

RESEARCH LETTER

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Key Points:

- Chemical alteration of glaciated volcanic bedrock is dominated by silica dissolution and precipitation
- Dissolved silica in glacial meltwater is greater at more mafic study sites and results in deposition of opaline silica rock coatings
- Past glacial chemical weathering may be responsible for some amorphous silica deposits on the highly mafic surface of Mars

Supporting Information:

- Supporting Information S1
- Data Set S1

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Silica Dissolution and Precipitation in Glaciated Volcanic Environments and Implications for Mars

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Abstract The surface of Mars exhibits strong evidence for a widespread and long-lived cryosphere. Observations of the surface have identified phases produced by water-rock interactions, but the contribution of glaciers to the observed alteration mineralogy is unclear. To characterize the chemical alteration expected on an icy early Mars, we collected water and rock samples from terrestrial glaciated volcanics. We related geochemical measurements of meltwater to the mineralogy and chemistry of proglacial rock coatings. In these terrains, water is dominated by dissolved silica relative to other dissolved cations, particularly at mafic sites. Rock coatings associated with glacial striations on mafic boulders include a silica-rich component, indicating that silica precipitation is occurring in the subglacial environment. We propose that glacial alteration of volcanic bedrock is dominated by a combination of high rates of silica dissolution and precipitation of opaline silica. On Mars, cryosphere-driven chemical weathering could be the origin of observed silica-enriched phases.

Plain Language Summary The planet Mars has glaciers and ice sheets on its surface and probably did in the past. Minerals on the planet's surface form in the presence of water, but it is unclear which minerals may have formed due to liquid water under warm climates versus those formed under much colder climates. In order to study this problem, we collected rocks and water from Mars-like analog sites: glaciated volcanoes. We measured the chemistry of the water and the mineralogy and chemistry of rock coatings found near the glaciers. Both the water and the rock coatings were high in silica. We propose that glaciers alter volcanic bedrock by dissolving and precipitating noncrystalline silica. Silica detected on the surface of Mars could have formed due to similar processes.

1. Introduction

Water ice has significantly modified the surface of Mars, based on features that have been interpreted as residual glacial landforms or ground ice deposits (Lucchitta, 1984; see also Colaprete & Jakosky, 1998; Head et al., 2005; Mangold, 2003; Milliken et al., 2003; Pierce & Crown, 2003; Rossbacher & Judson, 1981; Sharp, 1973; Squyres, 1978, 1979; Squyres & Carr, 1986). Geomorphic and radar data support the presence of near-surface, present-day ice, including mantled scarps with deposits of water ice >100-m-thick, glacier-like forms, viscous flow features, and lobate debris aprons, some of which are thought to be debris-covered glaciers (Dundas et al., 2018; Holt et al., 2008; Levy et al., 2007, 2010, 2014; Pierce & Crown, 2003; Plaut et al., 2009; Souness et al., 2012). These glaciers most likely formed during climate excursions during the Middle to Late Amazonian (Head et al., 2006; see also Fassett et al., 2014; Fastook & Head, 2014) and were covered with debris during or toward the end of their emplacement (Fastook et al., 2014). However, the areal extent and duration of glaciers and ice sheets on the surface of early Mars is poorly constrained.

Recent climate modeling favors a *cold and icy* scenario for early Mars (Forget et al., 2013; Kite et al., 2014; Wordsworth et al., 2013), leading some to propose an early Mars primarily affected by extensive glaciation with transient ice and snow melting (Cassanelli & Head, 2015; Fastook & Head, 2015; Kite et al., 2013; Wordsworth et al., 2013). However, it is unknown what chemical alteration a long-lived cryosphere and associated intermittent glacial meltwater would have caused on the mafic surface of Mars. Understanding the distribution of mineral deposits due to glacial weathering on Mars will help us understand past climates of Mars. The nature of the early Martian climate is a critical unresolved issue in planetary science.

