First results from Atmospheric Observations of CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub> and CO Abundances with SuperCam on Mars 2020. F. Montmessin<sup>1</sup>, T. McConnochie<sup>2,6</sup>, T. Fouchet<sup>3</sup>, C. Royer<sup>3</sup>, E. Knutsen<sup>1</sup>, T. Bertrand<sup>3</sup>, O. Forni<sup>4</sup>, P. Pilleri<sup>4</sup>, O. Gasnault<sup>4</sup>, G. Lacombe<sup>1</sup>, J. Lasue<sup>4</sup>, C. Legett<sup>5</sup>, M. T. Lemmon<sup>2</sup>, R. T. Newell<sup>5</sup>, D. M. Venhaus<sup>5</sup>, S. Maurice<sup>4</sup>, R. C. Wiens<sup>5</sup>, and the SuperCam team <sup>1</sup>LATMOS, 11 bd d'Alembert, 78280 Guyancourt, France (franck.montmessin@latmos.ipsl.fr), <sup>2</sup>Space Science Institute, Boulder, CO, USA, <sup>3</sup>LESIA, Meudon, France, <sup>4</sup>IRAP, CNRS, Université de Toulouse, UPS-OMP, Toulouse, France, <sup>5</sup>Los Alamos National Laboratory, Los Alamos, NM, USA, <sup>6</sup>University of Maryland, College Park, MD, USA

**Introduction:** The SuperCam instrument [1,2] onboard Mars2020 is capable of a variety of active and passive techniques, including passive spectroscopy in the 0.40-0.85 (VIS) and 1.3 to 2.6 microns (IR, [3,4]) wavelength ranges. Since the landing on Mars of Perseverance in February 2021, Supercam has acquired numerous observations of its near and distant environment, exploring the geological and mineralogical context of Jezero crater.

In addition, several measurements were devoted to probing the atmosphere surrounding the Perseverance rover. The technique of using sky spectra in passive mode, known as "passive sky", has already been demonstrated with ChemCam on the Mars Science Laboratory (MSL) rover [5]. SuperCam provides a superset of the ChemCam capabilities used in [5], and in particular adds a near-infrared component that includes absorption and scattering characteristics of key gases and aerosols/clouds.

"Passive sky" measurements have typically been performed every other week to allow a consistent monitoring of the seasonal evolution of the main quantities (CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO, aerosols/clouds). Particular attention was given to joint measurements of O<sub>2</sub> and CO, as they appear as key components of the Martian chemical cycle and have never been measured together at the same time on the surface of Mars. As the 2  $\mu$ m wavelength region is used for the first time at the surface of Mars, it enables the detection of CO (around 2.35  $\mu$ m). CO possesses a small absorption that has made it difficult to identify in SuperCam spectra so far.

An overview of SuperCam's progress to date in its characterization of the Martian atmosphere at Jezero will be presented.

## **Objectives:**

O<sub>2</sub> column abundance. O<sub>2</sub> (like H<sub>2</sub>O) is a key player in Martian photochemical cycles, and its chemistry is crucial to the long term stability of CO<sub>2</sub> [6]. It had been universally expected to have such a long chemical lifetime [7,8,9] that it behaves like an inert trace gas on timescales relevant to atmospheric circulations and annual cycles. However, in-situ atmospheric sampling by the Sample Analysis at Mars (SAM) Quadrupole Mass Spectrometer (QMS) on the MSL rover showed unexpected seasonal and interannual variability in the O<sub>2</sub> mixing ratio [10]. The magnitude of the unexpected

variability was too large to be explained by any purely atmospheric source or sink because CO<sub>2</sub> photolysis is known to be too slow and water vapor abundances are too small [10]. This led [10] to suggest sources and sinks in surface soils and to note that perchlorates represent a sufficiently large reservoir of oxygen atoms, albeit one lacking a known mechanism for sufficiently rapid exchange with the atmosphere.

Recent numerical modeling of perchlorate chemistry showing the release of oxygen from perchlorates in the combined presence of silicates, water vapor, and UV radiation [11] in Mars-like conditions suggests a potential way forward for the O<sub>2</sub> variability problem. Our objectives for O<sub>2</sub> measurements are therefore to confirm the surprising results of [10] at a second site, and to test potential correlations between excess O<sub>2</sub> variability and local or global water vapor abundance as well local or global aerosol opacity (which modulates surface UV flux). The desired precision for O<sub>2</sub> measurements is +/- 50 ppm in terms of columnaveraged volume mixing ratio, comparable to the typical precision in [10].

*CO column abundance.* In contrast to O<sub>2</sub>, CO has been observed [12] to follow the expected seasonal cycle of a chemically-inert non-condensable trace gas. To resolve the expected seasonal cycle of CO, our target measurement precision is +/- 100 ppm.

Water vapor column abundance. Local water vapor measurements are particularly valuable for assessing exchanges of water vapor between the atmosphere and surface materials. Our primary objective for water vapor is therefore to routinely sample the daytime water vapor column, for direct comparison with nighttime mixing ratio measurements made by the Mars 2020 Mars Environmental Dynamics Analyzer (MEDA) humidity sensor [13], but also to help connect in-situ measurement by MEDA with measurements from orbit. We target a precision for precipitable water column of +/- 1 precipitable microns, comparable to ChemCam [10].

