THE EFFECTS OF TEMPERATURE ON THE RAMAN SPECTRUM OF LABRADORITE CRYSTALS.

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Introduction: Labradorite ($(Ca,Na)(Al,Si)_4O_8$) is a type of plagioclase feldspar. Labradorite has been identified on the Martian surface by the Thermal Emission Spectrometer onboard the Mars Global Surveyor mission [1]. The *ExoMars* rover, due to launch in 2018, will carry the first Raman spectrometer to be deployed on another planetary body [2, 3].

Rationale: Raman spectroscopy is generally regarded as a nondestructive technique; this statement is incorrect. Concentrated laser power can generate localized heating leading to devolatisation, crystalline changes, and even melting of the sample [3]. These heating effects, coupled with the large fluctuation of Mars' surface temperature over the course of one Sol, could lead to misinterpretation of spectral data. This study aims to investigate how changes in temperature affect the Raman spectrum of labradorite; either due to changes in the ambient temperature, and/or changes due to localized heating caused by the exciting laser.

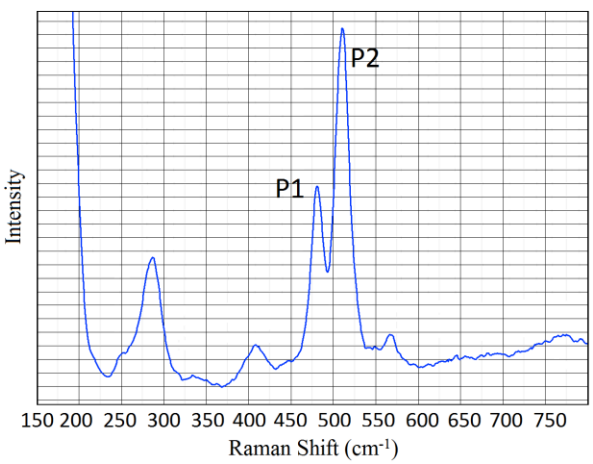

Fig. 1: Raman spectrum of Labradorite at 30°C with the main peaks at 481.27 and 509.59 cm^{-1} labelled as 'P1' and 'P2' respectively.

Raman spectroscopy uses monochromatic laser light to illuminate a sample. When the laser light strikes a molecule in the sample, most of the light is unaffected and can be detected at its original wavelength. A very small amount of the light, however, shifts due to interaction with the molecule and can be detected at wavelengths specific to the composition of the sample. This is known as Raman scattering [4]. Because the Raman scattering is specific to the composition of the sample, Raman spectroscopy can be used to identify specific molecular bonds within the sample.

The University of Kent's Raman spectrometer is a Horiba LabRam-HR equipped with four lasers: near infrared (785 nm), red (633 nm), green (532 nm), and blue (473 nm). In addition, it has a *Linkam* temperature controlled stage which can be used to cool/heat samples between -180°C and 600°C. The work carried out in this investigation used the 532 nm green laser that mimics the laser which will be carried on *ExoMars*. The Raman spectrum for labradorite at 30°C can be seen in Fig. 1, with the main peaks located at 481.27 and 509.59 cm^{-1} labelled as 'P1' and 'P2' respectively.

Methodology: A 4.70 mm diameter labradorite gemstone was placed in the *Linkam* temperature stage and heated to 30°C at a rate of 1°C per minute. Once 30°C had been reached the sample was allowed to stabilise for one hour before Raman spectra were obtained. The sample was then heated by 10°C at a rate of 1°C per minute and again allowed to stabilise for one hour before another spectrum was acquired. This process continued up to a maximum temperature of 550°C. To obtain data for temperatures below room temperature the labradorite sample was cooled in the *Linkam* stage using a liquid nitrogen pump. At the beginning of this experimental run, the sample was first heated to 40°C (in the same manner as before) to allow for a comparison between the two experimental runs. Once these two data points were obtained, the sample was then cooled by 10°C at a rate of 1°C per minute and the sample was allowed to stabilise for one hour before Raman data was obtained. This process continued down to a minimum temperature of -150°C.

These Raman data were then processed using a Python script which uses the least-squares fitting routine to find the exact position of the P1 and P2 peaks at each temperature, and then plots this position against the sample temperature.

Results: The graphs of temperature vs. P1 position and temperature vs. P2 position can be seen in Fig. 3. Although the peaks shuft by varying amounts, the plot shows that both peaks follow the same definite trend. The plot indicates that as the temperature of the sample is increased the peak positions decrease in wavenumber, while as the temperature decreases the position of the peaks increases in wavenumber.

The P1 position at -150°C is 482.15 cm^{-1}, and at 550°C the position is 478.01 cm^{-1}, giving a total variation of 4.14 cm^{-1} across a 700°C temperature difference. While the P2 position at -150°C is 509.93 cm^{-1}, and at 550°C the position is 507.97 cm^{-1}, giving a total

variation of 1.96 cm^{-1} across a 700°C temperature difference.