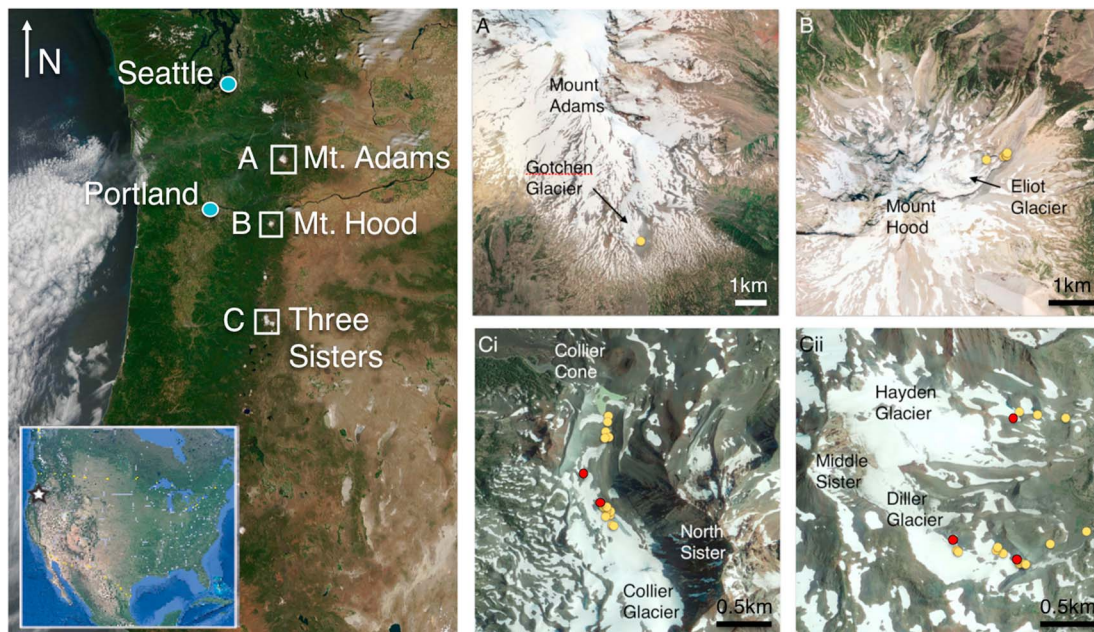


Figure 1. Locations of field sites in the Cascades Range, northwestern United States. The yellow dots indicate water sample locations at each individual site, and the red dots indicate the rock and sediment samples of interest in this study. (a) Gotchen Glacier; (b) Eliot Glacier; (Ci) Collier Glacier; and (Cii) Diller and Hayden Glaciers.

On Earth, comminution of bedrock in wet-based subglacial environments promotes high rates of physical and chemical weathering because it results in a greater amount of reactive mineral surface area (Anderson, 2005; Hallet et al., 1996). In terrestrial glaciated terrains where bedrock is primarily sedimentary, metamorphic, and/or granitic in composition, outwash contains dissolved silica an order of magnitude lower than total dissolved cations (Anderson, 2005; Anderson et al., 1997). In contrast, the few studies of glaciated volcanic systems have reported outwash with dissolved SiO_2 concentrations compared to dissolved total cations (Gíslason et al., 1996; Hodson et al., 2000; Yde et al., 2005). However, studies of glaciated basalts, particularly in Iceland, can be greatly influenced by inputs from hydrothermal systems, making it difficult to discern which solutes or precipitates are directly due to glacial weathering (Cousins, 2015; Cousins et al., 2013). This makes it difficult to tie precipitates directly to glacial alteration. George et al. (2007) calculated that 50% of primary weathered silica in Icelandic basalt catchments should be precipitated into secondary weathering products but did not directly tie them to glacial alteration. The glaciated volcanoes of the Cascades Range, which have little to no input from active hydrothermal systems, are an ideal location to study glacial alteration of Mars-like rocks.

We hypothesize that silica dissolution and precipitation should be predominant alteration processes occurring on actively glaciated volcanic bedrock and that SiO_2 abundance in the parent lithology should control SiO_2 dissolved in glacial meltwaters. To test this hypothesis, we examine glacial weathering of volcanic terrains at four distinct lithologic sites in the Cascades Range, USA. We use water geochemistry and infrared spectroscopy of geologic samples to examine weathering at these sites. Finally, we discuss implications of the observed alteration trends for interpreting remotely measured chemistry and mineralogy on Mars.

2. Site Descriptions and Methods

2.1. Field Sites

To investigate aqueous dissolution and precipitation of silica on a range of volcanic compositions, rock, sediment, and water samples were collected in June 2015 and July 2016 from glaciated volcanics in the Cascade Volcanic Arc (Figure 1). On Mt. Adams, two water samples were collected at Gotchen Glacier ($46^{\circ}9'N$, $121^{\circ}27'W$) in June 2015. On Mt. Hood, five water samples were collected at Palmer and Eliot Glaciers ($45^{\circ}21'N$, $121^{\circ}42'W$) in June 2015. On North Sister, 23 water samples were collected from Collier Glacier ($44^{\circ}10'N$, $121^{\circ}47'W$) in June 2015 and July 2016, and geologic samples were collected in July 2016. On

Middle Sister, 13 water and geologic samples were collected from Diller and Hayden Glaciers (44°9′N, 121°46′W) in July 2016.

