FROM HYDRATED SILICA TO QUARTZ: POTENTIAL HYDROTHERMAL PRECIPITATES FOUND IN JEZERO CRATER, MARS

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Introduction: NASA's Mars2020 Perseverance rover has been exploring Jezero crater on Mars since February 2021, with one aim being to collect a set of samples that shall be returned to Earth in a later mission, where they will be scrutinized to search for organic traces of ancient life, as part of the M2020 mission and the Mars Sample Return Program (e.g., [1]). One of the four major science goals of the mission is also to assess the biosignature preservation potential of the landing site [1]. To this end, rocks containing hydrated silica and other silica-rich phases currently represent one of the most promising astropaleontological targets [2]. Here, we report on the detection of three types of silica-dominated targets found in Jezero crater at three different locations: opaline silica, chalcedony, and quartz, the latter being observed in nearly pure form for the first time at the surface of Mars.

Methods: High-silica targets were identified using the combination of VISIR (visible/near infrared) spectroscopy, Raman spectroscopy, and chemistry data from the SuperCam instrument. The RMI (Remote Micro Imager) mosaics of the targets are shown (Fig. 1), and LIBS (Laser-Induced Breakdown Spectroscopy) and VISIR (visible/near infrared) reflectance spectra were obtained on several locations on the targets (Fig. 1). SuperCam provides information on the chemistry of rocks within about 10 meters of the rover using LIBS. The plasma emission generated by focusing a pulsed laser onto the target is analyzed by multiple spectrometers and emission lines can be used to derive the elemental composition for each point [3]. The SuperCam InfraRed Spectrometer (IRS) measures reflected sunlight in the 1.3-2.6 µm range [4], with a spectral resolution ranging from 5 (at 1.3 µm) to 20 nm (at 2.6 µm). Reflectance spectra from the targets were calibrated using the procedures described in [5]. SuperCam visible (VIS) spectra were also collected (0.40-0.85 µm), but are not used here.

Observations: The first detection of high-silica material (target *AEGIS_0910A*) occurred on sol 910 using AEGIS automated targeting software shortly after Perseverance entered the "Margin Unit" of Jezero crater [6]. This rock was selected by the "AEGIS" autonomous targeting software onboard the rover. The second observation (target Elves_Chasm) was also made close the edge of the Margin Unit, but within the northern-most part of the unit (Fig. 1). The third occurred during the Crater Rim Campaign, when the rover was climbing through a suite of igneous rocks of ultramafic to felsic chemistry. Four targets were analyzed by SuperCam and found to be silica-dominated: *Emmons_Glacier*, *AEGIS_1331B*, *Margaret_Falls* and *Owyhigh_Lakes*. The silica-rich material was found as light-gray float rocks, with a lustrous appearance.

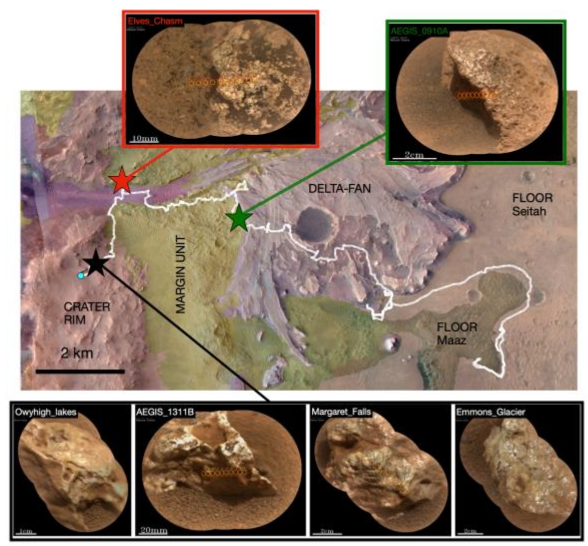

Figure 1: Annotated geologic map of units within Jezero crater, superimposed on color imaging, with the location of the high-silica targets indicated by red (opal), green (chalcedony- and black (quartz) stars. The white line is the rover traverse since landing. For each of the three locations, RMI images of high-silica targets are also shown, where red circles correspond to the field of view of SuperCam IR spectrometer.

