation are significantly different even after accounting for silica content and surface area differences ($P = 0.002$). Bulk mineralogy analyses (x-ray diffraction and petrography) were used to determine the mineral composition of the basalt samples in order to test the relevant minerals for hydrogen production. Plagioclase produces hydrogen at a rate similar to that of the basalt and lower than that of quartz. However, the hydrogen production from clinopyroxene was greater than the production from quartz by a factor of five. When the cumulative hydrogen production of clinopyroxene is normalized to silica content (54%), the production from clinopyroxene is still 5 times greater than hydrogen production from basalt. Production from plagioclase, normalized to silica content (54%),

is still on par with production from basalt when normalized to silica content (16.6 nmol H₂ g⁻¹ versus 14.1 nmol H₂ g⁻¹). Stevens and McKinley (2000) report that crushed olivine, when wetted and incubated at 60°C for four days, produced ~10 nmol H₂ g⁻¹. This indicates that mineral structure likely played a role in the amount and rate of hydrogen production.

Dry grinding experiments conducted by Kameda et al. (2004) using phyllosilicates, specifically biotite and muscovite, indicated that hydroxyl groups within the crystal structure could contribute up to 90% of the produced hydrogen. Hydroxyl groups within the crystal structure react with silyl radicals to produce hydrogen in the absence of water (Equation 4.1) (Kameda et al. 2003).



Macdonald et al. (2018) observed hydrogen production after mechanical activation of silicate rocks under dry conditions suggesting that the primary mechanism for hydrogen production in the absence of water involved the reaction of hydroxyl groups within the crystal structure with the silyl radicals (Equation 4.1). Macdonald et al. (2018) demonstrated a correlation between the abundance of micas in a sample and the production of hydrogen during dry grinding. Samples with <5% mica, quartzite and granite, produced 31 and 21 nmol H₂ g⁻¹ sample, respectively. However, two different schists, with 60% and 70% estimated mica by area, produced 164 nmol H₂ g⁻¹ sample

and 407 nmol H₂ g⁻¹ sample, respectively, but no basalts were tested in Macdonald et al. (2018). Future research on pure silicate mineral samples from each of the structural families would help examine potential links between hydrogen production and mineral structure.

Results from this work show no hydrogen production was observed after dry grinding but before wetting from Sólheimajökull and Kotlujökull bedrock and only 0.08 nmol H₂ per gram rock from Kaldalónsjökull (compared to 0.15 nmol H₂ per gram rock immediately after wetting). Only the sample from Leirufjarðarjökull produced greater amounts of H₂ per gram rock from the dry crushing prior to wetting, 0.63 nmol compared to an additional 0.36 nmol H₂ immediately after wetting. This may indicate that hydrogen production from the reaction of hydroxyl groups occurred in this sample. The Leirufjarðarjökull bedrock sample contains trace olivine, which has been altered and may account for this difference. Hydrogen production was not observed in the dry rock control vials throughout the seven day incubation. Therefore, the primary mechanism for hydrogen production from basalt is likely from the reaction of radicals with water (Equations 1.1, 1.4, and 1.5). Differences in mineral structure and composition may account for differences in hydrogen production observed between the crushed clinopyroxene and plagioclase when reacted with the Ar-sparged deionized water. Clinopyroxene, unlike plagioclase, can undergo serpentinization, which has been shown to generate hydrogen through the hydration of Fe(II), albeit not at subglacially relevant temperatures (Mayhew et al. 2013). Hydrogen generation from serpentinization is

constrained by temperature (Klein et al. 2013) and has not been tested at temperatures relevant to the subglacial environment.

Hydrogen Production from Mineral Shearing Requires Fresh Mineral Surfaces

The average cumulative hydrogen production from mechanically activated subglacial sediments over 7 days of incubation at 2°C with anoxic water (1.1 nmol H₂ per gram sediment) was lower than that from basalt (6.8 nmol H₂ per gram rock). This implies that the reaction is greatly enhanced with fresh mineral surfaces. Flowing basal ice and the grinding action of sediments embedded within this ice on underlying sediments and/or bedrock could provide fresh mineral surfaces by comminution (Anderson 2005). Hydrogen production from glacial comminution of silicate bedrock could therefore be active over time scales of tens of thousands of years (Telling et al. 2015), or possibly longer if fresh mineral surfaces are continually being exposed.