Mt. Hood is a composite stratovolcano made up of dacite pyroclastic flows and lavas with smaller outcrops of basalt and andesite (Wise, 1969). Mt. Hood contains the highest silicic composition bedrock in this study (62–66% SiO₂). Eliot Glacier is a 1.6-km² glacier on the northeast flank of Mt. Hood adjacent to and partly overlying dacitic block and ash flows (Crandell, 1980; Hamilton & Havig, 2017; Jackson & Fountain, 2007).

Mt. Adams is a composite stratovolcano composed of andesite, basaltic andesite, and basalt flows, with small amounts of dacite (53–65% SiO₂; Hildreth & Lanphere, 1994). Mt. Adams represents an intermediate composition between the mafic Three Sisters complex and the silicic Mt. Hood. Gotchen Glacier is on the southeast flank of Mt. Adams (Sitts et al., 2010).

The Three Sisters volcanic complex encompasses the most mafic presently glaciated mountains in the mainland United States. North Sister and Middle Sister are composite stratovolcanoes. North Sister is primarily composed of basaltic andesite with relatively small exposures of dacite and andesite (Hildreth et al., 2012; Schmidt & Grunder, 2009). Collier Glacier on North Sister overlies a combination of basaltic andesite, andesite, and dacite (54.5–64.5% SiO₂), whereas Diller and Hayden Glaciers on Middle Sister have a more mafic substrate (52.2–56.2% SiO₂; Hildreth et al., 2012; Mercer & Johnston, 2008; Schmidt & Grunder, 2011). Subglacial and proglacial bedrock exposures in the Three Sisters are dominated by unaltered mafic units (Hildreth et al., 2012; Scudder et al., 2017).

2.2. Methods

Measurements of temperature, pH, dissolved oxygen, and conductivity were made in meltwaters at the Three Sisters using a YSI Professional Plus meter and probes (YSI, Yellow Springs, OH, USA) and at Mt. Adams and Mt. Hood using a WTW 330i meter and probe (Xylem Analytics, Weilheim, Germany). Figure 1 details the sampling locations. Dissolved silica was measured in the field using a Hach DR 1900 portable spectrophotometer (Hach, Loveland, CO, USA). All water was filtered through 25-mm-diameter, 0.2 μm polyethersulfone syringe filters (Whatman, GE Healthcare Bio-Sciences, Pittsburgh, PA, USA) and stored in presoaked (18-mΩ/cm deionized water) centrifuge tubes until analysis. Major cation (Na⁺, K⁺, Ca²⁺, and Mg²⁺) and anion (SO₄²⁻, Cl⁻, Br⁻, and F⁻) concentrations of the collected water samples were measured with ion chromatography (Dionex IonPac AS11 analytical and IonPac AG11 guard columns for anions; Dionex IonPac CS12A analytical and IonPac SG11 guard columns for cations; conductivity detection) at Arizona State University (ASU), and trace elements (e.g., Al and Fe) were determined with high-resolution inductively coupled plasma mass spectrometry (iCap-Q ICP-MS; Kinetic Energy Discrimination mode) at ASU. Dissolved inorganic carbon (DIC) was determined through elemental analysis coupled to isotope-ratio mass spectrometry (OiWet oxidation total organic carbon analyzer coupled to a Thermo Delta Plus Advantage mass spectrometer; see Havig et al., 2011, for details) at ASU. DIC represents the combination of dissolved CO₂ (as H₂CO₃) and bicarbonate (HCO₃⁻), the predominant forms of DIC present over the pH ranges observed (~4.0–9.0).

Visible to near infrared (VNIR; 0.35- to 2.5-μm spectral range; 3- to 10-nm spectral sampling) reflectance spectra of rock outcrops and proglacial sediments were collected in situ at the Three Sisters using a TerraSpec contact field spectrometer (ASD, Inc., Boulder, CO, USA). Rock and sediment samples were collected concurrently for laboratory analysis. Whenever possible, samples were collected at the same location at water samples (Figures 1 and S2). Thermal infrared (TIR; 5–25 μm) emission spectra of these samples were collected in ASU's SpecLab facility at the Mars Space Flight Facility using a Nicolet Nexus 670 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) configured to measure emitted energy (Ruff et al., 1997). In order to increase the signal-to-noise ratio, samples were heated to 80 °C. Over the course of ~3 min, 128 spectra were collected and averaged, from 400–2,000 cm⁻¹ (5–25 μm) with 2-cm⁻¹ spectral resolution. In order to calibrate raw data to radiance, blackbodies at 70 °C and 100 °C were measured (Christensen & Harrison, 1993). Radiance values were then normalized to the Planck curve for the derived sample temperature and transformed to emissivity spectra (Ruff et al., 1997).

