

DETECTIONS AND INITIAL INTERPRETATIONS OF AMORPHOUS SILICATES IN JEZERO CRATER, MARS. R. J. Smith¹, K. R. Moore², J. Razzell Hollis³, S. Sharma³, E. Cardarelli³, E. Scheller², M. Tice⁴, N. Tosca⁵, F. Poulet⁶, R. Weins⁶, Y. Liu³, B. Horgan⁷, and A. Steele⁸, ¹Department of Geosciences, Stony Brook University, USA (rebecca.j.smith@stonybrook.edu), ²Division of Geological and Planetary Sciences, California Institute of Technology, USA (krmoore@caltech.edu), ³Jet Propulsion Laboratory, California Institute of Technology, USA, ⁴Geology & Geophysics, Texas A&M, USA, ⁵Department of Earth Sciences, Cambridge University, UK, ⁶Los Alamos National Laboratory, ⁷Earth, Atmospheric, and Planetary Sciences, Purdue University, USA, and ⁸Earth and Planets Laboratory, Carnegie Institution for Science.

Introduction: The Mars 2020 Perseverance rover instrument suite has detected potential amorphous silicates in Jezero crater rocks. These detections are notable because: (1) every Mars mission has detected amorphous silicates, indicating they are important surface components at orbiter and rover scales [e.g. 1-5]; (2) like crystalline minerals, the types of amorphous phases present can inform on past geologic processes (e.g., volcanism, impacts, aqueous alteration, primary precipitation) and habitable environments.

Natural amorphous silicates include: glass (e.g., volcanic, impact), alteration products (e.g., weathering products, leached rinds), and chemical precipitates (e.g., sinter, cements, chert precursors in ancient terrestrial seawater). Amorphous silicates have high chemical and structural variability [e.g. 6] and lack long-range order, leading to spectral and diffraction properties that are relatively non-unique (broad and low intensity features) for chemically similar phases. As a result, textures, morphologies, and geologic context of amorphous silicates can be key to helping identify phases.

Here we report on potential detections of amorphous silicates in Jezero crater rocks from multiple instruments and use estimates of their compositions, along with their textures and morphologies, where possible, and the geologic context of the rocks to place some initial constraints on what these phases might be and what geologic processes they might represent.

Methodology: Perseverance has two methods capable of determining crystallinity: Raman spectroscopy (SHERLOC) and diffracted X-rays (PIXL). This investigation focuses on abraded rock surfaces because these targets have co-located datasets from the SuperCam, PIXL, and SHERLOC/WATSON instruments.

SuperCam – the SuperCam instrument has several remote-sensing techniques and we focus on results from the laser-induced breakdown spectroscopy (LIBS) technique that provides quantitative major and minor elemental abundances from targets up to 7 m away and has a spot size < 600 µm depending on the distance (~400 µm at 2 m distance) [7].

PIXL – the PIXL (Planetary Instrument for X-ray Lithochemistry) instrument is a micro-focus X-ray fluorescence spectrometer that detects major and minor

elements, as well as many trace elements. PIXL provides detailed geochemical maps of a prepared (abraded) rock surface at high spatial resolution (< 120 µm spot size) [8]. PIXL also detects the presence or absence of diffracted X-rays, which indicate crystalline or noncrystalline (amorphous) states, respectively.

SHERLOC – the SHERLOC (Scanning Habitable Environments with Raman & Luminescence for Organics and Chemicals) instrument is a Deep UV native fluorescence and resonance Raman spectrometer capable of detecting most major mineral groups as well as organics [9]. The laser is focused using the Autofocus Context Imager (ACI), which acquires grayscale images at a spatial scale of ~10.1 µm/pixel. Another imaging subsystem, WATSON (Wide Angle Topographic Sensor for Operations and eNginEering), allows for spectra to be correlated with surface textures, color, morphology, and visible features. SHERLOC collects grids of Raman spectra from ~7x7mm observation regions and can obtain spectra from grains as small as 50 µm [10].

Geologic Context: Thus far, Perseverance has traversed two rock formations: the Máaz formation that covers most of the crater floor and the Séítah formation. Presently, the rover has abraded two targets in the Máaz formation (named Guillaumes and Bellegarde) and three targets in the Séítah formation (named Garde, Dourbes, and Quartier).

Both formations are interpreted to be igneous in origin based on outcrop expressions, primary mineralogy and grain textures observed in the abraded patches; Máaz rocks are mafic in composition while the olivine-rich Séítah rocks are ultramafic in composition [e.g., 11-13]. Both formations have mineral and textural evidence for aqueous alteration, including Ca- and Mg-sulfates, possible Fe-phyllsilicates, NaCl, and Na-perchlorate in Máaz rocks and Mg- and Fe-carbonates, possible Fe-phyllsilicates, Ca- and Mg-sulfates, and phosphates in Séítah rocks [14-16].

