**Mineralogical Signatures Of Cold And Icy Climates On Ancient And Modern Mars.** N. A. Scudder<sup>1</sup>, B. Horgan<sup>1</sup>, A. Rutledge<sup>2</sup>, E. B. Rampe<sup>3</sup>, R. J. Smith<sup>4</sup>, J. Graly<sup>5</sup>, <sup>1</sup>Purdue University (nscudder@purdue.edu), <sup>2</sup>Northern Arizona University, <sup>3</sup>NASA Johnson Space Center, <sup>4</sup>Stony Brook University, <sup>5</sup>Indiana University Purdue University Indianapolis.

**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]. However, any model for the early climate on Mars must be reconciled with the chemical record. We currently do not understand how alteration mineralogy formed in snow and icedominated conditions compares to that of warmer climates, and it is unclear whether cold climate weathering could form all or any of the aqueous alteration phases expressed on early martian surfaces [2]. To help resolve this knowledge gap, we synthesize results from glacial Mars analog sites at the Three Sisters, Oregon and mafic regions of the Antarctic ice sheet, and compare them to the surface mineralogy of Mars. These sites provide the opportunity to investigate weathering in environments analogous to glacial environments on Mars throughout geologic time, including snowpacks or smaller wet-based or polythermal glaciers [3, 4] as well as the proposed extensive ice sheets of the late Noachian icy highlands model [e.g., 1].

**Snowpack and alpine glacial weathering:** The Three Sisters volcanic complex in the Oregon Cascades is the most mafic glaciated terrain in the continental U.S. [5], and recent glacial retreat has freshly exposed glaciated material in a Mars-analog environment. We collected rocks, sediments, and water samples from the 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 ions and determined the chemistry and mineralogy of rocks and sediments with VNIR spectroscopy, XRD, microscopy (SEM, TEM, EDS), and thermal-IR spectroscopy.

The predominant form of chemical weathering in these periglacial mafic systems is dissolution of feldspar and volcanic glass by carbonic acid, which releases relatively large quantities of silica into solution compared to other ions [6]. When these reactions occur under the glacier, silica is precipitated at the ice-rock contact, resulting in extensive hydrated silica coatings on glacially scoured bedrock. These rock coatings exhibit silica signatures in VNIR and TIR spectra [6], and scanning electron microscopy (SEM) shows that the <1 mm thick coatings are composed of glacial flour cemented by a high-silica phase. 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 weathering occurs due to diurnal snow melt in the proglacial terrain, silica is precipitated on glacial sediments in the form of silica-rich poorly crystalline phases. In proglacial 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 all sediments contain higher abundances (15-40+ wt%) of Xray amorphous materials compared to local bedrock sources [7]. Energy dispersive spectroscopy (EDS) with TEM of individual amorphous particles in the glacial sediments indicates that the amorphous component includes bedrock-sourced volcanic glass alongside a variety of neoformed amorphous silicates and protoclays [8]. These particles have variable Fe-Al-Si compositions and are consistent with weathering observed in other cold, icy mafic environments [e.g., 9]. By comparing predicted bulk crystalline chemistry from XRD models to actual measured bulk chemistry [10], we also observed that the bulk composition of the amorphous materials are enriched in silica relative to



**Fig. 1.** Collier glacial valley at the Three Sisters, OR. The glacier has retreated >1 km to its present position in the past 100 years, exposing fresh subglacial/proglacial sediment, with annual ice/snowmelt feeding the proglacial lake.

the parent material [10]. Based on these observations, X-ray amorphous hydrated silica-rich materials appear to be the major weathering product formed in mafic glacial/proglacial ice/snowmelt-driven systems.

Chemical weathering under ice sheets: In small glaciers and snowpacks, water and sediment move through the system very quickly and alteration occurs rapidly during daily melt cycles. These are scenarios that favor poorly crystalline phases, which form when kinetics dominate over thermodynamic reactions [11]. Large ice sheets can harbor water and sediments for orders of magnitude longer: in Antarctica, typical ice streams discharge water over decades, and the largest subglacial lakes have residence times of  $\sim 10^5$  years [12]. 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 applied VNIR and TIR spectroscopy, XRD, and XRF to a suite of samples from warm- and cold-based locations across the Antarctic ice sheet where mafic, Marsrelevant substrates dominate.