Shearing of Silicate Minerals Results in Radical Production

The consumption of 2,2-diphenyl-1-picrylhydrazyl (DPPH) consumption was used as a measure of radical production in the experiments on crushed rock, individual minerals and glacial sediment (following Damm and Peukert 2009). The calcite mineral control did not produce radicals as no consumption of DPPH was observed after mechanical activation. No correlation between DPPH consumption and hydrogen production was observed in these experiments ($R^2 = 0.003$; Appendix A); though radical

production is a requirement for hydrogen production from silicate mineral shearing (Equations 1.4 and 1.5). Crushed plagioclase consumed over three times the amount of DPPH relative to the crushed clinopyroxene, despite clinopyroxene producing about four times more hydrogen. DPPH consumption, and thus radical production, should be correlated to hydrogen production if the only process for hydrogen production is from radical – H₂O reactions (Equation 1.4). This does not appear to be the case; implying that additional controls on the reaction may be impacting hydrogen production such as hydroxyl reactions with silica radicals (Equation 4.1) (Kameda et al. 2003, 2004; Hirose et al. 2011, Macdonald et al. 2018). Additionally, despite micromolar concentrations of radicals produced during grinding, only nanomolar concentrations of hydrogen were produced per gram sample. Telling et al. (2015) observed similar results, in which radical concentrations were three orders of magnitude greater than hydrogen concentrations. This may be due to the effects of temperature, as the reaction rate decreases with temperature (Telling et al. 2015) or due to reactions of the formed radicals with each other and other components of the minerals and grinding bowl (Damm and Peukert 2009; Telling et al. 2015). There was no correlation between the production of radicals and the production of hydrogen peroxide from the mechanical activation of basalts ($R^2 = 0.01$) or from minerals and sediment ($R^2 = 0.04$).

Hydrogen Peroxide Produced during Mineral Shearing

The production of hydrogen peroxide from mechanical activation of silicates is unsurprising given that previous studies have shown hydrogen peroxide production from mechanical activation of quartz and reaction with oxygen (Damm and Peukert 2009), simulated wind saltation of quartz and basalt (Bak et al. 2017), and mechanical activation of gabbro (Balk et al. 2009). Peroxide production followed the chemical groupings of the basalt samples, with the younger samples (from Solheimajökull and Kotlujökull) producing over twice the amount produced from the older samples (from Kaldalónsjökull and Leirufjarðarjökull), 0.082 ± 0.005 mM compared to 0.030 ± 0.007 mM per gram, respectively. The two silicate minerals tested, clinopyroxene and labradorite produced about half as much peroxide (0.015 to 0.018 mM per gram) as the older bedrock samples and over four times less than the younger samples. This implies that hydrogen peroxide production may occur from minerals other than silicates. Calcite also produced hydrogen peroxide, albeit at levels four times lower than the lowest bedrock value. Though hydrogen peroxide is bactericidal, the concentrations produced from grinding (0.056 mmol/L on average) are an order of magnitude lower than even bacteriostatic concentrations (0.15 mmol/L) (Baldry 1983).

Milling of Bedrock and Sediments Liberates Methane

Although not the primary gas of interest for this thesis, methane, was observed after grinding and wetting of bedrock, sediment, and mineral samples. The cumulative

methane production from Icelandic basalt over 7 days incubation at 2°C with anoxic water, 2.6 nmol CH₄ per gram rock on average, was less than that produced from the sediments, 4.4 nmol CH₄ per gram sediment on average. Additionally, methane was released after dry crushing of basalt from Kaldalónsjökull (0.07 nmol CH₄ per gram) and Leirufjarðarjökull (0.44 nmol CH₄ per gram). Macdonald et al. (2018) milled rock samples (igneous, metamorphic and sedimentary) from glaciated catchments in Norway, Greenland, and Canada under dry conditions and measured releases of 3-20 nmol CH₄ per gram and also observed significant releases of hydrogen, carbon dioxide, and minor volumes of other short-chained hydrocarbons during the dry crushing of the rocks. The source of the methane released during the course of these experiments is not known and future work could attempt to determine this by measuring the isotopic ratio of the carbon in the produced methane.