In order to perform microscopic analysis, rock samples were prepared using methods similar to Minitti et al. (2007). Microscopic texture and chemistry of polished cross sections were collected with a JOEL 7600F scanning electron microscope at National Aeronautics and Space Administration Johnson Space Center. Backscattered electron imaging allowed composition and texture to be determined, and

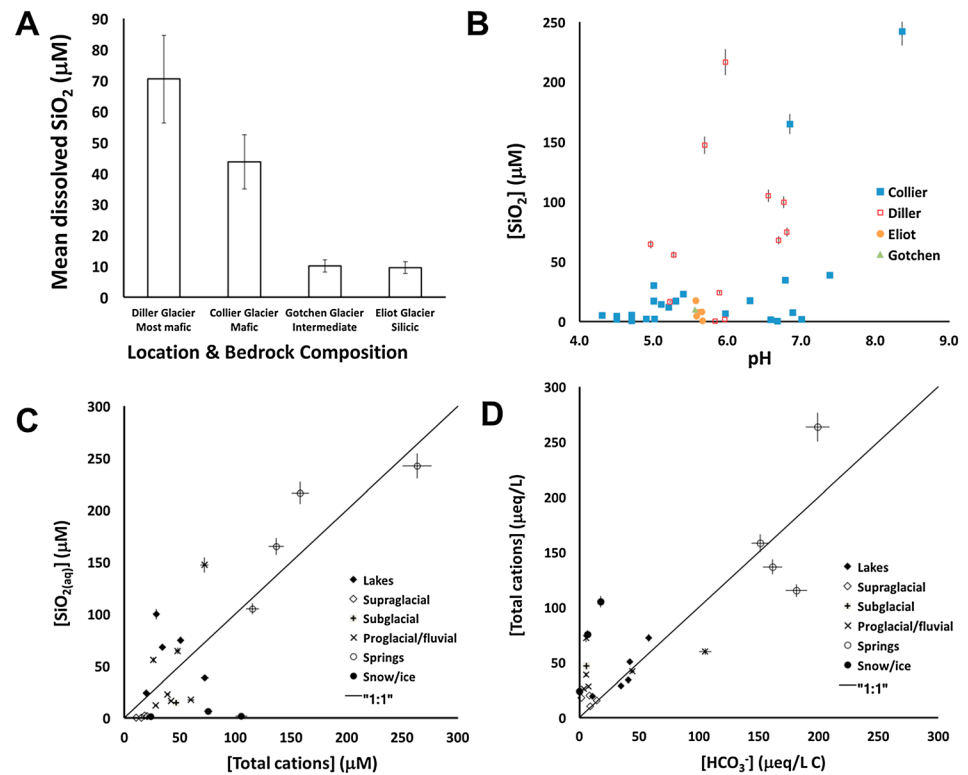


Figure 2. (a) Mean dissolved silica in water samples at each of the four field sites. (b) pH versus dissolved silica concentration at the field sites. (c) Concentration of total dissolved major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) versus dissolved silica concentration for various parts of the hydrologic systems at the Three Sisters. (d) Concentration of bicarbonate versus concentration of total cations at the Three Sisters.

qualitative chemistry was measured using electron-dispersive spectroscopy. All scanning electron microscope measurements were made at current levels between 0.5 and 0.7 nA and an accelerating voltage of 15 kV with a focused beam (~1- to 2-mm spot).

3. Results

3.1. Aqueous Geochemistry

Across the four studied sites, aqueous geochemical measurements indicate that dissolved silica ranges from 0.399 μM to 242.2 μM (Figures 2a and 2b). At Diller Glacier, dissolved silica concentrations range from 0.183 to 216.4 μM , pH ranges from 5.22 to 6.82, summed dissolved major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) range from 15.4 to 158.2 μM , and DIC concentrations range from 14.32 to 181.43 $\mu\text{mol C/L}$, which equates to calculated HCO_3^- concentrations of 3.72 to 181.43 $\mu\text{eq/L}$. At Collier Glacier, dissolved silica concentrations range from 0.74 to 242.2 μM , pH ranges from 4.3 to 8.36, total dissolved major cations range from 10.4 to 263.3 μM , and DIC concentrations range from 0.00 to 221.17 $\mu\text{mol C/L}$, which equates to calculated HCO_3^- concentrations of 0.00 to 199.05 $\mu\text{eq/L}$. At Gotchen Glacier, dissolved silica concentration was 10.03 μM , and pH was measured as 5.56. One sample was collected from Gotchen Glacier from the proglacial lake (no other proglacial outwash present); it is considered representative of average proglacial runoff. At Eliot Glacier, dissolved silica concentrations range from 0.63 to 17.28 μM , and pH measurements range from 5.57 to 5.66. For all sites, dissolved SO_4^{2-} ranges from not detectable to 1.07 μM . Dissolved chemical concentrations are reported in Data Set S1 in the supporting information.

