

Characterisation of Raman spectra of high purity olivine as a function of temperature and shock history.

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1. Introduction

ExoMars' Raman Laser Spectrometer (RLS, [1], [2]) will be the first Raman spectrometer deployed on another planetary body. It is probable the rover will land on the ancient terrain (TBD) within transverse distance to several impact craters where the rocks are estimated to be >3 billion years old. These ancient terrains have been subjected to impacts, and work at Kent has shown such impacts result in modification of minerals and organics [3, 4] and can induce a loss of volatiles [5, 6, 7]. This highlights some problematic scenarios for the interpretation of Raman spectra collected by *ExoMars*:

- i) The spectra of impact generated minerals may be misinterpreted since their signatures have not been systematically characterised;
- ii) The materials produced by the degradation of organic (biologically significant) compounds during impact are unknown, and consequently may be overlooked as evidence for life;
- iii) Shocked hydrated minerals may be erroneously identified as anhydrous, since it is currently unknown whether there is a spectral difference between volatile rich minerals that have been shocked and their anhydrous counterparts.

Our primary goal is therefore to study impact modification. Using the Light Gas Gun at Kent [8], we have shocked minerals under Martian conditions and compared their Raman spectra from before and after impact. Thus far, we have conducted experiments by a firing a buckshot of ~50 μm molybdenum spheres onto gem quality olivine (peridot, which have a very clean and consistent composition) and analysing the impact craters on the surface of the sample using Raman spectroscopy.

Raman spectroscopy is generally regarded as a non-destructive technique, however, concentrated laser power can generate localised heating leading to devolatilisation, crystalline changes, and even melting of the sample. This can lead to misinterpretation of spectral data (such as incorrect mineralogical composition). Therefore, we have also set out to study and quantify any alterations of the spectra of Martian analogue minerals due to their temperature.

We have subjected samples at temperatures between -150 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$ on a temperature controlled stage whilst illuminating them with a 500 mW, 532 nm laser, which mimics the RLS laser.

2. Results (Shock)

To date, shots have been performed at 0.61, 1.57, 3.03, and 4.17 km s^{-1} . The peridot from the 4.17 km s^{-1} shot was disrupted by the impact and as a result it fractured into pieces with no discernible craters to analyse. However, spectra taken from the surface of the remaining fragments has shown shifts of up to 2.0 cm^{-1} (Fig. 1) in the positions of the P1 and P2 olivine peaks ('P1' at, notionally, 826.0 cm^{-1} and 'P2' at, notionally, 858.6 cm^{-1} for Fo_{100} , [4]).

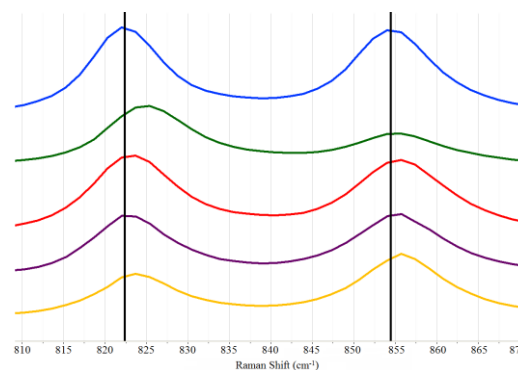


Fig. 1: Spectra showing the shift in peak position from peridot samples that have received different degrees of shock pressure compared to an un-shocked sample (blue). 0.61 km s^{-1} (green), 1.57 km s^{-1} (red), 3.03 km s^{-1} (purple), and 4.17 km s^{-1} (yellow).

By comparing spectra taken from inside the craters of the 1.57 and 3.03 km s^{-1} shots to those taken from the surface before the impact occurred, shifts of the P1 and P2 lines of up to 1.5 cm^{-1} have been observed (Fig. 1).

The impact velocity was not great enough to generate craters on the surface of the 0.61 km s^{-1} shot - instead small circular impressions have been made on the surface and comparison of spectra taken from the centre of the impression and from the pre-shocked peridot show peak shifts of up to 3.0 cm^{-1} (Fig. 1).

