

CHARACTERISATION OF RAMAN SPECTRA OF HIGH PURITY OLIVINE AS A FUNCTION OF TEMPERATURE AND SHOCK HISTORY: PREPARATION FOR EXOMARS.

R. Hibbert¹ and M. C. Price¹

¹School of Physical Sciences, University of Kent, Canterbury, CT2 7NH, UK (rh443@kent.ac.uk)

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 of Mawrth Vallis (TBD in 2014), 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 our initial experiments by firing gem quality olivine (peridots, which have a very consistent composition, Fig. 1) into aluminium plates and looked at the shocked residue. Our ultimate aim is to develop and validate data collection and analyses methods that will be used for the more representative mineral samples.

Raman spectroscopy is generally regarded as a non-destructive technique; this statement is incorrect. 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), but these heating effects have not been comprehensively studied. 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 cooled samples on a temperature controlled stage whilst illuminating them with a 500 mW, 532 nm wavelength laser, which mimics the one that will be used on RLS. This will allow us to develop

'best practice' protocols to be adopted during analyses, ensuring minimal modification of samples, and maximal scientific return.



Fig. 1: An example (3.0 mm diameter) peridot projectile.

Results (shock): The preliminary impact experiments have shown that the greater the peak pressure, the greater the shift in the position of the P1 and P2 olivine peaks ('P1' at 826.0 cm^{-1} and 'P2' at 858.6 cm^{-1} for Fo_{100} , [4]). To date, shots have been performed at 0.30 , 0.90 , 1.74 , 2.11 and 4.08 km s^{-1} . Analysis of the 0.30 and 0.90 km s^{-1} shocked peridots showed no discernible shift when compared to data from pre-shocked. The 1.74 and 2.11 km s^{-1} shots showed possible shifts in the olivine peaks but these were small (Fig. 2.), and more data and statistical analyses are required. The 4.0 km s^{-1} shot, however, showed a definite shift of ~ 3 wavenumbers (Fig. 3.).

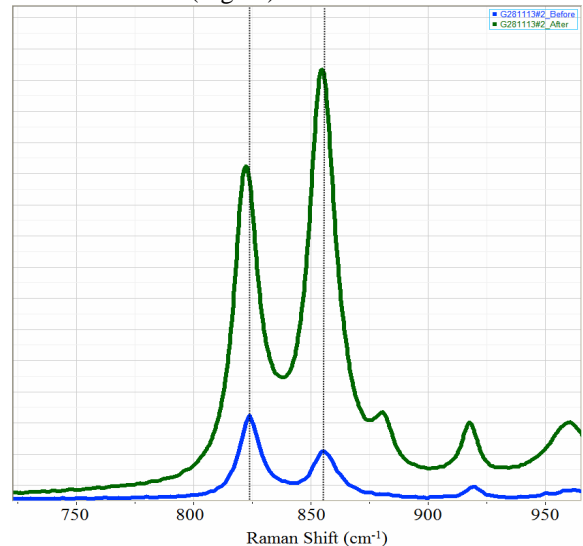


Fig. 2: Shot G281113#2. $V = 2.11\text{ km s}^{-1}$. The blue line is the pre-shocked spectrum, and the green line is the post-shock spectrum of peridot residue contained within the impact crater. Note the shift in the green spectra to the left by 1.5 wavenumbers.

