FREEZE-THAW CYCLING AS A CHEMICAL WEATHERING AGENT ON A COLD AND ICY MARS.

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Introduction: Liquid water was abundant on early Mars, but whether the climate was warm and wet or cold and icy with punctuated periods of melting is still poorly understood. Modern climate models for Mars tend to predict a colder, icier early climate than previously imagined [e.g., 1]. In addition, ice and glaciation have been major geologic agents throughout the later Hesperian and Amazonian eras [e.g., 2]. One process that can act in such climates is repeated freezing and thawing of water on the surface and in the subsurface, and is significant because it can occur anywhere with an active layer and could have persisted for a time after liquid water was no longer stable on Mars' surface. As freeze-thaw is the dominant mechanical weathering process in most glacial/periglacial terrains, it was likely a significant geomorphologic driver at local to regional scales during past climates, and would potentially have been most active when day-average surface temperatures exceeded 0 °C for part of the year [3]. Indeed, freeze-thaw involving liquid water in the Amazonian is evidenced by abundant geomorphic features including polygonal ground and solifluction lobes requiring seasonal thawing [3,4].

In addition to physical modification, freezing can drive solutions towards supersaturation and force dissolved solutes out as precipitates [5]. In Mars-like terrains, dissolved solutes are typically dominated by silica [6, 7]. In polar regions on Earth, freeze-thaw cycles have been shown to promote deposition of silica [8], and freeze-thaw experiments on synthetic solutions found stable amorphous silica that built up over multiple cycles [5]. Freeze-thaw may therefore be an important but overlooked chemical weathering process on Mars. However, our ability to assess its impact on alteration of martian terrains is majorly limited by the current lack of understanding of the alteration phases produced (and formation rates) under controlled freeze-thaw weathering of Mars-relevant materials. To address this knowledge gap, we report results from (1) freeze-thaw weathering products found at a glacial Mars analog site at the Three Sisters, Oregon, and (2) new controlled freeze-thaw experiments on basaltic material.

Methods: The Three Sisters volcanic complex in the Oregon Cascades is the most mafic glaciated terrain in the continental U.S. [9], and recent glacial retreat has freshly exposed glacial/periglacial material in a Mars-analog environment. We collected sediment and subglacial rocks from the two major glacial valleys in order to characterize the weathering products forming in this environment. The proglacial sediment is subjected to annual and diurnal freeze-thaw cycling at this site, and the bedrock is exposed to freeze-thaw at the base of the glaciers. We determined the chemistry and mineralogy of the rocks and sediments there using visible/near-infrared (VNIR) and thermal-infrared (TIR) spectroscopy, X-ray diffraction (XRD), and microscopy.

New freeze-thaw experiments on Hawaiian basalt, glassy tephra, and Three Sisters basaltic andesite are ongoing at Purdue University. Sealed aliquots of rock chips or <250 µm powdered rock mixed with DI water are subjected to continuous cycling between appx. -20 to +5 °C over 5-hour periods. To explore a range of scenarios (e.g. subglacial, proglacial, closed/open system), we vary the water/rock ratio and whether the water is replaced. CO_2-atmosphere (Mars-like composition) experiments are also planned. We currently have 10 days of data and plan to run these experiments for multiple months to maximize detectable change. Nevertheless, VNIR spectra of samples after only 10 days of cycling already exhibit significant spectral changes.

Field results: The predominant form of chemical weathering at the Three Sisters glaciers is dissolution of feldspar and volcanic glass by carbonic acid, which releases relatively large quantities of silica into solution compared to other ions [7]. When these reactions occur under the glacier, precipitates may form during pressure-controlled freeze-thaw precipitation (regelation; [10]). Subglacial rocks from the Three Sisters have regelation coatings that exhibit silica signatures in VNIR spectra (Fig. 1a), and TIR spectra and scanning electron microscopy (SEM) show that the <1 mm thick coatings are composed of glacial flour cemented by a high-silica material [7]. Glacially polished bedrock shows the same signature as these coatings in VNIR and TIR, indicating that silica is also precipitated as widespread optically thin coatings under the glacier.

In proglacial sediments from the glacier termini, moraines, and proglacial lakes, we found higher abundances (15-40+ wt.%) of X-ray amorphous materials compared to local bedrock sources [11]. Energy dispersive spectroscopy (EDS) with transmission electron microscopy (TEM) of individual amorphous particles in the glacial sediments indicates that the amorphous component includes some bedrock-sourced volcanic glass alongside a variety of authigenic Fe-Si-Al amorphous silicates, clay mineral precursors, and nanophase iron oxides [12]. These particles are consistent with

weathering observed in other cold, icy mafic environments [*e.g.,* 13]. We also found dissolved silica and cations in waters throughout the proglacial environment, most strongly in moraine-sourced springs, where partial freezing of solute-enriched fluids could precipitate these amorphous materials.

