SuperCam detections of hydrated-silica in the Jezero crater. P. Beck<sup>1</sup>, E. Dehouck<sup>2</sup>, O. Beyssac<sup>3</sup>, O. Forni<sup>4</sup>, E. Clavé<sup>5</sup>, S. Bernard<sup>3</sup>, E.A. Cloutis<sup>6</sup>, L. Mandon<sup>1</sup>, C. Royer<sup>7</sup>, W. Rapin<sup>4</sup>, S. Schröder<sup>5</sup>, R. Francis<sup>8</sup>, N. Mangold<sup>9</sup>, J. Johnson<sup>10</sup>, C. Quantin-Nataf<sup>2</sup>, F. Poulet<sup>11</sup>, T. Fouchet<sup>12</sup>, C. Pilorget<sup>11</sup>, C.C. Bedford<sup>7</sup>, T.S.J. Gabriel<sup>13</sup>, J.M. Madariaga<sup>14</sup>, G. Arana<sup>14</sup>, S. Clegg<sup>15</sup>, A. Cousin<sup>4</sup>, R.C. Wiens<sup>7</sup>, S. Maurice<sup>4</sup> & the SuperCam Team. <sup>1</sup>IPAG, Univ. Grenoble Alpes. <sup>2</sup>LGL-TPE, Univ. Lyon. <sup>3</sup>IMPMC, Paris. <sup>4</sup>IRAP, Toulouse. <sup>5</sup>DLR, Berlin. <sup>6</sup>Univ. of Winnipeg. <sup>7</sup>Purdue University. <sup>8</sup>NASA-JPL. <sup>9</sup>LPG Nantes.<sup>10</sup>APL John Hopkins Univ.<sup>11</sup>IAS, Univ. Paris-Saclay.<sup>12</sup>LESIA, Obs. Paris.<sup>13</sup>USGS, Flagstaff. <sup>14</sup>Univ. Basque Country. <sup>15</sup>LANL.

Introduction: Hydrated silica is a common product of both low to high temperature aqueous alteration of Si-bearing rocks. While this material is simple in its chemistry (silica + H<sub>2</sub>O), it can exist through a diversity of crystallinity, shapes, mesoscopic arrangements of the silica domains, or amounts of OH/H<sub>2</sub>O. This diversity is a result of the variety of protoliths, geological contexts, and alteration pathways from which it can form [1]. Opals are the less crystalline forms, and can be classified according to their diffraction spectra [2]. On Earth, opals are all less than a few Ma old [1] since they inevitably transform to more "crystalline" types upon burial-heating and interaction with water, eventually made of fibrous forming chalcedony, and cryptocrystalline quartz and moganite, or cherts made of massive cryptocrystalline quartz.

Hydrated silica has been detected from orbit in Jezero crater [3] and holds great promise for the astrobiology science goals of the M2020 mission and the Mars Sample Return Program (e.g.,[4]). In fact, early entombment within an hydrated silica matrix has been shown to minimize the molecular degradation of microorganisms during advanced diagenesis [5]. Consistently, ancient terrestrial cherts such as the 1.88 Ga Gunflint cherts or the 3.4 Ga Strelley Pool cherts, still contain (partially preserved) molecular biosignatures [6-7].



Figure 1: RMI image of the AEGIS\_0910A target Observation: On sol 0910, a float rock was automatically selected by the AEGIS system after a rover drive when entering the margin unit from the Jezero delta top. AEGIS is an automatic targeting

algorithm that has been implemented to SuperCam modes of operations [8-9]. The RMI (Remote Micro Imager) image of the target is shown (Fig. 1), and LIBS (Laser Induced Breakdown Spectroscopy) and VISIR (visible/near infrared) spectra were obtained on ten different locations of the target.

**RMI image:** The target is light-toned, partially buried float with lustrous appearance. It displays a pitted texture (typical pit size 1-2 mm), and the surface is partially covered by sand or dark dust coatings. Some of the VISIR analyses are unfortunately shadowed but spectra with good signal to noise ratio were obtained on locations 1 to 4 (Fig. 1).

**LIBS chemistry:** The chemistry of 9 out of 10 points reveal a homogeneous composition, enriched in SiO<sub>2</sub>. The average SiO<sub>2</sub> content for these 9 points is 75.0 wt.%, while the average total of quantified oxides is 83.5 wt. %. The low total may be due to the presence of one or a combination of the following non-quantified species: C, H, S, Cl (but neither S nor Cl emission lines were detected). Inspection of the LIBS spectra suggests that the rock is closer to pure silica than indicated by the composition provided by the quantification model.