Aqueous silica is found in meltwater across all measured pH values (Figure 2b), but dissolved silica concentrations generally increase with increasing pH, which is consistent with silica solubility increasing with pH (e.g., McLennan, 2003). However, the effects of pH cannot explain differences between the sites. Notably, the glacier with the most mafic substrate, Diller, also exhibits the highest silica concentrations. Mean

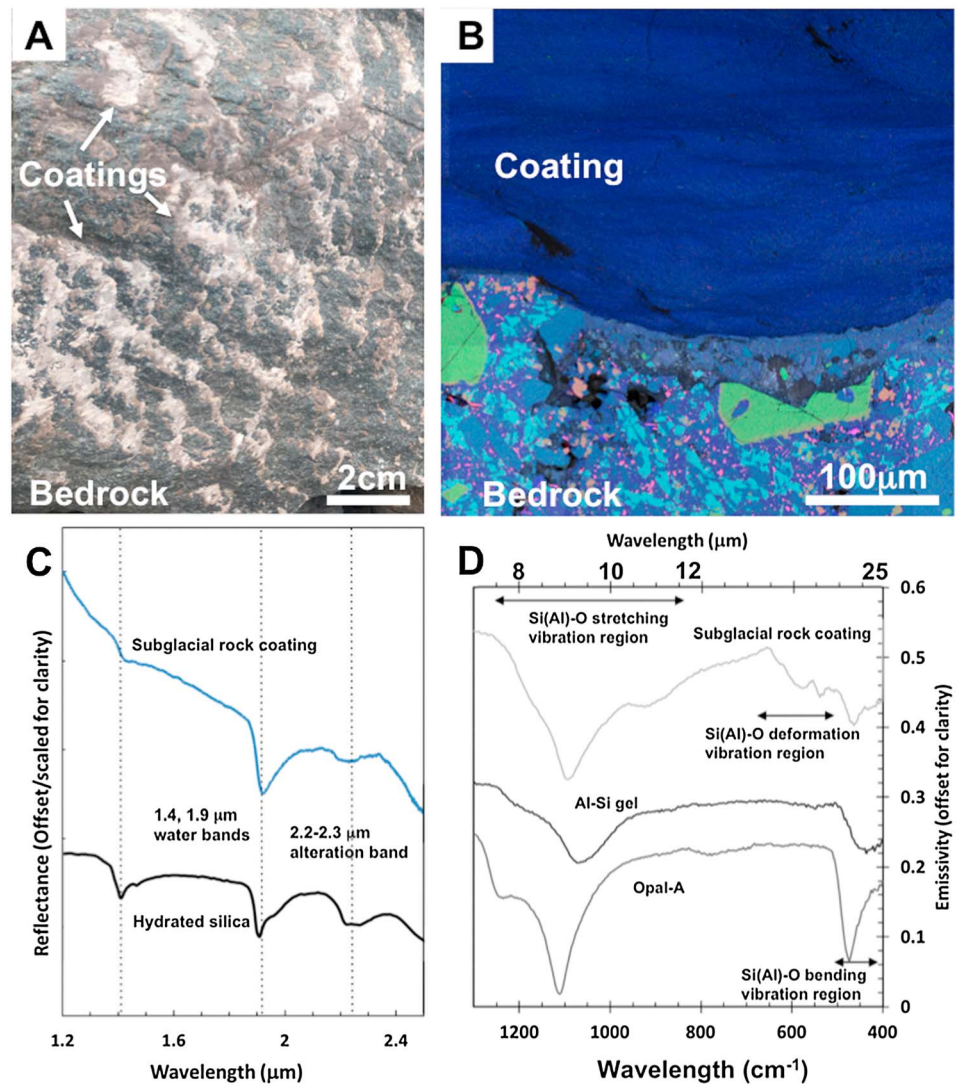


Figure 3. (a) Context image of rock coatings on recently deglaciated mafic bedrock. (b) An scanning electron microscope-derived false color image of the cross section of a rock coating. Image is composed of electron-dispersive spectroscopy chemical maps superimposed on a backscattered electron image. Colors represent elements: Fe is red; Mg is green; Si is blue; Ca is cyan; Ti is magenta; and P is yellow. (c) Representative visible to near infrared field spectrum of a rock coating, which displays similar absorptions to hydrated silica (U.S. Geological Survey Spectroscopy Laboratory Opal TM8896). (d) Representative thermal infrared spectrum of a rock coating which most resembles a combination of aluminosilicate gel and opaline silica (Michalski et al., 2003; Rampe et al., 2012).

dissolved silica concentrations increase as the underlying bedrock becomes more mafic (Figure 2a). One possible source of error with this result is the low sampling frequency at Eliot and Gotchen Glaciers, but these water samples can be considered representative of their watersheds.