Hydrogen Production Sufficient to Support Subglacial Microbial Communities

The rates of hydrogen production from weathering of Icelandic basalt in a simulated subglacial environment could be sufficient to support hydrogenotrophic microbes. Hydrogen production from basalt (an average of 6.6 nmol H₂ g⁻¹ after 168 hours) is equivalent to or lower than other rock types tested by Telling et al. (2015): gneiss (~6 nmol H₂ g⁻¹), shale (~6 nmol H₂ g⁻¹), quartzite (~15 nmol H₂ g⁻¹), granite (~ 20 nmol H₂ g⁻¹ sample), and schist (~40 nmol H₂ g⁻¹ sample). Telling et al. (2015) argued that the lowest amounts of hydrogen produced in their study, e.g. from the shale, were

sufficient to support a hydrogenotrophic methanogen population in the glacial sediments from that catchment. Using similar logic it would seem crushed basalts could also produce sufficient hydrogen to support hydrogenotrophic metabolism. Incubation studies performed with sediments taken from the same location (Kotlujökull) as the bedrock and sediments used in the weathering experiments were amended with 500 ppm hydrogen and incubated at 4°C in the dark (personal comm. Eric Dunham). These experiments demonstrated a maximum rate of hydrogen consumption of $\sim 13 \text{ nmol day}^{-1} \text{ gram}^{-1}$ dry weight sediment whereas sterilized sediments did not consume hydrogen (personal comm. Eric Dunham). This microbial consumption rate is significantly greater than the cumulative hydrogen production from the glacial sediments from Kotlujökull, $0.6 \text{ nmol gram}^{-1}$ after 7 days, but is unlikely to occur in situ, as the ecosystem would be limited by available hydrogen and nutrients (Hodson et al. 2008). Given that hydrogenotrophic bacteria have been enriched from these sediments, it is logical to assume that sufficient hydrogen must exist in the natural system to support them. Whether that hydrogen is sourced solely from silicate mineral weathering is unknown. Future work could supply the observed bacteria with hydrogen concentrations equivalent to those observed in the weathering experiments to determine if the hydrogen production from the sediments is sufficient to support a community of hydrogenotrophs.

Methane Production from Mineral Shearing Provides a Source of Hydrocarbons for Microbial Communities

Reservoirs of methane have been hypothesized to exist beneath Antarctica (Wadham et al. 2012) and confirmed through fieldwork at least for the Whillans Ice Stream, West Antarctica (Michaud et al. 2017). Subglacially produced methane has been observed emanating from the margin of the Greenland Ice Sheet, in west Greenland (Dieser et al. 2014; Christiansen and Jorgensen 2018; Lamarche-Gagnon et al. 2019). Molecular evidence for an active community of microbes in the glacial sediments, including those capable of utilizing methane, has been demonstrated for both Greenland (Dieser et al. 2014) and Antarctica (Michaud et al. 2017). Glacial comminution of rock can release trapped gases that could potentially be utilized by subglacial microbial communities (Macdonald et al. 2018). The methane released from the reaction of crushed Icelandic basalt with water under anoxic conditions could provide a carbon source for subglacial microbial communities as methane acts as a carbon source for microbial communities underneath the Antarctic Ice Sheet (Michaud et al. 2017) and the Greenland Ice Sheet (Dieser et al. 2014).

Hydrogen Production from Silicate Mineral Shearing Could Support Subglacial Communities on Mars

Cousins and Crawford (2011) hypothesize that hydrogen from volcanic gas could support chemosynthetic metabolisms in the subglacial environments on Mars, both past and present. This work demonstrates that hydrogen gas could be formed, at rates that

might be sufficient to support microbial hydrogenotrophy, in the absence of volcanic hydrogen. This greatly increases the available habitats for life on Mars given that where contact between actively-moving ice and basalt or silicate minerals exists, hydrogen gas could form from mechanical activation and contact with water (Kameda et al. 2003; Telling et al. 2015; Bak et al. 2017). Hydrogen production from mechanically activated basalt could also extend the viability of potential ecosystems supported by periods of glaciovolcanic activity long after volcanism has ceased.