The higher the impact velocity the larger the shock pressures that the peridot targets have had to endure. As such, it is expected that the peridots that have been subjected to higher velocity impacts would show larger shifts. This trend has been shown to be true, with the exception of the 0.61 km s^{-1} shot. We believe that this is because no crater has been formed and, as such, no shocked material has been lost. Therefore, we are able to observe the material that has sustained the greatest shock pressures due to the impact, whereas, in the shots where cratering has occurred, the material that has sustained the greatest shock pressures has been ejected and we only observe that has been subject to lower shock pressure.

3. Results (Temperature)

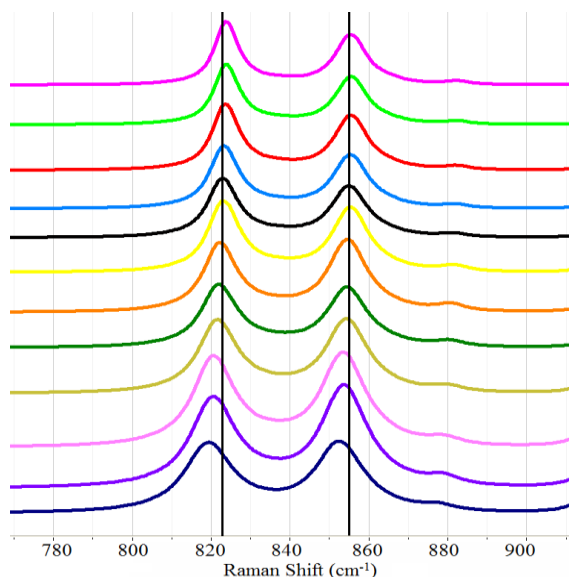


Fig. 2: Spectra showing the shift in peak position at different temperature in relation to room temperature (25 °C – black). -150 °C (purple), -100 °C (green), -50 °C (red), 0 °C (blue), 40 °C (yellow), 80 °C (orange), 120 °C (dark green), 160 °C (gold), 200 °C (pink), 240 °C (dark purple) and 280 (dark blue).

From Fig. 2 we can see that as the temperature is decreased, the values for the P1 and P2 peaks move to higher wavenumbers; while as the temperature is increased the values for the P1 and P2 peaks move to lower wavenumbers. The peak values for a peridot at 25 °C were 822.9 cm^{-1} and 854.8 cm^{-1} (corresponding to Fo_{80}). At the lowest temperature (-150 °C) these had changed to 823.8 cm^{-1} and 855.3 cm^{-1} respectively, equating to a total shift of $+0.9 \text{ cm}^{-1}$ and $+0.5 \text{ cm}^{-1}$, while at the highest temperature (280 °C) these had changed to 819.5 cm^{-1} and 852.5 cm^{-1}

respectively, equating to a total shift of -3.4 cm^{-1} and -2.3 cm^{-1} . While these are not large shifts, this could lead to an erroneous determination of the mineralogical composition of an olivine: e.g. using equations given in [4] of >5 molar units. Conversely, care has to be taken in ensuring that laser power does not cause significant heating of a cold (i.e. on Mars) sample. We observe localised heating, and shifting of peaks, when using laser powers of a few mW on a sample held at -100 °C. Stoke/anti-Stokes line ratios are therefore required to calculate the temperature of the sample under the laser.

4. Conclusions

We have shown that both temperature and shock history change the position of the fingerprint Raman peaks of gem quality olivine. The impact work is continuing, in parallel with hydrocode modelling, to calculate peak pressures, to generate a quantification of the shift in the olivine peaks as a function of shock history. The temperature work has shown if a sample of gem quality olivine is taken to extreme temperatures, the P1 and P2 peaks shift by amounts proportional to the degree of heating, or cooling, the sample is subjected to.

5. Further Work

Once our experimental programme has been completed, we will apply the analysis techniques used here to examine other Martian analogue minerals (such as: gypsum, orthopyroxene, serpentine, iron oxides, etc) in forms that will be more typical of the Martian surface i.e: powders with varying grain sizes.

Finally, we are also studying what effects atmospheric pressure (and composition) has on mineral spectra. Preliminary results obtained from the spectra of olivine have shown no detectable difference in the spectra between Earth atmosphere and pressure and Martian ($\sim 7 \text{ mPa}$ of CO_2); these experiments will be repeated using different mineral samples and presented.

References

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