ANALYSIS OF MARS OLIVINES WITH THE RAMAN SPECTROMETER IN THE PERSEVERANCE ROVER SUPERCAM INSTRUMENT.

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Introduction: The Perseverance rover has been in Jezero crater, Mars, since February 2021; investigating the geology of the site, looking for biosignatures, assessing habitability and studying Mars' climate. Within the rover's payload is the SuperCam instrument, a suite of six remote characterization techniques including a telescopic Remote Micro Imager (RMI), a microphone and four spectroscopies: Laser Induced Breakdown (LIBS), Visible and Near Infrared Reflection and Raman [1,2]. During the Perseverance rover mission, SuperCam has taken Raman spectral linear raster sequences of over 30 Martian rocks, including undisturbed samples and abrasion patches. These measurements resulted in olivine being the most detected mineral phase using the Raman spectrometer. All the detections were in the Seitah formation, visited between sols 200 and 340 of the mission. However, most of these spectra showed only weak olivine Raman signal, with noise, spurious spikes, shot to shot intensity and wavelength variations and Raman background arising from the optic fiber connecting the mast (MU) and body units (BU) of the instrument [3] further complicating the analysis of the Raman signals of Jezero crater olivine. As Raman spectra can provide unequivocal mineral identification besides adding information on crystallinity, new data processing approaches are needed to extract the maximum information for the Raman spectra obtained in Mars. In the case of olivine ($FeMgSiO_4$), falling on the mixing line between forsterite ($MgSiO_4$) and fayalite ($FeSiO_4$), the Raman spectra has been found to shift in wavelength with composition [4]. This study looks at characterizing the Jezero Mars olivine from the available data to further constrain Jezero crater geological history.

Methods: SuperCam Raman spectra containing signatures of olivine were analyzed to extract accurate peak positions and spectral shapes. The Raman spectra contained two major sources of inaccuracies affecting the position of the two major olivine Raman peaks in the range 815-857 cm^{-1}: the Raman signal of the optical fiber connecting the BU and the MU, and the presence of spurious spikes. The optical fiber shows its fused silica composition with a broad Raman feature in the Range 790-860 cm^{-1} present in all the spectra, confounding the olivine signal. Random spurious spikes in each spectrum added variability to the final averaged point spectra. Raman spectra were taken with 532 nm excitation, typically in rasters of 9 different points in the rocks, resulting from the co-addition of 20 laser shots.

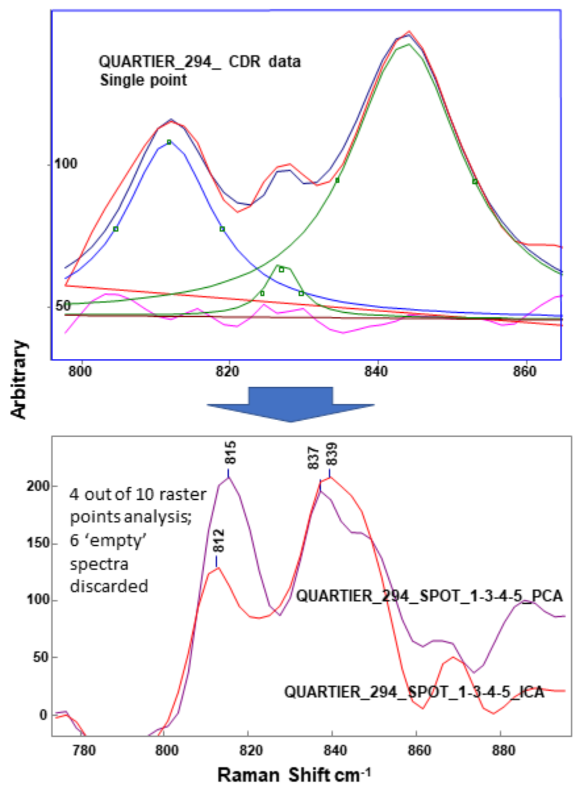

Figure 1: Example of the ICA/PCA analysis results obtained in this study. Top panel: CDR SuperCam Raman data for one point showing olivine Raman signal in Quartier 294. Bottom panel: PCA and ICA derived spectra for points 1, 2, 4 and 5 obtained in this study.