Conclusions

This research has demonstrated that mechanically activating basalt, basaltic sediment, and common silicate minerals under conditions relevant to subglacial environments produces hydrogen gas, radicals, hydrogen peroxide, and methane. Hydrogen gas, a powerful reductant, and methane, a potential carbon source, could help to support microbial ecosystems in subglacial environments. Previously, rates of hydrogen production at subglacially-relevant temperatures from basalt and basaltic minerals were unknown. Additionally, radicals and hydrogen peroxide are produced during grinding of basalt. Previous work (Telling et al. 2015) implied that silica content and surface area were the primary controls on the generation of hydrogen from the reaction of mechanically activated silica and water; however, experiments with pure mineral specimens indicate a role for crystal structure in the reaction.

Future Directions

Though this work used specific parameters (2°C, deionized water, anoxic atmosphere) to simulate a subglacial environment and test for hydrogen production from basalt, future work could focus on quantifying hydrogen production from varied subglacial environments. Though this work used deionized water, subglacial melt waters generally contain micromolar to millimolar concentrations of dissolved ions (i.e. CO_3^{2-} , Ca^{2+} , etc.) from the weathering of rock (Torres et al. 2017). In Iceland, meltwaters are affected by volcanic outgassing of H_2S which increases sulfate concentrations and decreases pH (Lawler et al. 1996). On Mars, near-surface water may be in the form of brines (Martin-Torres et al. 2015). Future experiments could use artificial brines and subglacial water, or even meltwater samples from the Icelandic glaciers to simulate a variety of water chemistries. Additional variables that could be tested include differing basalt geochemistry, water pH, the concentration of oxygen and other atmospheric gases or volcanic gases. The possibility of serpentinization occurring at subglacially-relevant temperatures could also be studied; isotopic studies could be used to differentiate between hydrogen produced from serpentinization and hydrogen produced from the reaction of silicon-based radicals and water. The origin of the methane liberated from the basalt and sediment samples could also be determined via isotopic analysis of the carbon and hydrogen atoms in methane.

Broader Impacts

Mechanical activation of Icelandic basalt under simulated subglacial conditions produces hydrogen at rates that might be sufficient to support hydrogenotrophic bacteria. The abiotic production of hydrogen from the reaction of mechanically-activated basalt and water has implications for maintaining microbial life beneath ice during periods of widespread glaciation on Earth, as well as for the potential for life on Mars and other icy, rocky planetary bodies (Smith and McKay 2005; McKay 2010; Cockell et al. 2011). Isolated and protected from radiation and the thin atmosphere, subglacial environments on Mars could offer refuge to microbial life (Price 2007). Mars was previously likely warmer and wetter (Arvidson 2016; Jakosky et al. 2017), with evidence for subglacial volcanism (Ghatan and Head 2002) and currently there may exist liquid water beneath the southern polar ice cap (Orosei et al. 2018). There exists, then, the possibility of interfaces between rock, water, and ice, both in the past and in the present on Mars, where the process of silicate mineral shearing in the presence of liquid water might be occurring. Where silicate rock, water, and flowing ice co-exist there is the potential for abiotic generation of hydrogen and thus, the potential for life on icy worlds.

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APPENDICES

APPENDIX A

GEOLOGIC AND GLACIOLOGICAL HISTORY OF ICELAND

A Brief Geologic History of Iceland

Iceland is primarily formed of basalt, with thin sediment layers composed of weathered basaltic minerals (Saemundsson 1979). Construction of the basalt plateau that now forms Iceland likely began around 24 million years ago (Thordarson & Larsen 2007). The plateau now stands about 3000m above the sea floor and is about 350,000km² in area, although only about 30% of this total area is above the current sea level. The oldest exposed rocks on Iceland are between 14 and 16 million years old and are present in the volcanically extinct northwest of the island (Thordarson & Larsen 2007). Several active zones of spreading account for the current volcanism in Iceland; these are the Reykjanes Volcanic Belt (RVB), West Volcanic Zone (WVZ), Mid-Iceland Belt (MIB), East Volcanic Zone (EVZ), North Volcanic Zone (NVZ), and two intraplate zones, the Öräfi Volcanic Belt (OVB) and Snæfellnes Volcanic Belt (SVB) (Thordarson & Larsen 2007). The bedrock underneath Drangajökull is likely between 3.3 to 16 million years old and underneath Mýrdalsjökull, the bedrock is less than 0.8 million years old (Thordarson & Larsen 2007).

