The effect of Martian conditions on the stoichiometry calculation of olivine (Fo-Fa) compositions using a combined Raman-Laser Induced Breakdown spectroscopy instrument. K. Motamedi[1], A. Colin[1], I. Hutchinson[2], R. Ingley[2] and G. Davies[1]. [1]Faculty of Earth and Life Sciences, De Boelelaan 1085, 1081HV Amsterdam, Netherlands; [2] Department of Physics & Astronomy, University of Leicester, University Road, Leicester LE1 7 RH, UK.

Introduction: To better understand the mineralogy of other planets we need to fully understand the crystal structure of all minerals so as to predict the signatures obtained by spectroscopic instruments utilised on space missions. Olivine is a mineral particularly influenced by breakdown under wet conditions, hence the detection of olivine on the surface of the Earth and other planets can help us to assess how long it has been at the surface and provide suggestions about the climate history of the planet. Olivine crystal characteristics can be determined by different spectroscopy such as adsorption, reflectance and Raman spectroscopy.

A combined Raman-laser induced breakdown spectroscopy (LIBS) instrument (RLS) was initially chosen as one of the analytical instruments of the rover's Pasteur instrument package of the ExoMars mission [1]. As such it was proposed to be one of the most important analytical tools on the mission being a first contact instrument. Raman spectrometry would be used to characterize mineralogy and organic compounds and simultaneously, the LIBS would determine multi-elemental compositions [2]. Due to scaling back of the ExoMars mission, the RLS has been replaced by a Raman only instrument. However, the potentially powerful analytical capability of a combined RLS system is widely recognized and development of a RLS continues in the context of potential future missions to both Mars and Moon [3].

Here, we study how olivine structure is affected by different chemistry and assess if these variations can be detected using the RLS. In addition, to simulate Mars condition, experiments are carried out in our Mars atmosphere simulation chamber (MASC) chamber, to assess the effect of low temperature and pressure on olivine Raman spectra.

Samples and analytical methods: In this study we use two olivine compositions with fosterite contents Fo value of 64 and 93 (molar ratio; Fo=Mg/(Mg+Fe) mol %) and we labelled them as olivine number 1 and 2. The Fo values were determined on a JEOL JXA-8800M Superprobe with four wavelength dispersive spectrometer (WDS) at VU University.

The RLS spectrometer uses a 659 nm wavelength laser for Raman analysis that weighs less than 30 g with an output of 20 mW. The spectrometer determined the Raman spectra of the two different olivine compositions under Martian condition within the MASC. These experiments are also effectively a test of the ability of the Raman spectrometer to act as a field instrument for planetary missions.

Raman spectra of olivines under vacuum condition (10^{-5} mbar) at +10^{0}C: Raman Peaks in the region of 700-1100 cm^{-1} are attributed to the internal symmetric and asymmetric stretching modes of the SiO_4 tetrahedra in olivine structure. The dominant feature within this region is a "doublet" of two peaks between 815– 825 cm^{-1} and 838 – 857 cm^{-1} and the positions of the major doublet peaks are more strongly controlled by composition of the olivine mineral. [4].

The Raman spectra of the two olivine compositions were determined at room temperature and under vacuum conditions to provide reference spectra. The spectra in Fig. 1 confirm the presence of a doublet peak circa 825 and 856 cm^{-1} in olivine 1, and 820 and 848 cm^{-1} in olivine 2. In our study the selected olivine samples have Fo values of 64 and 93. These compositional differences are clearly detected in the Raman spectra with shifts in Raman peaks with change of composition in olivine composition and hence structure.

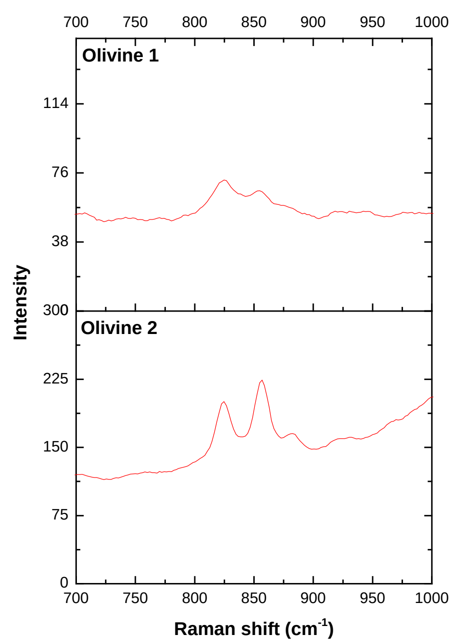

Figure 1. Raman spectra of olivine number 1and 2 in the range 700 – 1000 cm^{-1} at 10 ^{o}C, vacuum condition (10^{-5} mbar).

Raman spectra of olivine under 8 mbar CO_2 pressure between +10 and -20 ^{0}C: In the second part of the project, we examined possible variations in Raman spectra related to temperature variation. Temperature was varied between +10 and -20^{0}C. Doublet peaks near 825 and 856 cm^{-1} in olivine 1, 820 and 848 cm^{-1} in olivine 2 remain unchanged in wave number under different temperatures (Fig.2).

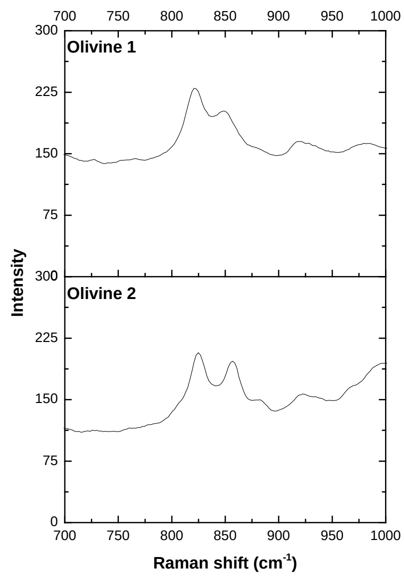

Figure 2. Raman spectra of olivine number 1and 2 in the range 700 – 1000 cm^{-1} at -20 ^{0}C, vacuum condition.

The experiments also establish that there is no variation in peak positions with the presence of CO_2 (Fig. 3)

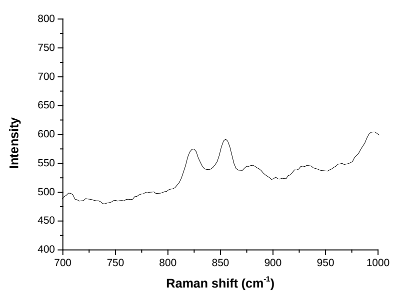

Figure 3. Raman spectra of olivine number 1 in the range 700 – 1000 cm^{-1} at -20 ^{0}C, 8 mbar CO_2

Conclusion: The analyses of the olivine Raman spectra under Marin conditions using the RLS system allow us to distinguish the peaks that allow characterize olivine with different composition under vacuum conditions and Martian analogue atmosphere (at 10 and -20^{o}C). In addition, varying temperature under Martian conditions did not effect Raman peak positions of the samples under study.

In comparing the frequencies of the various mode categories, the frequency ranges for the doublet peaks found in this study are indistinguishable to those found by Wang et al. 2006.

References: [1] K. E. Kuebler et al. (2006) *Geochimica et Cosmochimica Acta. Volume 70, Issue 24.* [2] F. Rull et al. (2012), *EPSC Abstracts, Vol. 7 EPSC2012-740.* [3] B. Ahlers et al. (2008), *VII ICSO.* [4] E. Laan et al. (2009), *XL LPSC, Abstract # 1836.*