Across the hydrologic systems at Three Sisters, dissolved silica concentrations are comparable to the sum concentrations of major dissolved cations (Figure 2c). Lakes, moraine-sourced springs, and proglacial streams exhibit dissolved silica concentrations that are greater than those observed in melted snow and glacial ice. The highest silica concentrations at the Three Sisters were measured in moraine-sourced spring waters.

3.2. Infrared Spectroscopy

At North and Middle Sisters, white and brown striated rock coatings on recently deglaciated lava flows (Figure 3a) were found, indicating subglacial precipitation of dissolved phases. While these types of coatings were not collected from Mt. Hood or Mt. Adams, observations by Hallet (1975) suggest that they exist throughout the Cascades. The rock coatings are characterized by pronounced lineations parallel to the

local glacial striations, suggesting that they formed in direct contact with actively sliding ice. The thickest coatings are found on the lee sides of local topographic highs on the abraded rocks, consistent with subglacial regelation films described by Hallet (1975, 1976). VNIR and TIR spectra of the coatings are both consistent with hydrated silica (Figures 3c and 3d). In the VNIR spectrum (Figure 3c), the Si-OH combination bands near 2.21 and 2.25 μm are consistent with hydrated silica (e.g., Rice et al., 2013). In the TIR spectrum (Figure 3d), the sharp, V-shaped absorption in the Si(Al)-O stretching region ($\sim 950\text{--}1,250\text{ cm}^{-1}$) is consistent with highly polymerized silicate phases (i.e., poorly crystalline secondary silicates) similar to opal or aluminosilicate gel (Michalski et al., 2006; Rampe et al., 2012). Additionally, spectra of proglacial sediments, glacial flour generated through subglacial grinding, are also consistent with a hydrated silica component (Figure S2).

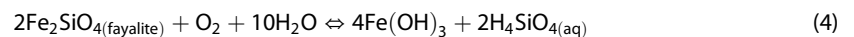
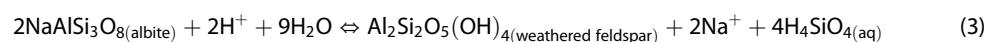
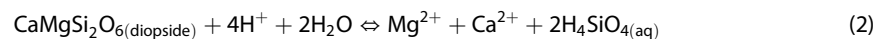
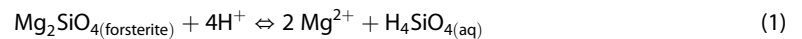
3.3. Scanning Electron Microscopy

Backscattered electron images indicate that the coatings range from 30 to 225 μm in thickness and drape over the substrate microtopography (Figures 3b and S1). Electron-dispersive spectroscopy mapping indicates that the rock coatings are enriched in silica compared to the underlying bedrock. The coatings contain internal laminations and unconformities (Figure S1). These measurements are consistent with those described by Hallet (1975) of silica-rich subglacial regelation films.

4. Discussion

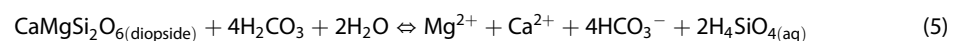
Silica dissolution and precipitation is a predominant alteration process in the volcanic field sites studied here. On average, higher concentrations of dissolved silica are found at the more mafic glaciated volcanic sites compared to more felsic glaciated volcanic sites (Figure 2a). These results are most likely broadly applicable to glaciated volcanic regions, as Cascadia represents a wide range of typical volcanic compositions (Hildreth et al., 2012).

Weathering at these volcanic sites is thought to be due to one or more of the following hydrolysis (McLennan, 2003) and oxidation reactions expected for minerals found in basaltic rocks:



Free hydrogen ions in reactions (1)–(3) are produced from dissolution of CO_2 into water and subsequent deprotonation of the resulting carbonic acid ($\text{H}_2\text{CO}_3 = > \text{H}^+ + \text{HCO}_3^-$). Reaction (4) is most likely primarily driven by subglacial microbial communities dependent on oxidation reactions for energy (e.g., Boyd et al., 2014; Hamilton et al., 2013; Mitchell et al., 2013; Raiswell et al., 2008), which are likely to be occurring at the Three Sisters based on water chemistry (Fe concentrations are comparable to major dissolved ions at some locations; see Data Set S1).