A Brief Glacial History of Iceland

Glaciation in the Pliocene-Pleistocene (3.1-0.7 Ma) covered the volcanoes throughout central Iceland with ice and subglacial volcanism resulted in uneven topography formed by hyaloclastite and pillow lava (Saemundsson 1979). Subglacial volcanism continued through the Upper Pleistocene (younger than 0.7 Ma)

(Saemundsson 1979). Presently, subglacial volcanism occurs under all Icelandic ice caps except Drangajökull (Thordarson & Larsen 2007). During the Last Glacial Maximum (LGM) around 25 kyr ago, an ice sheet covered almost the entirety of Iceland and marine components of the sheet extended onto the shelves (Figure 1.1) (Ingólfsson et al. 2009). The ice sheet began retreating from its LGM position on the northern Iceland shelf between 18.7 and 16.1 kyr ago, followed by a retreat of the ice sheet from the western Iceland shelf prior to 14.9 kyr ago (Ingólfsson et al. 2009). Global eustatic sea level rise due to the melting of large ice sheets (e.g. Laurentide, Fennoscandian, Barents, Greenland, and Antarctica) (Fairbanks, 1989; Huybrechts, 2002) resulted in sections of the marine components of the Icelandic ice sheet to begin floating, resulting in calving and subsequent collapse of those sections, resulting in retreat beginning at 18.7 kyr (Ingólfsson et al. 2009). Subaerial lava flows in northern Iceland indicate that the portions of the interior of Iceland became ice-free between 15.4 and 13.0 kyr ago (Ingólfsson et al. 2009).

