

**MINERALOGICAL SIGNATURES OF COLD AND ICY ALTERATION ON THE SURFACE OF MARS.**

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**Introduction.** The significant effects of water and ice on the surface of Mars throughout its history is well documented [e.g., 1]. Geomorphic features show evidence for abundant liquid water on early Mars, but whether the climate was warm and wet or cold and icy with punctuated periods of melting is not well understood. Some atmospheric models for early Mars predict a cold, icy climate [e.g., 2], but any model for the early climate on Mars must be reconciled with the observed chemical record, which strongly indicates aqueous alteration [e.g., 3]. Climate models for the Amazonian era also predict periodic ice ages [4, 5], and the mineralogical record on these surfaces supports these models, with sulfates and high-silica surfaces modeled in high latitudes [e.g., 6-8]. However, alteration mineralogy formed in snow and ice-dominated conditions is poorly understood compared to that of warmer climates, and it is unclear whether or not cold climate weathering could form the aqueous weathering products preserved on ancient martian surfaces [3]. To address this knowledge gap, we synthesize results from glacial Mars analog sites at the Three Sisters, OR, USA, and mafic regions of the Antarctic ice sheet, and compare them to the surface mineralogy of Mars. These sites provide the opportunity to characterize weathering in environments analogous to glacial environments on Mars throughout geologic time, including small warm-based glaciers and perennial snowfields [9, 10] as well as the proposed extensive ice sheets of the late Noachian icy highlands model [e.g., 2].

**Alpine glacial and periglacial alteration.** The Three Sisters volcanic complex in the Cascade Volcanic Arc is the most mafic glaciated terrain in the contiguous U.S. [11], and recent ice retreat has made freshly deglaciated materials accessible. We collected rocks, sediments, and water samples, and made in situ measurements (temperature, pH, dissolved O<sub>2</sub>) in two major glacial valleys in order to characterize weathering products and infer chemical reactions in this cold and wet environment. We analyzed water samples for major and minor dissolved ions (IC, ICP-MS), and determined the chemistry and mineralogy of rocks and sediments with VNIR/TIR spectroscopy, XRD, and electron microscopy (SEM, TEM, EDS).

The predominant form of chemical weathering in these mafic glacier-dominated systems is dissolution of feldspar and volcanic glass by carbonic acid, which releases relatively large quantities of silica into solution compared to other ions [12]. When these reactions

occur under the glacier, silica is precipitated at the ice-rock contact, resulting in extensive hydrated silica coatings on glacially striated bedrock. These rock coatings exhibit silica signatures in VNIR and TIR spectra, and scanning electron microscopy (SEM) shows that the <1 mm thick coatings are composed of glacial flour cemented by a high-silica phase [12]. Glacially polished bedrock shows the same signature as these coatings in VNIR and TIR, indicating that silica is also present as widespread optically thin coatings under the glacier.

Where alteration occurs due to diurnal and seasonal snowfield melt in the proglacial plain, silica is precipitated on glacially derived sediments as silica-rich poorly crystalline phases. In sediments from the glacier terminus, moraines, and proglacial lakes, we found no evidence for authigenic formation of crystalline alteration phases, but XRD and TIR spectra indicate that, on average, sediments contain greater abundances (by ~10-20 wt.%) of X-ray amorphous materials compared to local bedrock [13]. TEM-EDS (transmission electron microscopy with energy dispersive spectroscopy) of the <2 μm and <150 μm size fractions of glacial sediments indicates that the amorphous component includes bedrock-sourced volcanic glass alongside a variety of secondary amorphous silicates and clay mineral precursors [14-16]. These particles have variable Fe-Al-Si compositions and are consistent with weathering observed in other cold, icy mafic environments [e.g., 17]. By comparing predicted bulk crystalline chemistry from XRD models to actual measured bulk chemistry [18], we also observed that the bulk composition of these amorphous materials are enriched in silica relative to the parent material [18]. Based on these observations, X-ray amorphous, hydrated silica-rich materials appear to be the predominant weathering product deposited in alpine glacial and perennial snowfield ice/snowmelt-driven systems on mafic bedrock.

**Chemical weathering under large ice sheets.** In small glaciers and perennial snowfields, water and sediment move through the system very quickly and alteration occurs rapidly during daily melt cycles. These conditions favor the formation of poorly crystalline phases, which form where kinetic effects dominate over thermodynamic reactions [19]. Water and sediments can remain under large ice sheets for orders of magnitude longer: in Antarctica, typical ice streams discharge water over decades, and the largest subglacial

cial lakes have residence times of  $\sim 10^5$  years [20]. We hypothesize that while initial weathering reactions under large ice sheets might be similar to those under small glaciers, the persistence of water and sediments over longer timescales may lead to more crystalline alteration phases. To test this hypothesis, we used VNIR and TIR spectroscopy, XRD, and XRF to characterize a suite of sediment samples from warm- and cold-based locations across the Antarctic ice sheet where mafic, Mars-relevant basal bedrock dominates.