Experimental results: Freeze-thaw experiments are ongoing. However, in under two weeks of cycling under ambient Earth atmosphere, detectable visual and spectral changes have already occurred in all samples. While the spectral character beyond 0.75 µm remained nearly identical, the Day 10 spectra show a strong absorption edge in the visible that is attributable to ferric iron (Fig. 1b). The appearance of this absorption edge indicates that oxidation of Fe^{2+} to Fe^{3+} has occurred during the freeze-thaw cycling. The ratio spectrum showing the change between Day 0 and Day 10 does not exhibit the distinctive absorptions indicative of crystalline iron oxides (e.g. goethite; Fig. 1b), suggesting that the Fe^{3+} is forming as noncrystalline (including amorphous and nanophase) iron oxides instead [14]. We interpret this spectral change to indicate that Fe^{2+} was dissolved from the ferrous minerals and volcanic glass in the fresh rock powder, was oxidized to Fe^{3+}, and precipitated rapidly as a noncrystalline product. Immediate changes in iron are not unexpected due the oxygen-bearing Earth atmosphere inside the tubes as well as the highly insoluble nature of Fe^{3+}. Weathering of ferrous igneous minerals (e.g., olivine, pyroxene) also releases silica and other cations into solution [6,7], so as cycling continues, other dissolved cations may begin to precipitate as part of
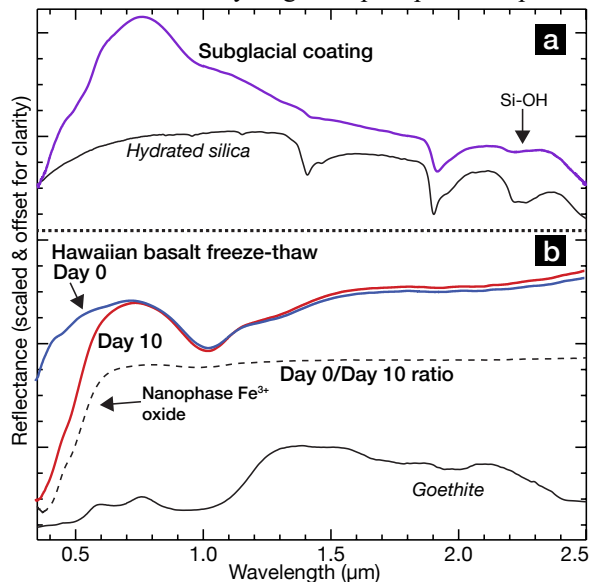
Fig. 1. (a) Subglacial regelation film from Three Sisters displaying absorptions similar to hydrated silica. (b) Current freeze-thaw experiment VNIR results showing a ferric iron absorption after 10 days resembling nanophase rather than bulk oxides.

detectable products. CO_2-atmosphere experiments will be started before the time of the conference and provide an oxygen-poor Mars-like freeze-thaw environment.

Implications for Mars: Results from glacial Mars-analog sites and experiments indicate that high abundances of poorly crystalline silicates and nanophase amorphous iron oxides can form during cyclic freeze-thaw of Mars-like materials. The decrease in dissolved solutes caused by each thaw cycle results in a solution that is undersaturated with respect to the minerals with which it is in contact, promoting further mineral dissolution [5] and driving the process forward.

Silica-rich poorly crystalline phases are common in Amazonian and Hesperian sediments on Mars, consistent with melt-driven weathering under cold climates. Silica has been detected in Amazonian periglacial sediments [15], and our glacial coatings could be analogous to the silica-rich rinds hypothesized in the Amazonian northern lowlands [16]. Poorly crystalline phases are also a major component of Gale crater Hesperian lake sediments [17] and possibly of martian global sediments [18]. Freeze-thaw weathering could have contributed to the amorphous products observed in these cases. In addition, our experiments show that freeze-thaw may be one way to form the amorphous nanophase oxides found in martian dust and soil [19]. However, a melt-driven alteration model cannot easily explain the abundant crystalline alteration minerals found across Noachian terrains [20], suggesting that these minerals did not form from ice/snow melt or freeze-thaw events.

Since freeze-thaw processes were regionally active on Mars and could have occurred throughout much of its history, it is likely that freeze-thaw-related chemical weathering has also occurred. The young age of our field site suggests that this can be a relatively rapid process under Earth-like water/rock ratios, leading to significant amounts of secondary material build-up over time. So, freeze-thaw chemical weathering may be a more significant process in Mars' geologic history than previously considered.

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