**Reflectance spectra:** The reflectance spectra of well-illuminated points from the target (1-4, Fig.1-2) share an overall blue slope, and exhibit absorptions at 1.9  $\mu$ m (H<sub>2</sub>O), 2.2  $\mu$ m (Si-OH or Al-OH) and 1.4  $\mu$ m (OH & H<sub>2</sub>O). The chemistry derived from LIBS (mean Al<sub>2</sub>O<sub>3</sub>< 2 wt.%) leads to the attribution of the 2.2  $\mu$ m band to Si-OH. All such absorptions are present within spectra of terrestrial hydrated silica (Fig. 2).

**AEGIS 0910A and relation to high-Si and high-Al points:** This target selected by AEGIS is unique so far in having almost all points showing a strong enrichment in SiO<sub>2</sub>. The exception is point 2. (dark tones in the RMI images) that has a chemistry in line with dust/coatings [10]. While AEGIS\_0910A is a float rock, it was detected in an area that shows an increase in carbonate-signature and an increase in high-SiO<sub>2</sub> points within the bedrock. Several light-toned floats have been observed in the crater ([11-13] al., this meeting), and their chemistry suggests a mixture of silica and an Al-rich phase. It is not clear whether this AEGIS target is related to this family of rocks. It lacks elevated Ni as seen in the Al-rich rocks [13] potentially indicating a unique geological history.



Figure 2: IRS spectra of AEGIS\_0910A compared to opals (C-TAPE spectra in black and grey) and chalcedony (USGS).



Figure 3: Major element chemistry of AEGIS\_0910A compared to all other SuperCam targets.

What type of hydrated silica? Given the LIBS derived chemistry dominated by high SiO<sub>2</sub>, we can reasonably attribute all absorption bands to the hydrated silica ([14-15]). The reflectance spectra show that this target contains both Si-OH (silanol) and molecular water. The position of absorption bands departs from what is typically observed for opals A or CT (i.e., the 1.9-µm band is at higher wavelength in AEGIS 0910A, lack of 1.46-µm feature) and chalcedony is at present the closest spectral analogue in term of band depths and position. The position of the 1.9 band indicates that most water molecules are free (not bonded to silanol). Interestingly, the hydrogen signal derived from LIBS analysis is quite low suggesting a relatively water-poor type of silica, in agreement with chalcedony, but the quantification is still in progress.

What origin? A 2.2 µm band has been observed in the IR spectra from the upper fan and the margin unit, together with carbonate and phyllosilicate signatures. The LIBS derived chemistry of the targets suggest that this 2.2 band is related to hydrated silica though we cannot strictly exclude a contribution from an Al-OH phase. This suggests that the formation of the hydrated silica is associated with carbonate formation (locally or in the catchment) and that AEGIS 0910A may have the same origin. One possible scenario that is being investigated is that this silica material could represent the precipitates from a fluid that dissolved the ubiquitous olivine found in Jezero floor and delta (and regionally), and concomitantly precipitated carbonates that are abundant in the upper-fan and marginal unit rocks ([16-17]).

**Comparison to other silica observations on Mars:** Here, reflectance spectroscopy reveals that this hydrated silica-rich material is more crystalline that the hydrated silica deposits previously reported on Mars from orbit and *in situ* at Marias Pass, Gale crater [18-21]. CheMin analyses revealed that a silica-rich amorphous material is present but in association with cristobalite [22]), and suggested that a fraction of hydrated silica could contribute to the amorphous component identified in most samples.

Summary: Two independent lines of evidence, VISIR and LIBS, reveal that the float rock analyzed on sol 910 is made of hydrated silica. This target is unique so far in the SuperCam dataset (> 500 targets), but may be linked to high Al<sub>2</sub>O<sub>3</sub> and high SiO<sub>2</sub> points observed in the carbonate-rich delta bedrock units. Based on the reflectance spectra, this rock seems more akin to a micro-crystalline type of silica, in contrast to previous observations of hydrated silica from the ground. Such a target may have trapped and preserved biosignatures, information together with unique on the paleoenvironmental conditions of the Jezero crater. Perseverance will thus be on the lookout for similar targets in the future.

**References:** [1] Rice et al., *Icarus* (2013) [2] Williams et al., *J. Sed Pet.* (1985) [3] Tarnas et al., *GRL* (2019). [4] Farley et al., *SSR* (2021) [5] Alleon et al., *Chem Geol.* (2016) [6] Alleon et al., *Nat. Com.* (2016) [7] Alleon et al., *GPL* (2018) [8] Francis et al., Sci. Rob. (2017) [9] Wiens et al., *SSR* (2021) [10] Garczynsky et al., JGR Planets (2023) [11] Royer et al., this meeting. [12] Bedford et al., this meeting. [13] Forni et al., this meeting. [14] V. Sun PhD (2017) [15] B. Chauviré PhD (2016) [16] Wiens et al., GRL 2021, [19] Gabriel et al., JGR 2022 [20] Ruff et al., JGR Planets (2011) [21] Rapin et al., JGR Planets (2018). [22] Morris et al., PNAS (2016).