Sediments from warm-based portions of the Antarctic ice sheets remain in contact with liquid water for long periods of time. Both VNIR and TIR spectra confirm that mafic subglacial sediments from warm-based sites like Mt. Achrenar contain significant Al-clays and chert that are not observed in their source rocks. While the source rocks do contain some phyllosilicates, they have significantly different spectral signatures and compositions from the Al-clay minerals in the sediments, 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 [13] but we expect that chemical alteration rates are far slower than those in warm-based zones [14]. Indeed, sediments from the cold-based glacial/periglacial site Basen Nunatuk exhibit no clear evidence for crystalline alteration phases in TIR or XRD. Instead, these sediments contain high abundances of high-silica amorphous materials, perhaps analogous to the poorly crystalline silicates at our alpine glacier site.

**Implications for Mars**: Results from glacial Mars analog sites show that transient ice/snowmelt-driven weathering on a cold and icy Mars, whether at small alpine glaciers or under large cold-based ice-sheets, should produce high abundances of poorly crystalline materials. 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. Similar trends are observed in terrestrial mafic soils, from crystalline clay minerals in warm climates to poorly crystalline phases in cold climates [15]. Thus, alteration product crystallinity may be an important indicator of past climatic conditions.

Silica-rich poorly crystalline phases are common in Amazonian and Hesperian sediments on Mars, consistent with ice/snowmelt-driven weathering under cold climates. Silica has been detected in Amazonian periglacial sediments [16], and glacial coatings could be analogous to the silica-rich rinds hypothesized in the Amazonian northern lowlands [17-19]. Poorly crystalline phases are also a major component of Gale crater Hesperian lake sediments [20] and possibly of martian global sediments [21]. However, this ice/snowmelt-driven alteration model cannot easily explain the abundant crystalline alteration minerals found across Noachian terrains [2], suggesting that these minerals did not form from ice/snow melt events.

The low geothermal gradient predicted for ancient Mars means that most large ice sheets were likely coldbased [1]. Chemical alteration could have been driven by localized subglacial melting, as well as by the widespread top-down melt that has been predicted for large ice sheets on Mars [22]. Alteration in these melt-driven systems should have produced poorly crystalline phases as the dominant alteration material. While this style of alteration may be consistent with observations of Hesperian and Amazonian sediments, it is not consistent with the abundant crystalline alteration minerals found across Noachian terrain [2]. This suggests that if cold, icy climates dominated the Noachian, their chemical record is largely lost, and punctuated and persistent warm periods would be required to produce the observed crystalline clay mineral record. References: [1] Fastook & Head (2015) PSS, 106, 82-98. [2] Ehlmann & Edwards (2014) Ann. Rev. EPS, 42, 291-315. [3] Kite et al. (2013), Icarus, 223, 181-210. [4] Scanlon et al. (2015), Icarus, 250, 18-31. [5] Hildreth et al. (2012) USGS Map 3186. [6] Rutledge et al. (2018), GRL, 45. [7] Scudder, et al. (2018) LPSC XLIX, #2913. [8] Rampe et al. (2017), AGU Fall Meeting, P33C-2892. [9] Hausrath et al. (2008), Astrobio, 8, 1079-1092. [10] Smith et al. (2018), JGR, 123. [11] Ziegler et al. (2003), Chem. Geol. [12] Bell et al., (2002), Nature, 416, 307. [13] Atkins et al. (2002), Geology, 30, 659-662. [14] Margreth et al. (2014), Quat. Sci. Rev., 91, 242-256. [15] Alexander et al. (1993), Catena, 20, 113-128. [16] Sun & Milliken (2018), GRL, 45, 10,221-10,228. [17] Kraft et al. (2010), LPSC XLI, #2600. [19] Ruff & Christensen (2007), GRL, 34, 6. [19] Horgan & Bell (2012) Geology, 40, 391-394. [20] Rampe et al. (2017), EPSL, 471, 172-185. [21] Rampe et al. (2012), Geology, 40-, 995-998. [22] Cassanelli & Head (2015), Icarus, 253, 243-255.