Amorphous silicate detections: The Perseverance instrument suite has detected potential amorphous silicates in every abrasion patch examined to-date. All five abrasion targets have 1-2 pixels where SHERLOC Raman spectra have a general background signal consisting of broad and diffuse peaks centered around ~1060-

1070 cm^{-1} . In general, Raman peak centers for amorphous silicates depend on composition [17] and the peak positions noted here are best matched with obsidian or a synthetic Mg-silicate made in the lab. Note that these positions are not consistent with pure opaline silica ($\sim 1078 \text{ cm}^{-1}$) [9].

Only one target, Dourbes, has PIXL measurements that overlap with areas identified by SHERLOC as potential amorphous silicates. PIXL shows these regions have high-Si and low other elements (e.g., Fe, Mg) compared to identified endmember minerals. The potential amorphous silicate areas are very small (a few pixels) and so the uncertainty in the compositions of the amorphous silicate regions is very high. Because only one abrasion patch has instrument overlap on potential amorphous silicates, it is uncertain if all of the potential amorphous silicate areas measured by SHERLOC have similar compositions. However, PIXL has noted “high-Si and low Fe, Mg” areas in most abrasion patches [16].

The SuperCam LIBS technique has detected one LIBS spot in Guillaumes (Cf-fr) and four LIBS spots in Quartier (S  t  h) with compositions indicating mixing of a Si-rich component with felsic and mafic minerals. The spot in Guillaumes indicates relatively high-Si and some Fe, Mg, K, Ca, and Na, whereas the spots in Quartier have relatively high-Si, some Fe and Mg, and low Al and alkalis. The general dearth of high-Si detections with SuperCam LIBS is likely due to the large spot size compared to the other techniques and to the small areas of potential amorphous silicates. The fact that there are a higher number of relatively high-Si LIBS spots in the Quartier sample suggests that this target has larger areas of amorphous silicates than other abraded patches. Also notable are a number of LIBS points with high-Si measured in Cf-fr rocks along the traverse [17].

Discussion: In all cases, SHERLOC and PIXL indicate that the potential amorphous silicates are found in very small areas between mineral grains, generally found in no more than two pixels per targets. It is challenging to constrain compositions of the potential amorphous silicates, but both Raman and chemical measurements indicate that the amorphous phases are not pure silica and are instead mixed cation-bearing silicates (mostly Mg and Fe, but also potentially Ca, Na, and K). Both Cf-fr and S  t  h rocks have igneous textures and show evidence for aqueous alteration. At first glance, glass and aqueous alteration products are equally plausible candidate phases.

The S  t  h rocks are hypothesized to be cumulates, which cool slowly, lessening the likelihood of glass as a candidate phase. Additionally, the relatively high-Si compositions for these phases makes for an unlikely, but not impossible, glass composition for mafic/ultramafic rocks. It should be noted that olivine crystals in the

Quartier target show some evidence for undercooling/fast cooling that might have allowed glass to form.

A simpler explanation is that these phases formed through aqueous alteration of mafic minerals, which releases cations and silica into solution. If the cations are not removed from the system (“closed system”), amorphous cation-bearing silicates can form along with phases like Ca- and Mg-sulfates and carbonates, depending on conditions. The textures and mineral associations of the potential amorphous silicates (grain interstices proximal to olivine grains and crystalline alteration products) resemble those observed in Martian meteorites attributed to olivine carbonation on Mars [18].

Implications: Most other locations on Mars also show evidence for amorphous silicates (as opposed to pure amorphous silica) that are likely alteration phases [3-5]. The return of cores bearing amorphous silicates to Earth will greatly enhance our knowledge of what phases are possible for the Martian surface and will increase our understanding of amorphous phases in other locations on Mars.

Furthermore, amorphous phases are metastable materials and eventually yield to more crystalline phases. Like at Gale crater, the rocks of Jezero crater are likely billions of years old, making amorphous alteration phases in Martian rocks some of the oldest known, persisting up to 10^2 years longer than amorphous alteration phases on Earth [6]. Investigations of returned samples can allow for these materials to be dated and fully characterized using power and labor-intensive techniques (e.g., TEM and synchrotron).

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References: [1] Bandfield J. (2002) *JGR*, 107. [2] Sun V. and Milliken R. (2018) *GRL*, 45. [3] Glotch T. et al. (2006) *JGR*, 111. [4] Ruff S. J. et al. (2006) *JGR*, 111. [5] Rampe E. B. et al. (2020) *Geochem.*, 80. [6] Smith R. J. and Horgan B. (2021) *JGR*, 126. [7] Weins R. et al. (2021) *Space Sci. Rev.*, 217. [8] Allwood A. et al. (2020) *Space Sci. Rev.*, 216. [9] Razzel Hollis J. et al. (2021) *Planet. and Space Sci.*, 209. [10] Bhartia R. et al. (2021) *Space Sci. Rev.*, 4. [11] Udry A. et al. (2022) *this meeting*. [12] Wiens et al. (2022) *this meeting*. [13] Schmidt et al. (2022) *this meeting*. [14] Scheller E. et al. (2022) *this meeting*. [15] Poulet F. et al. (2022) *this meeting*. [16] Meslin, P. -Y. et al. (2022) *this meeting*. [17] Di Genova D. et al. (2015) *J. Raman Spectrosc.*, 46, 1235–1244. [18] Steele et al. (2018) *Sci. Adv.*, 10.