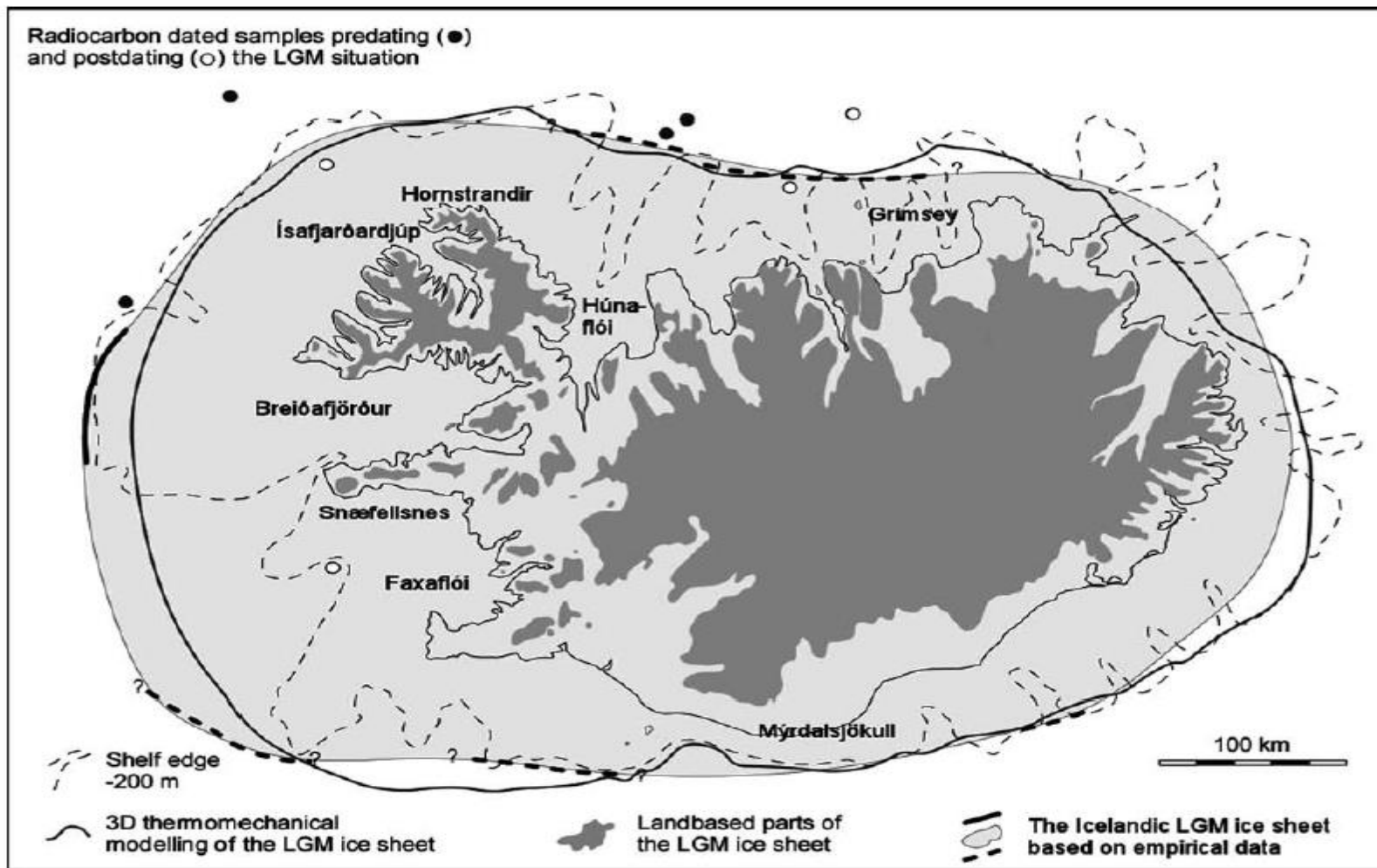


FIGURE 1.1. Extent of the Iceland ice sheet during the Last Glacial Maximum (Ingólfsson et al. 2009). © Elsevier. Reprinted with permission.

During the Younger Dryas (13.0 to 11.5 kyr ago), the Icelandic ice sheet advanced again to cover much of Iceland's land mass; however, throughout north-central Iceland, ice-free regions along the coast still existed (Ingólfsson et al. 2009). The ice sheet began retreating once more between 11.5 to 10.1 kyr ago and the ice caps reached a minimum during the Holocene Thermal Maximum (HTM) at 5.0 kyr ago (Ingólfsson et al. 2009). After the HTM, the ice caps advanced during the Neoglacial period; advances occurred in two main stages, during the Sub-Atlantic period (2.6 to 2.0 kyr ago) and the Little Ice Age spanning from the sixteenth century to the mid nineteenth century (Ingólfsson et al. 2009). Most of the Icelandic ice caps reached their maximum Neoglacial extent at the end of the Little Ice Age and in the time after; outlet glaciers of Mýrdalsjökull did not begin retreating until after 1900 (Ingólfsson et al. 2009). The ice caps began retreating at the end of the Little Ice Age and have continued retreating through to the present day (Ingólfsson et al. 2009). The glaciers and ice caps of Iceland presently cover about 11% of the landmass and are classified as temperate glaciers (Björnsson & Pálsson 2008).

APPENDIX B

SUPPLEMENTARY METHODS AND DATA

Meltwater Chemistry Analyses

Field Measurements

The pH and electrical conductivity (EC) were measured in the field using a Mettler Toledo SevenGo DuoPro pH/Ion/Cond probe.

Meltwaters crimp sealed in clean glass vials were measured for dissolved oxygen within five hours of sampling. Samples were allowed to equilibrate to the surrounding temperature in the sealed vials prior to taking measurements. Dissolved oxygen was measured using a Mettler Toledo OptiOx™ probe.

Meltwaters crimp sealed in clean glass vials were measured for alkalinity within five hours of sampling. A Hach digital titrator was used to titrate samples with 1.6N sulfuric acid to an endpoint of pH 4.5. The pH was monitored using a Mettler Toledo SevenGo DuoPro pH/Ion/Cond probe.

Ion Chromatography

Meltwaters were gulp sampled using clean 1L polyethylene bottles. Bottles were rinsed 3x with sampled waters between each site. Subglacial waters were sampled from flowing outlets as close as possible to the glacial terminus. Supraglacial water from Leirufjarðarjökull was collected from waters flowing over the ice surface at the glacier terminus. Samples were filtered in the field using 0.22µm Sterivex filters, placed into clean 20mL HDPE vials and kept chilled during transport to Montana State University where samples were stored at 4°C.

Analysis of the major anion and cation concentrations were determined via ion chromatography at University of Bristol, UK by Mark Skidmore using a Dionex Ion Chromatograph.