Aerosol particle sizes and composition. Both MEDA and Mastcam-Z [14] on the Mars 2020 payload provide direct measurements of column aerosol opacity in addition to sky brightness measurements that can substantially constrain particle sizes. SuperCam, will contribute to constraining particle sizes and will with its

broad spectral range and near-infrared coverage be uniquely well-suited to constraining the relative contributions of water ice and dust to column opacity, and to distinguishing the dust aerosol particle size distribution from that of water ice.

Relationship to Mars 2020 mission objectives. Since both O<sub>2</sub> and H<sub>2</sub>O cycle into and out of Martian soil, that soil is currently or was in the recent past in some kind of equilibrium with these atmospheric volatiles. Thus the atmospheric H<sub>2</sub>O and O<sub>2</sub> cycles are an important part of the geochemical and geological context for near-surface samples and the Jezero field site. Aerosols, too, are relevant geological context because some portion surface-accumulated aerosols will inevitably be present in returned samples. Evaluation of airborne dust hazards is also an important precursor to human exploration, and aerosols are important diagnostics of atmospheric dynamical processes, as are water vapor and carbon monoxide, and thus the are important for validating global atmospheric models

## Measurement approach:

SuperCam VISIR Spectrometers: ChemCam-heritage reflection spectrometer, 385–465 nm ("violet"), < 0.2 nm res. [3]; intensified transmission spectrometer, 536–853 nm, 0.3-0.7 nm res. [3]; acousto-optic-tunable-filter (AOTF) -based IR spectrometer on the rover mast, 1300-2600 nm, 20-30 cm<sup>-1</sup> res. [2,4].

Primary "passive sky" observing strategy. Our primary observing strategy is the same approach used for MSL ChemCam "passive sky" observations [10]: we point SuperCam at two different elevation angles in the sky that yield two different path lengths through the gas absorptions of interest. Due to sun-safety constraints, all sky spectra are effectively out of focus yielding an effective field of view of ~3° diameter. Ratioing instrument signals from the two pointing positions eliminates solar spectrum and instrument response uncertainties that are  $\sim 100x$  and  $\sim 10x$  larger than signals of interest for the transmission and AOTF IR respectively. spectrometers, For the intensified transmission spectrometer, instrument response fluctuates significantly with instrument temperature and so we must ratio different atmospheric pointings acquired within minutes of each other. To obtain the desired sensitivities for O<sub>2</sub> and H<sub>2</sub>O vapor, we use ~20 minutes of total integration time to provide multiple visits to each pointing position.

First results (Fig. 1). We have retrieved a water vapor mixing ratio (VMR) varying between 24 to 147 ppmv with a 5 ppmv uncertainty out of H<sub>2</sub>O and CO<sub>2</sub> infrared signatures, in rough agreement with MEDA RH measurements [15]. CO has been tentatively estimated on a restricted number of occasions, resulting in a VMR ranging between 900 to 1700 ppmv that corresponds to

the concentration that is observed from orbit, in particular by ACS on TGO [16]. However, many flaws in the processing still remain that have prevented the extraction of the majority of the potential information contained in the dataset. A number of improvements still need to be implemented to permit full use of SuperCam VISIR spectrometers for atmospheric observations.

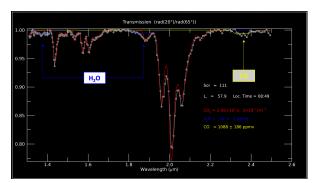


Figure 1: Fitting attempt on the IRS part of SuperCam performed on the data collected on Sol 111.

References: [1] Wiens, R.C., et al., 2021. Space Sci Rev 217, 4, [2] Maurice, S., et al., 2021. Space Sci Rev 217, 47, [3] Royer, C., et al., 2020. Review of Scientific Instruments 91, 063105, [4] Fouchet, T., et al., 2021, Icarus, 373, 114733. [5] McConnochie T. H et al., 2018. Icarus 307, 294. [6] Atreya S. K. and Gu Z. G. (1994), JGR 99, 13133. [7] Atreya S. K. and Gu Z. G.(1995), Adv. Space Res, 16, #6, 57. [8] Clancy R. T. and Nair H. (1996), JGR 101, 12785. [9] Lefèvre F. and Krasnopolsky V. (2017), in The Atmosphere and Climate of Mars, Cambridge U. Press, 374. [10] Trainer M. G. et al. (2019), JGR 124, 3000. [11] Escamilla-Roa E. et al. (2020) Applied Surface Science, 512, 145634. [12] Smith M. D. et al. (2018), Icarus 301, 117. [13] Rodriguez-Manfredi et al. (2021) Space Sci Rev, 217, 3, 48. [14] Bell et al. (2021), Space Sci Rev, 217, 1, 24. [15] Tamppari et al. (2021), AGU fall meeting, New Orleans P251-2253. [16] Fedorova et al. (2022), in prep..