The LIBS-derived elemental chemistry revealed strong enrichment in SiO_2 for all the 6 targets. These rocks clearly stand out among the >950 individual targets analyses performed by SuperCam since the beginning of the mission. The reflectance spectra of well-illuminated points (1-4) from *AEGIS_0910A* share an overall general blue slope and exhibit well-resolved absorptions at 1.9 µm (H_2O), 2.2 µm (Al-OH) and 1.4 µm (OH and H_2O). The reflectance spectra of *Elves_Chasm* also shows absorption bands at 1.4, 1.9 and 2.2 µm, but the exact position of these bands differs from *AEGIS_0910A*. The use of spectral criteria (band depth, position and concavity) [7-9] indicate that *AEGIS_0910A* has spectral properties close to terrestrial chalcedony and that *Elves_Chasm* is similar to desiccated opals-A or CT.

While the LIBS-derived chemistry points toward very high SiO_2 compositions for the four targets encountered in the crater rim (Fig. 1), the VISIR spectra do not show any evidence for Si-OH which suggests a mature form of silica. Absorptions at 2.31 and 2.39 µm are likely related to impurities in the quartz such as Mg-bearing clay minerals, similar to those found in the Margin Unit and some locations of the crater rim. Absorption bands at 1.4, 1.9 and 2.1 µm may be related to the contribution from mono-hydrated Fe- sulfate.

Among the four targets from the crater rim, only *Emmons_Glacier* was analyzed by Raman. The four points yield very similar strong spectra (peak positions, flat continuum background), and the absence of hydration features suggested that the mineralogy is the same for these points. When averaging these four spectra all the peaks are attributed to quartz as listed by [10]. Noticeably, no peak assignable to any other SiO_2 polymorph is observed in this [10], nor is hydration assignable to opaline silica [11]

Discussion: Quartz can be found on Earth in igneous, metamorphic, sedimentary or hydrothermal rocks. If the quartz was of igneous origin, we may however expect to find it in association with other silicates (feldspar, mica) as well as with late-stage minerals such as phosphates or Fe-Ti oxides. However, LIBS and VISIR show that the targets are fairly homogeneous (with the exception of superficial dust coatings) and that these phases are absent. Quartz may also be found in sandstones, but we do not see evidence for grains, cement, or other minerals phase that would support a sandstone hypothesis. Quartz and amorphous silica are stable under current Mars conditions, while other silicates, such as opal can dehydrate over time [12]. Quartz may also be encountered in cherts, rocks formed by the massive precipitation of silica. However, cherts are very fine-grained and may produce a strong fluorescence-like background in remote Raman such as SuperCam which is not observed in the spectrum obtained by SuperCam on *Emmons_Glacier*.

Our preferred hypothesis is therefore that the quartz was initially formed by hydrothermal processes. On Earth quartz veins are commonly observed as fracture fills in crustal rocks, and are formed by the hydrothermal precipitation of silica. Such a formation scenario is consistent with well crystalized silica, and fairly coarse grain sizes that explain the lack of fluorescence-like background in the Raman spectra.

Furthermore, if the three types of silica (quartz, opal, chalcedony) observed in Jezero are related to a single system and a single formation process, the observations would be consistent with a hydrothermal origin, and their variation in texture and composition could be explained by different temperature-pressure of precipitation. The texture and crystallinity of the quartz-dominated float rocks argues toward a direct precipitation of SiO_2 at pH<8 and relatively high-T, and in a confined environment. Conversely, the "popcorn" texture of *Elves_Chasm*, may suggest precipitation under low-P, at the surface, and the texture is more akin to a surficial hydrothermal sinter deposit. In that model, the quartz-rich targets would have formed at some depth, within the bedrock, while *Elves_Chasm* may represent surface precipitates from a similar and/or related source. The chalcedony target *AEGIS_0910A* would represent an intermediate between the other opaline silica and the quartz.

Interestingly, the quartz float rocks were found in the crater rim, close to a suspected inverted fracture network [13]. On Earth, impact cratering is known to generate hydrothermal systems within and around the crater, when the heat deposited by the cratering process is lost through water circulation [14]. Hydrated silica and quartz are among the mineral phases that can be produced by such impact-induced hydrothermalism [14-15]. In the case of terrestrial craters, deep faults are present on the crater rim/wall and at least in one well documented case, the Haughton crater, these faults were found to act as conduits for the development of hydrothermal vents [16]. Given the proximity of all high-silica targets with the Jezero crater wall, they may be related to a noachian hydrothermal system, triggered by the Jezero crater-forming event – a hypothesis addressable with upcoming observations.

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