Dissolved Organic Carbon

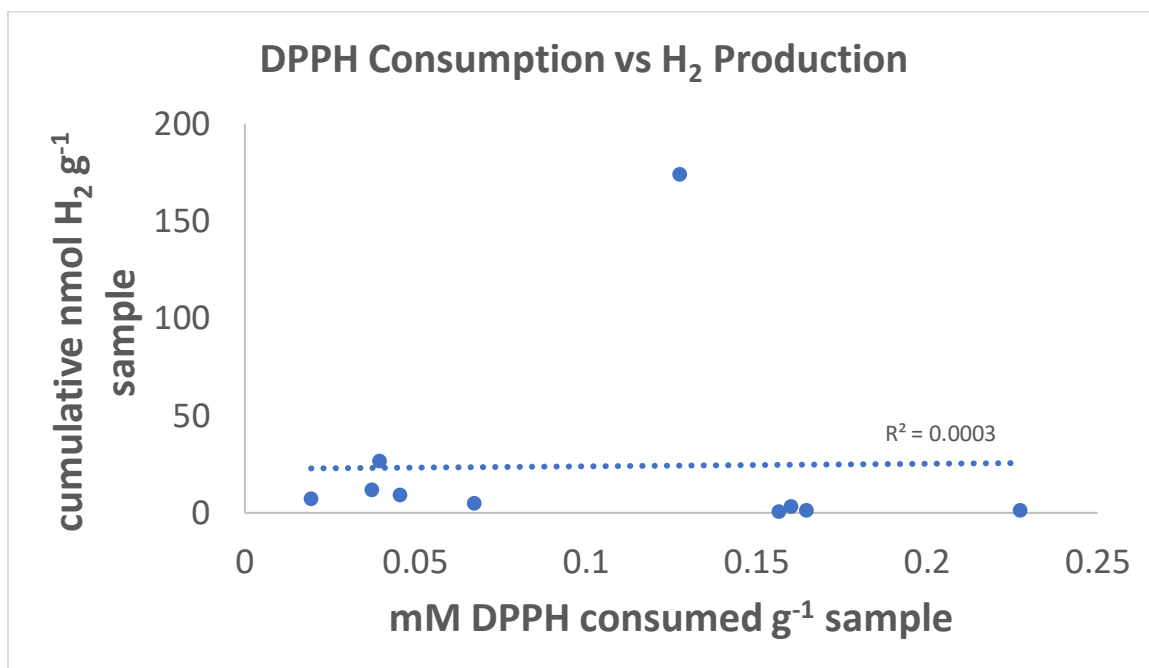
Meltwater samples were crimp sealed into glass vials and filtered within five hours of sampling. Meltwater was filtered using a furnaced glass filter apparatus (rinsed with hydrogen peroxide and sample water between samples) and pre-combusted GF/F filters. Samples were then stored in clean amber glass vials, kept chilled during transport to Montana State University where samples were stored at 4°C. Samples were analyzed by August Steigmeyer at Montana State University via high-temperature oxidation using a Shimadzu organic carbon analyzer.

Meltwater Chemistry Data

Meltwater Chemistry						
	Kotlujökull *	Sólheimajökull *	Kaldalónsjökull North*	Kaldalónsjökull South*	Leirufjarðarjökull subglacial	Leirufjarðarjökull supraglacial
pH	6.76	7.9	6.6	6.5	6.4	6.0
Electrical conductivity, ($\mu\text{S}/\text{cm}$)	82.1	35.8	15.5	15.3	20	4.2
Dissolved oxygen, ppm	10.26	8.47	13.04	Not measured	12.1	Not measured
Alkalinity, CaCO_3 (mg/L)	36.2	11.9	1.4	1.1	3.1	0.6
Non- purgable organic carbon, (ppm)	0.11	0.13	0.15	0.07	0.16	0.51
Total nitrogen, (ppm)	0.11	0.07	0.02	0.02	0.03	0.01

Mineral XRF Data

Major elements, wt% oxide, normalized				
Mineral samples				
	quartz	calcite	clinopyroxene	plagioclase
SiO₂	99.47	0.00	53.88	54.39
TiO₂	0.04	0.03	0.06	0.22
Al₂O₃	0.14	0.29	1.30	23.36
FeO*	0.21	0.11	9.55	4.28
MnO	0.01	0.12	0.24	0.07
MgO	0.05	0.53	11.96	4.20
CaO	0.12	98.91	22.32	9.02
Na₂O	0.00	0.00	0.55	4.01
K₂O	0.00	0.01	0.12	0.42
P₂O₅	0.01	0.01	0.02	0.02
Total	100.00	100.00	100.00	100.00

Hydrogen Production is not Correlated with DPPH Consumption

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