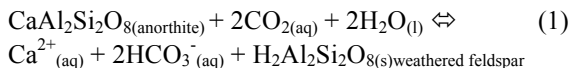DOES MELT-DRIVEN SILICA CYCLING DOMINATE WEATHERING IN GLACIATED VOLCANIC TERRAINS? A. M. Rutledge[1], N. A. Scudder[1], J. R. Havig[2], B. Horgan[1], E. B. Rampe[3], and T. L. Hamilton[2], [1]Dept. of Earth, Atmospheric and Planetary Sciences, Purdue University (alicia.rutledge@gmail.com), [2]University of Cincinnati, [3]NASA Johnson Space Center.

Introduction: New results show that terrestrial cold-climate silica cycling is more efficient than previously reported, and in some settings, particularly glaciated mafic volcanics, can be the dominant weathering process. Based on field work at glaciated volcanic sites, we hypothesize that this is due to a combination of high rates of silica dissolution from mafic bedrock and reprecipitation of silica in the form of opaline silica coatings and other poorly crystalline silicate alteration phases. Widespread evidence for past and present-day glaciation on Mars [1-4] means that this cycle must be investigated in order to better interpret silica deposits on the surface of Mars [5-9].

Silica cycling in terrestrial glacial systems: The high rate of bedrock comminution in subglacial environments results in high rates of both chemical and physical weathering, due to the increased reactive mineral surface area formed through glacial grinding. In most bedrock types, carbonate weathering is enhanced and silica fluxes are depressed in glacial outwash compared with global average riverine catchment runoff due to low temperatures and short residence times [10]. However, in mafic systems, higher dissolved SiO_2 concentrations have been observed [11-13]. Additionally, remote sensing has identified high-silica zones in proglacial outwash plains on mafic bedrock [14].

Water composition. The major difference between glacial alteration of volcanic bedrock and more typical continental terrains is the absence of significant dissolved carbonate in the former. In the absence of carbonate minerals which normally dominate dissolution processes at glacier beds [10], carbonation of feldspar can become the dominant weathering process [11]:

$$CaAl_2Si_2O_{8(anorthite)} + 2CO_{2(aq)} + 2H_2O_{(l)} \Leftrightarrow \qquad (1)$$
$$Ca^{2+}_{(aq)} + 2HCO_3^-_{(aq)} + H_2Al_2Si_2O_{8(s)weathered\ feldspar}$$

This reaction coupled with futher alteration can result in a high proportion of dissolved silica fluxes in glacial outwash waters compared to the total cation flux. It is thought to be the dominant reaction in volcanic systems due to the lack of carbonate mineral dissolution, which would otherwise quickly saturate the aqueous system. Mafic volcanic rocks are particularly susceptible to silica mobility, due to the high concentration of soluble minerals (i.e. plagioclase) as compared to the high concentration of insoluble quartz found in felsic rocks [15].

Subglacial deposits. Silica concentrations are measured from glacial outwash samples, and thus reflect only the dissolved silica that is actively removed from the subglacial environment. Based on multiple observations of subglacially precipitated silica phases, we hypothesize that subglacial precipitation of silica-rich secondary minerals likely contributes to lowering silica fluxes in glacier outwash waters [16]. Subglacially-deposited silica coatings have been observed at mafic volcanic glacial margins [17,18], subglacially-sourced fluvial deposits in basaltic terrain in Iceland were found to have a poorly crystalline silica alteration component [19], and new analyses of mafic glacial flour appear to include a silica-rich poorly crystalline alteration phase [20,21]. Thus, dissolved silica concentrations in subglacial zones are most likely greater than measured in glacial outwash studies.

Field study: To investigate melt-driven silica cycling on mafic volcanics, water and rock samples were collected during June 2015 and July 2016 from glaciated volcanic bedrock in the Cascade Volcanic Arc: Mount Adams (46º9'N, 121º27'W), Mount Hood (45º21'N, 121º42'W), Middle Sister (44º9'N, 121º46'W) and North Sister (44º10'N, 121º47'W). Dominant bedrock compositions for each site are detailed in Table 1. Evidence for subglacial precipitation of poorly crystalline silica was found at North and Middle Sisters in the form of striated rock coatings with greasy lustre on recently deglaciated lava flows (Fig 1) [18] and in a silica-enriched poorly crystalline component of glacial flour from moraine deposits [20].