Raster points showing the main olivine doublet were selected for each Martian sample showing olivine Raman features: Garde, Penne, Dourbes, Castellet and Quartier, in addition to the olivine calibration target onboard the rover. The latter has been characterized as having a forsterite ratio Fo65 before flight using EPMA and LA-ICP-MS [5]. Candidate spectra were despiked by performing a sigma-clipping algorithm, which is effectively used by the SuperCam team and is a common algorithm used in Astronomy [6]. The presence of olivine signal was confirmed by extracting one olivine component through independent component analysis (ICA). The contribution of the fused silica spectrum from the optic fiber was removed by including a modeled spectrum of fused silica as an ICA component. Principal component analysis (PCA) was applied to extract the olivine Raman component for a selection of several points showing the main olivine doublet from each sample along the modeled fused silica spectrum input into the PCA model. The modeled fused silica spectra were from the Mars target Guillaumes on Sols 163 and 168. These spectra were chosen as the fiber optic cable signal was pronounced as well as being the only feature present in the spectrum. The spectra were standardized and processed using the python package Scikit learn.

Results and discussion: ICA and PCA derived Raman spectra were obtained for Martian samples Garde sol 207, Garde 209, Garde 210, Penne, Dourbes, Castellet, Penne, Dourbes, Castellet, Quartier 294 and Quartier 303, in addition to the olivine calibration sample onboard the rover. The forsterite ratio of most olivine detections in the Seitah formation within Jezero crater, Mars, falls in the range Fo53-60, Table 1. This is consistent with other data provided by the SuperCam instrument, with Fo54-72 obtained from LIBS [7], and with the Fo55 characterization provided by the PIXL instrument onboard the rover from data taken on the same samples [8,9]. These are also consistent with the interpretation of the Seitah formation being an igneous cumulate [7 ,9].

Target	**Fo %**
Garde, Sol 207	**57**
Garde Sol 209	**53**
Garde Sol 210	**59**
Penne Sol 211	**55**
Dourbes Sol 259	**58**
Castellet Sol 248	**60**
Olivine SCCT	**69**

Table 1: Calculation results of Forsterite ratios for Seitah olivine and the olivine on the SuperCam calibration sample set.

The Raman derived forsterite olivine ratio for the calibration sample, Fo69, is higher but within 5% of the EPMA/LA-ICP-MS value obtained before the mission, Fo65. That precision is consistent with that reported for the olivine composition Raman calibration used in this study [4, 10].

The Raman spectra of the olivine from the sample Quartier show unusually low Raman shifts consistent with possible Ca, Mn or other ions within the olivine. The spectra from Quartier were obtained from an abrasion patch drilled on the Issole outcrop within the Seitah formation. We found olivine on the measurements taken in same sample at different times, in sols 294 and 303, to show the same unusually low Raman shifts for olivine, confirming the Raman spectrum of Quartier. Manganese in the composition of the Quartier olivine was found to be too low to explain the unusual Raman shift using the LIBS measurements obtained from points colinear and overlapping the Raman raster points. Nevertheless, the unusual olivine Raman shift in Quartier suggests that the parent magmas of the Issole outcrop are slightly different than that of the rest of the Seitah formation.

Conclusions: The SuperCam Raman instrument onboard the Perseverance rover obtained olivine Raman spectra for samples located in the Seitah formation, Mars. This study proves that ICA and PCA analysis can help retrieve the information on otherwise unreliable Raman data. According to olivine Raman data and in concordance with other measurements onboard the rover, the Seitah formation is an igneous cumulate. The ICA and PCA analysis were able to characterize the slightly different Quartier Raman data, suggesting that Quartier might have a slightly different parent magma. The same technique could be applied to other SuperCam Raman spectra obtained during the mission.

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References: [1] Wiens, R. C et al. (2020) *Space Sci. Rev. 217*, 4. [2] Maurice, S. et al. (2021*) Space Sci. Rev*. 217, 47. [3] Kelly, E. et al. (2023), *this conference*. [4] Kuebler, K.E. et al. (2006) *Geochim. Chosmochim. Acta*, *60*, 6201. [5] Cousin, A. et al. (2022) *Spectrochim. Acta B*, *188*, 106341. [6] Akhlaghi, M. and Ichikawa, T. (2015) *Astrophys. J. Suppl. Series*, 220, 1, 33. [7] Wiens, R.C. et al (2022) *Sci. Adv*. *9*, abo3399. [8] Tice M.M. et al. (2022) *Sci. Adv. 8*, eabp9084 [9] Liu, Y. et al. (2022) *Science, 377*, abo2756. [10] Acosta-Maeda et al. (2013) *Amer. Min. 98*, 859.