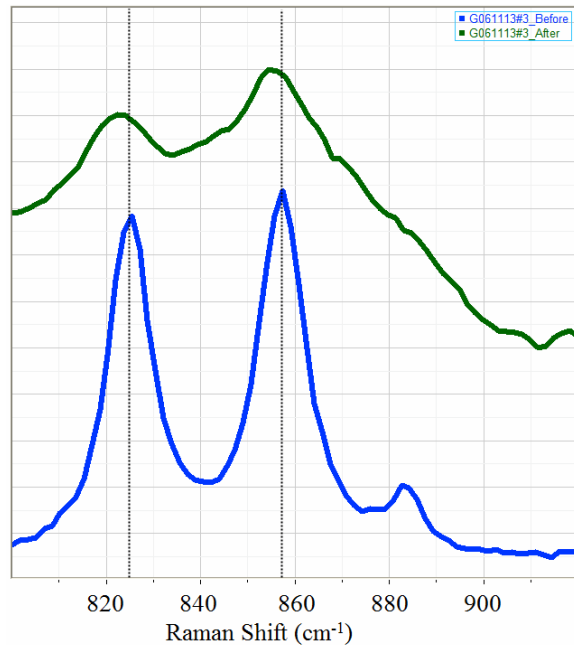


Fig. 3: Shot G061113#2. $V=4.08 \text{ km s}^{-1}$. The blue line is the pre-shocked spectrum, and the green line is the post-shock spectrum of peridot residue contained in the impact crater. Note the shift in the green spectra to the left by 3 wavenumbers.

These data are complementary to data reported in Ramkissoon N. et al. (these proceedings) [9], which also shown changes in the Raman spectra of shocked goethite and gypsum.

Once our experimental methodology has been tested and validated, it will be applied to other Martian analogue minerals (such as: olivine, orthopyroxene, serpentine, iron oxides, etc) in forms that will be more typical of the Martian surface i.e: powders with varying grain sizes.

Results (temperature): From Fig. 4. we can see that as the temperature is decreased, the values for the P1 and P2 peaks move to higher wavenumbers. The peak values for a peridot at 25 °C were 822.9 cm^{-1} and 854.8 cm^{-1} (corresponding to Fo_{80}), while 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 this is not a large shift, 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. Thus Stoke/anti-Stokes line ratios are also required to calculate the temperature of the sample under the laser.

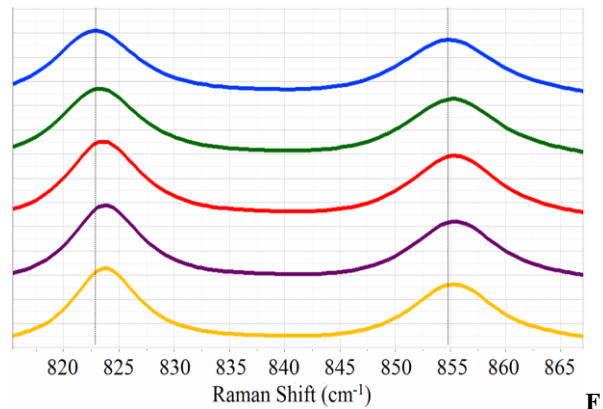


fig. 4: The P1 and P2 peaks of olivine as obtained from a peridot at various temperatures; 25 °C (purple), 0 °C (blue), -50 °C (green), -100 °C (red), -150 °C (yellow).

Conclusions and Further Work: Initial results 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. Further work involves looking at the Raman spectra of mineral powders of different grain sizes, which will be prepared by grinding and sieving high purity bulk mineral samples provided by collaborators at the Natural History Museum, London.

Finally, we are studying what effects of atmospheric pressure (and composition) has on mineral spectra. Preliminary results obtained from the spectra of olivine has 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.

Acknowledgements: RH thanks the Uni. of Kent for receipt of a PhD. tuition fees scholarship. MCP thanks the STFC, UK.

References: [1] Rull F. et al. (2011). *42nd LPSC abstract #2400*. [2] Rull F. et al. (2013). *44th LPSC abstract #3110*. [3] Wozniakiewicz P. et al. (2012). *MAPS*, 47, 4, 660 – 670. [4] Foster N. et al. (2013). *GCA*, 121, 1 – 14. [5] Wozniakiewicz P. et al. (2011). *MAPS*, 46, 7, 1007 – 1024. [6] Miljković K. et al. (2013). *44th LPSC abstract # 1940*. [7] Price M. C. et al. (2013). *Int. J. Astrobiology*, DOI: 10.1017/S1473550413000384. [8] Burchell M. J. et al. (1999). *Meas. Sci. & Tech.*, 10, 41 - 50. [9] Ramkissoon N. et al. (2014). *45th LPSC abstract*.