Basal sediments from warm-based portions of the Antarctic ice sheets remain in contact with *liquid* glacial meltwater longer (sediment flux rate:  $\sim 100$  m<sup>3</sup>/m/yr) than sediments from cold-based ice ( $\sim 5$  m<sup>3</sup>/m/yr) [21]. VNIR/TIR spectra confirm that mafic subglacial sediments from warm-based sites like Mt. Achrenar contain significant Al-clays. The source rocks contain some Fe/Mg-phyllosilicates but not Al-, suggesting that the Al-clay minerals were formed during subglacial alteration.

Under cold-based portions of the ice sheet, temperatures at the base are below the freezing point of water such that the base is frozen to the rock or sediment below. Here subglacial sediment can still come in contact with liquid water and be moved [22] but we expect chemical alteration rates to be far slower than those in warm-based zones [23]. Indeed, sediments from the cold-based glacial/periglacial site Basen Nunatak exhibit no clear evidence for crystalline alteration phases in TIR or XRD. Rather, these sediments contain high abundances of high-silica amorphous materials [24], perhaps analogous to the poorly crystalline silicates at our alpine glacier Cascades field site.

**Implications for Mars.** Results from these two glacial Mars analog sites show that alteration product crystallinity is most likely an important indicator of past climatic conditions. Our study predicts that transient ice/snowmelt-driven weathering on a cold and icy Mars, whether during the Amazonian in widespread periglacial terrains and at small alpine glaciers, or in the Noachian/Hesperian under large cold-based ice-sheets, should have produced high abundances of poorly crystalline materials (Table 1). In contrast, sediments from warm-based portions of ice sheets with persistent liquid water are enriched in crystalline clay minerals, which we hypothesize form due to longer residence times under the ice sheet. Localized regions of warm-based ice may have existed on ancient Mars due to top-down melting induced by insolation and/or volcanic eruptions [2, 25], and we suggest that crystalline clay mineral formation in these locations as well as poorly crystalline phases from elsewhere in the ice sheet could have contributed to downstream lacustrine sediments.

Silica-rich, poorly crystalline phases are a significant component of Amazonian and Hesperian sediments on Mars, consistent with melt-driven glacial/periglacial weathering under cold climates. Silica has been detected in Amazonian periglacial sediments [26], and glacially-derived rock coatings could be analogous to the silica-rich rinds suggested in the Amazonian northern lowlands [6, 27, 28]. Poorly crystalline phases and clay minerals are also a major component of Gale Crater Hesperian lake sediments [29] and of extensive Northern Acidalia Amazonian sediments [8]. However, this ice/snowmelt-driven alteration model cannot easily explain the abundant crystalline alteration minerals found across Noachian terrains [3], suggesting that these surface minerals did not form due to ice/snow melt but rather during persistent warm periods on early Mars.

**References:** [1] B.L. Ehlmann et al (2011) *Nature*, 479, 53-60. [2] Fastook & Head (2015) *PSS*, 106, 82-98. [3] Ehlmann & Edwards (2014) *Ann. Rev. EPS*, 42, 291-315. [4] M.I. Richardson & R.J. Wilson (2002) *JGR*, 107. [5] J.W. Head et al. (2003) *Nature*, 426, 797-802. [6] Horgan & Bell (2012) *Geology*, 40, 391-394. [7] Horgan et al. (2009) *JGR*, 114, E01005. [8] Rampe et al. (2012), *Geology*, 40-, 995-998. [9] Kite et al. (2013), *Icarus*, 223, 181-210. [10] Scanlon et al. (2015), *Icarus*, 250, 18-31. [11] Hildreth et al. (2012) USGS Map 3186. [12] Rutledge et al. (2018), *GRL*, 45. [13] Scudler et al. (2018) *LPSC XLIX*, #2913. [14] Rampe et al. (2017), *AGU Fall Meeting*, P33C-2892. [15] Smith & Horgan (in review) *Geology*. [16] Smith et al. (2017) *AGU*, #216658. [17] Hausrath et al. (2008), *Astrobio*, 8, 1079-1092. [18] Smith et al. (2018), *JGR*, 123. [19] Ziegler et al. (2003), *Chem. Geol.* [20] Bell et al., (2002), *Nature*, 416, 307. [21] Gollege et al. (2013) *QSR*, 78, 225-247. [22] Atkins et al. (2002), *Geology*, 30, 659-662. [23] Margreth et al. (2014), *Quat. Sci. Rev.*, 91, 242-256. [24] Graly et al. (2019) Goldschmidt #868. [25] Cassanelli & Head (2015), *Icarus*, 253, 243-255. [26] Sun & Milliken (2018), *GRL*, 45, 10,221-10,228. [27] Kraft et al. (2010), *LPSC XLI*, #2600. [28] Ruff & Christensen (2007), *GRL*, 34, 6. [29] Rampe et al. (2017), *EPSL*, 471, 172-185.

**Table 1.** Terrestrial analog glacial environments and their associated alteration mineralogy.

Environment:	Major alteration product observed:
Warm-based alpine glacier or snowpack • Short residence time • High water/rock ratio	Poorly crystalline silicates
Cold-based ice sheet • Short residence time • Low water/rock ratio	Poorly crystalline silicates(?)
Warm-based ice sheet • Long residence time • High water/rock ratio	Al-clay phases