Table 1. *Dominant bedrock compositions [22,23] and mean dissolved silica concentrations in melt streams.*

Location	Composition	SiO_2 (µM)
Middle Sister	Basalt	25.84
North Sister	Basaltic andesite	15.19
Mt. Adams	Bas. andes. & dacite	10.03
Mt. Hood	Dacite	9.48

Results: Table 1 details the mean glacial outwash stream silica concentrations, as measured from water samples. All measured silica concentrations are shown in Figure 2. Note that silica concentration tends to increase with pH, which is consistent with silica solubility increasing with pH. Proglacial streams, springs, and lakes exhibit dissolved silica concentrations that are greater than observed in glacial snow/ice. The highest silica concentrations were measured in moraine-sourced springs (Fig 2).

Discussion: More mafic glaciovolcanic sites have,

on average, higher concentrations of dissolved silica compared to more felsic glaciovolcanic sites (Table 1). Though basalts have lower SiO_2 content than more felsic volcanic rocks, they are more susceptible to silica mobility due to their higher content of minerals such as olivine, pyroxene, and plagioclase, which are more soluble than quartz [15]. These mineral breakdown reactions are potentially enhanced by microbial populations at the glacier bed [22].

The measured high silica concentrations in springs are potentially due to moraines acting as sediment traps. Moraines are poorly sorted sediments with a high proportion of subglacially ground fine particles [24], and glacial flour accumulates by aeolian deposition [18]. The increased fine-grained component – and thus increased surface area – and longer residence times due to associated decreased permeability could contribute to the observed relatively high dissolved silica concentrations.

Finally, while high rates of subglacial silica dissolution are likely, subglacial precipitation of silica glaze through pressure melting and refreezing (Fig 1) is potentially decreasing the overall silica measured in solution in the glacier foreland, akin to the hypothesis proposed by [16].

Applications to Mars: The significant effect of water and ice on the surface of Mars is well documented [1]. Geomorphic and radar evidence exists for the presence of large volumes of near-surface, present-day ice [2], chemical evidence points to aqueous alteration on Mars [5], and atmospheric modeling shows evidence of a "cold and icy" early Mars [3]. Some studies have proposed an early Mars dominated by widespread glaciation with transient melting [4]. Additionally, silica is thought to be highly mobile on the surface of Mars [15]. Silica deposits should not be interpreted as only hydrothermal; rather, morphology and context should be used to rule out an origin related to glaciers or alteration of glacial sediments.

Silica deposits on Mars. Widespread poorly crystalline, high SiO_2 deposits have been modeled in Nothern Acidalia [5], consistent with low-T weathering of volcanic glass. Hydrated silica deposits have been identified in Valles Marineris [6], Nili Fossae [7], and Hellas Basin [8]. Additionally, poorly crystalline silicates have been identified as a major component of rock coatings in Gusev Crater [9].

Conclusions: Melt-driven silica cycling on low-carbonate, mafic rocks may be more important than previously thought, on both Earth and Mars. This cycle is most likely driven by the lack of immediately available carbonate minerals resulting in silicate-dominated weathering reactions, relatively high water-rock ratios, and/or long residence times.

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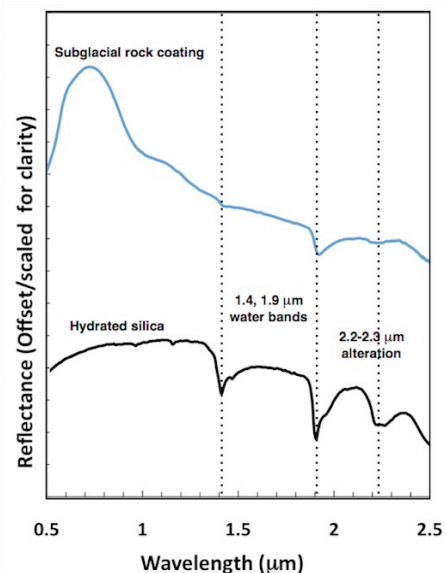

Figure 1. Rock sample measurement: representative VNIR field spectrum of subglacial rock coating exhibits similar absorptions to hydrated silica. From [18].
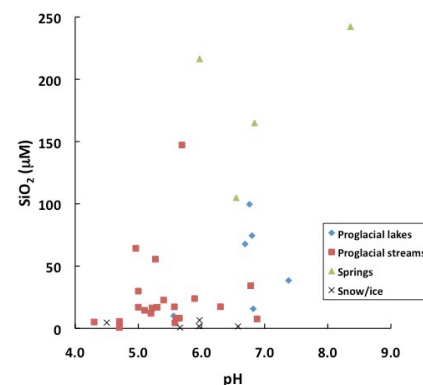

Figure 2. Water sample measurements: pH vs. dissolved silica at field sites. Data from [14, 22].