Figure 2d shows concentrations of bicarbonate with respect to concentrations of total cations at the Three Sisters. The measurements plot close to the 1:1 line, indicating that the total positive charge from cation release is balanced by negative charge produced from dissolution of CO_2 into water and subsequent deprotonation of the resulting carbonic acid ($\text{H}_2\text{CO}_3 = > \text{H}^+ + \text{HCO}_3^-$). Dissolved SO_4^{2-} is a minor component compared to bicarbonate in all sampled waters. This correlation thus implies that the majority of the weathering on glaciated volcanic bedrock at the Three Sisters is controlled by carbonic acid dissolution, as opposed to sulfide oxidation or carbonate dissolution. The full weathering reaction can be described by combining the dissolution reaction of (for example) diopside (reaction (2)) with the deprotonation of carbonic acid:



Silica is the most abundant dissolved constituent in these glacial meltwaters, and concentrations are comparable to the total dissolved cation concentrations (Figure 2c). This is a direct result of these hydrolysis reactions (e.g., reaction (5)), where dissolved silica ($\text{H}_4\text{SiO}_4(\text{aq})$) is produced in high quantities relative to other cations. In

previous studies on glaciated sedimentary or metamorphic lithologies, silica fluxes tend to be an order of magnitude lower than total cation fluxes (e.g., Anderson, 2007; Anderson et al., 1997; Hodson et al., 2002, 2000). Based on our results and previous studies, silica dissolution is the predominant reaction in these volcanic systems because of the absence of carbonate mineral dissolution, which would else result in CO₂ saturating the aqueous system and inhibiting silicate weathering (Taylor et al., 1999; Yde et al., 2005). Mafic volcanic rocks are exceptionally susceptible to silica mobilization during near-surface alteration, due to the high concentration of soluble minerals (e.g., plagioclase) versus the high concentration of relatively insoluble quartz found in felsic rocks (McLennan, 2003). Additionally, the bedrock at these sites contains reactive volcanic glass, which, Gíslason and Eugster (1987) and Hausrath et al. (2008) suggested, is more rapidly dissolved than olivine under conditions of low-temperature alteration.

Mafic rocks have a high abundance of soluble silicate phases compared to felsic rocks (McLennan, 2003). As a result, silica is expected to be highly mobile during near-surface alteration of Mars-like basaltic rocks (Soderblum, 1992), at a wide range of temperatures, pressures, and fluid chemistries. McLennan (2003) found that silica loss in basalt weathering profiles outstrip those of granodiorite and that silica is highly mobile during near-surface alteration of mafic rocks. Taylor et al. (1999) observed that terrestrial basalt weathered twice as fast as colocated felsic and intermediate bedrock, and Hodson et al. (2000) found that weathering of glacierized Icelandic basalts consumed more CO₂ than that of glacierized plutonic or metamorphic lithologies. Additionally, Stefánsson and Gíslason (2001) found that silica fluxes increased with increasing content of glass in deglaciaded Icelandic basalts. This field study is consistent with previous work and better constrains the effects of residence time and cold temperatures across four distinct volcanic lithologies: With similar weathering mechanisms at work, silica is more highly mobile in the mafic, cold, Mars-like system than at the more felsic sites.

There is considerable variability in dissolved silica concentrations throughout the proglacial environment; in particular, we measured greater silica concentrations in moraine-sourced springs (Figure 2c) than in proglacial fluvial and lake settings. Moraines are composed of poorly sorted sediments with a large amount of very fine particles (glacial flour), which decreases porosity and permeability and can increase the residence time of meltwater within moraines (Hooke & Iverson, 1995; Parriaux & Nicoud, 1990). Longer residence times and the increased surface area of the fine-grained component, including volcanic glass, could contribute to the relatively high dissolved concentrations of silica compared to total dissolved cations. While a significant portion of weathering is likely happening under the glacier where meltwater interacts with basal sediments, additional alteration is occurring in the proglacial plain, where dissolved ion concentrations are greater in streams, lakes, and springs than in subglacial or supraglacial meltwaters (Figures 2c and 2d).

Our observation of striated rock glazes suggests that significant silica is being precipitated in the subglacial environment as a result of the abundant dissolved silica. The observed coatings are interpreted to be hydrated silica films formed at the ice-rock contact through subglacial pressure melting and refreezing processes known as regelation (Hallet, 1975, 1976). The coatings measured in this study contain laminations and unconformities (Figure 3b), indicating that they were most likely emplaced during successive periods of deposition. These observations support the hypothesis that silica fluxes in glacier outwash waters are lowered by subglacial precipitation of silica-rich secondary phases (Crompton et al., 2015). Supporting these chemical observations, remote sensing of the most mafic glacial catchments also suggests enhanced silica deposits in the proglacial plains (Figure S3; Scudder et al., 2017) and mineralogical analyses have found evidence for poorly crystalline, silica-rich alteration phases in mafic glacial flour (Figure S2; Rampe et al., 2017; Smith et al., 2017). Detailed discussion of the methodology can be found in the supporting information (Gillepsie, 1992).