Conclusion: As can be clearly seen in Fig. 3, there is a strong negative trend showing the peak positions, decreasing in wavenumber as the temperature increases and the peak positions increasing in wavenumber as the temperature decreases. Using the Stokes and anti-Stokes ratio, the temperature of the sample itself will be calculated to compare with the ambient temperature of the stage to infer how much laser heating has occurred within the sample.

This work is a continuation of a series of Raman temperature experiments being conducted on various Martian analogue minerals. Pervious experiments have been conducted on Olivine [5] and Quartz [6]

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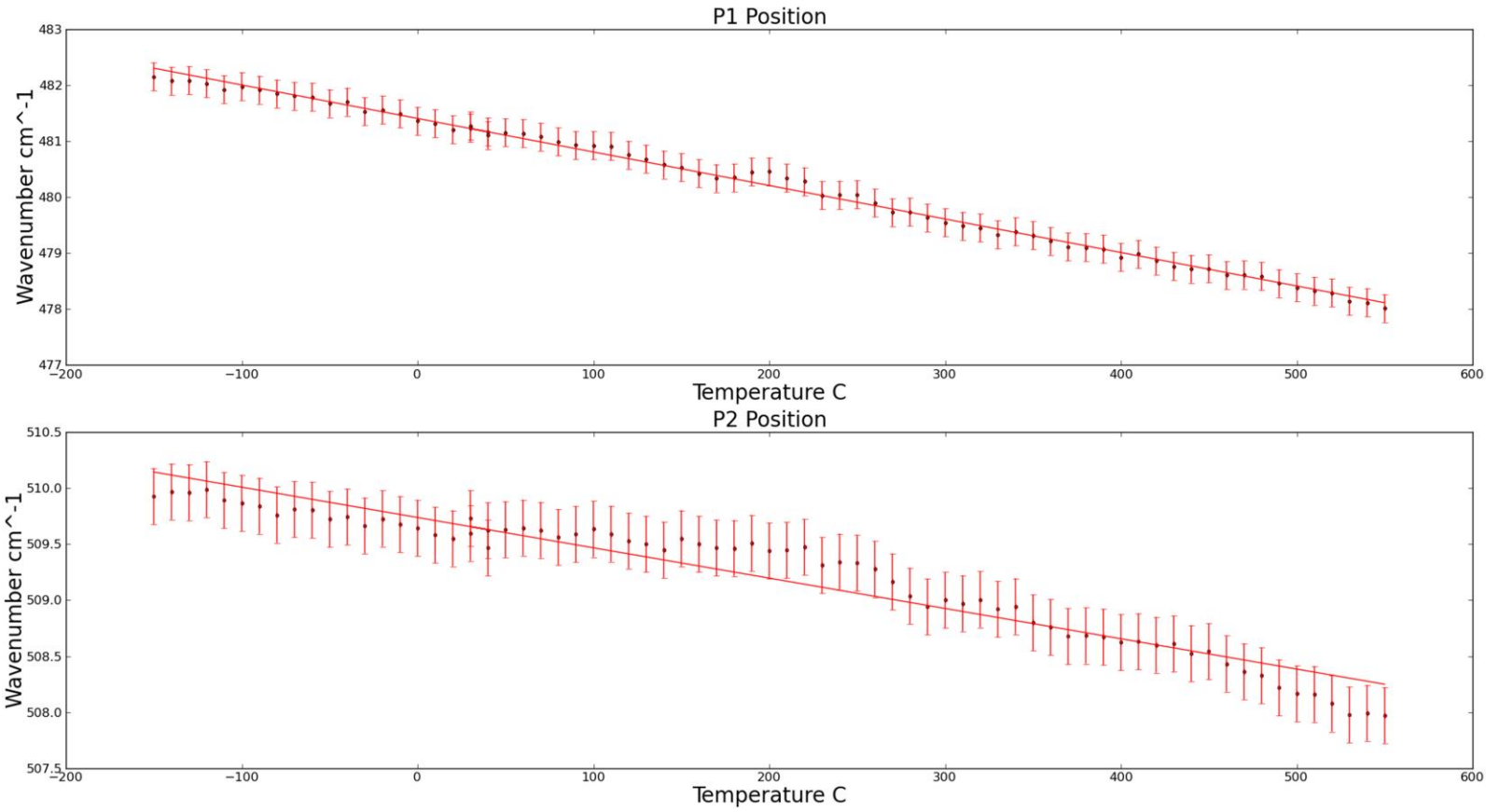

Fig. 3: (Top) A graph showing the P1 peak position when the labradorite sample is subjected to varying temperatures. (Bottom) A graph showing the P2 peak position when the labradorite sample is subjected to varying temperatures.