Our results demonstrate that terrestrial cold-climate silica dissolution and precipitation is more efficient than previously reported and can be a predominant weathering process compared to dissolution of other cations, especially in glaciaded mafic volcanic systems. We hypothesize that this is due to preferential silica dissolution from mafic bedrock in the absence of trace carbonates, resulting in precipitation of rock coatings composed of opaline silica and other poorly crystalline silicate alteration phases (Figure 3). The significant remaining dissolved silica and other dissolved ions that are carried out of the glacial system could also be precipitated as amorphous silicates or more crystalline secondary phases downstream of glacial environments in fluvial-lacustrine settings. Hydrated silica and other poorly crystalline silicates thus dominate the mineralogical record of glacial weathering in these systems.

Extensive evidence for present-day and past glaciation on Mars (e.g., Forget et al., 2013; Holt et al., 2008; Levy et al., 2014; Lucchitta, 1984; Pierce & Crown, 2003; Souness et al., 2012) means that chemical alteration related to glacial activity must be considered as a possible origin for silica deposits on the surface of Mars. Evidence for secondary silica and silicates on Mars has been documented by analysis of satellite VNIR and TIR spectroscopy and rover data (e.g., Ehlmann & Edwards, 2014; Milliken et al., 2008; Mustard et al., 2008; Smith et al., 2013) as well as Mars-relevant experiments (e.g., Hausrath & Brantley, 2010). Surfaces consistent with widespread poorly crystalline, high-silica phases have been identified in the northern plains using VNIR and TIR orbital spectra, and are consistent with silica rinds on volcanic glass (Horgan & Bell, 2012; Rampe et al., 2012). High-silica surfaces were identified in Hellas Basin with TIR orbital data (Bandfield, 2008). Near Valles Marineris, opaline silica was identified in VNIR orbital spectra and interpreted as evidence of low-temperature, acidic, regionally extensive aqueous alteration (Milliken et al., 2008). Hydrated silica identified in orbital VNIR spectra at Nili Fossae has been interpreted to be the result of weathering in a hydrothermal environment (Ehlmann et al., 2009). Additionally, a silicate amorphous phase of basaltic composition has been identified with TIR data from the Spirit rover in rock coatings at Gusev Crater (Ruff & Hamilton, 2013). While secondary silica deposits have been identified globally on Mars, their origin(s) have not yet been entirely explained. Our results suggest that low-temperature weathering under a range of pH induced by seasonal snow and ice melt could, over time, produce significant silica deposits akin to those identified on Mars. This formation mechanism has not been considered before when investigating silica deposits on Mars.

5. Conclusions

Glacial weathering of terrestrial volcanic terrains is understudied and poorly understood, and thus difficult to apply to Martian alteration models. This study directly addresses this problem through water, rock, and sediment sampling across a range of glaciated bedrock compositions. Aqueous geochemical analysis of meltwater and infrared spectroscopy of geologic samples were used to evaluate alteration processes at these sites. Silica dissolution through the carbonation of mafic minerals was found to be the predominant process at each site, with greater concentrations found in more mafic terrains. This seeming incongruence can be explained by the higher solubility of olivine, feldspar, and volcanic glass compared to quartz at surface temperatures. Additionally, the greatest dissolved silica concentrations were observed in moraine-sourced spring water, with lower concentrations found in proglacial streams and lakes. We hypothesize that this is due to the higher abundance of reactive fine-grained glacial flour in moraines as well as the associated long residence times of water in these deposits. Finally, striated silica coatings were observed in glacial foregrounds, indicating subglacial silica deposition is occurring during basal sliding through the process of regelation. This suggests that significant silica cycling is occurring within the glacial system. This study underscores the need for similar investigations in other glaciated volcanic terrains to better constrain these results.

Silica dissolution and precipitation on mafic, low-carbonate rocks may be more important than previously thought on both Earth and Mars. This cycle is most likely driven by silicate-dominated weathering reactions resulting from the absence of immediately available carbonate minerals, relatively high water-rock ratios and relatively long residence times. Silica deposits on Mars should therefore not be interpreted as only hydrothermal or metamorphic in nature; rather, morphology, context, and the associated mineral assemblages should be used to rule out an origin related to glaciation, glaciofluvial alteration, or postdepositional alteration of glacial sediments. For instance, outwash plains, ancient streambeds, and lake sediments associated with past ice sheet terrains and ancient glacial moraines (Arfstrom & Hartmann, 2005; Hubbard et al., 2011) could contain alteration products, which have been transported downstream. Future landed missions and returned sample investigations should consider high-silica phases as potential signals of glacial melt in an icy climate. Detailed investigation of these phases through landed measurements and eventual sample return would greatly inform our understanding of ancient glacial alteration on the surface of Mars and could help to constrain the extent and duration of past ice sheets and glaciers and thus the nature of past climates on Mars.

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