

RAMAN SPECTROSCOPY OF OLIVINE IN DUNITE EXPERIMENTALLY SHOCKED TO PRESSURES BETWEEN 5 AND 59 GPa S. Turner¹, W.U Reimold¹, M. Niewoudt² and R. Erasmus³, ¹Impact Cratering Research Group, School of Geosciences, Univ. of the Witwatersrand, Private Bag 3, P.O. Wits 2050, Johannesburg, South Africa (turners@geosciences.wits.ac.za); ²School of Physics, Univ. of the Witwatersrand, ³Raman and Luminescence Laboratory, School of Physics, Univ. of the Witwatersrand.

Summary: Raman spectroscopic analysis of olivine in dunite samples experimentally shock-loaded to pressures between 5 and 59 GPa showed no significant shift of the 824 and 856 cm^{-1} Raman bands with increasing shock pressure.

Introduction: This Raman spectroscopic study on olivine was carried out on a series of dunite samples progressively shocked to pressures from 5 to 59 GPa [1]. Previous investigations on experimentally shocked single crystal olivine as well as statically stressed single crystal olivine have shown that the major olivine Raman bands seemingly shift to a higher wavenumber in a characteristic manner with increase in pressure. Raman analysis of olivine **statically** deformed at high pressures (60.7 GPa) has also shown development of broad features that could be due to the formation of diaplectic olivine glass [2], indicated by the appearance of new bands.

Numerous studies of shock-metamorphism of olivine have been reported. A detailed petrographic classification of shock effects occurring at different shock pressures, mainly based on optical analysis, has been compiled [3, 4, 5, 6,]. In contrast, Raman and infrared spectroscopic studies of shocked olivine to date are still limited and do not provide conclusive information on the exact shift in wavenumber expected for a specific olivine composition and shock pressure, or effects of band broadening with pressure. Although the experimental work to date covers a large pressure range, individual studies often do not report the actual wavenumber shifts in the Raman lines for shocked olivine.

The purpose of this study was to provide a quantitative data base for Raman based shock barometry for progressively shock-metamorphosed olivine. If it was possible to positively relate Raman band shift or band broadening to shock pressure, a new shock barometry tool would become available.

Experimental work: Olivine in samples of dunite from Åheim (Norway) with olivine abundances of 84.28 to 86.16 vol. % and Fo concentrations of 90.64 to 92.00 mole % and that had been experimentally shocked to 5-59 GPa [1,7] was studied using a Jobin-Yvon T64000 Raman spectrometer. A number of other dunite specimens (Corundum Hill, Twin Sisters Peak and Mooihoek dunites) with olivine of different Fe/Mg ratios had also been shocked at 29.3 GPa [1] and were analyzed in this study to investigate possible

compositional effects on the Raman spectroscopic signatures. Raman spectroscopic analysis was carried out with an Ar^+ laser and calibration was done using the 520.3 cm^{-1} plasma line of the laser. The triple subtractive mode was used for all acquisitions. Laser power was varied from 200 to 500 mW depending on fluorescence of the sample and acquisition times were between 120 and 180s. Data were recorded using a liquid nitrogen-cooled CCD (charge coupled device) detector and the laser light was focused. For instrumental reasons, only the spectra $> 400 \text{ cm}^{-1}$ could be recorded.

Results: A shift in the bands at 824 and 856 cm^{-1} to higher frequencies with increased shock pressure is not evident from the Raman spectra of the progressively shocked Åheim samples (Fig. 1). The differences in Raman spectra of olivine shocked to different pressures are summarised below (also compare Fig. 1):

- Åheim 5 GPa – There is no change in band positions when compared to the unshocked sample. The ν_4 internal mode at 617 cm^{-1} is not apparent in the unshocked sample.
- Åheim 15.5 GPa – The Raman spectrum is the same as that for the 5 GPa sample.
- Åheim 20 GPa – There is a slight shift to lower frequencies for the 824 and 856 cm^{-1} bands when compared to the 15.5 GPa sample.
- Åheim 29.3 GPa – There is a slight shift to higher frequencies for the 824 cm^{-1} band, but no shift for the 856 cm^{-1} band, when compared to the 20 GPa sample. A band at 650 cm^{-1} is apparent in the spectra.
- Åheim 38.5 GPa – There is a slight shift to lower frequencies for the 824 and 856 cm^{-1} bands when compared to the 29.3 GPa sample.
- Åheim 45 GPa – There is a slight shift to higher frequencies for the 824 and 856 cm^{-1} bands when compared to the 38.5 GPa sample. An increase in the full width at half maximum (FWHM) is apparent at this shock pressure for the 824 cm^{-1} band and to a lesser extent for the 856 cm^{-1} band.
- Åheim 59 GPa – There is a slight shift to higher frequencies for the 824 and 856 cm^{-1} bands from the 45 GPa sample, but only for two grains.. FWHM's are of the same order

of magnitude as those found in the 45 GPa sample.

The shifts to higher frequencies reported by previous authors [8-10] were determined on single-crystal forsterite, incrementally stressed in a diamond anvil cell. Such consistent effects are not seen in the polycrystalline dunites, probably due to heterogeneous stress experienced by mineral grains within the samples during experimental shock loading. An extra band at 650 cm^{-1} was identified in Åheim dunite shocked to pressures of 5, 29.3 and 59 GPa, and in the unshocked Mooihoek dunite. An extra band at 696 cm^{-1} was identified in the 59 GPa sample. The closest band to 696 cm^{-1} identified in previous studies is a broad band at 689 cm^{-1} in shocked meteoritic olivine [11]. The samples shock-loaded to a pressure of 29 GPa (Åheim, Corundum Hill and Twin Sister Peak dunite samples) revealed similar peak positions. A consistent increase in FWHM for the 824 cm^{-1} band with increasing shock pressure was identified in the shocked Åheim samples above 45 GPa, and to a lesser extent for the 856 cm^{-1} band.

Conclusion A consistent shift in frequency with increased shock pressure in the Åheim samples shocked to pressures between 5 and 59 GPa was not detected. The vibrational effects seen in single crystal analysis (shifts to higher frequencies with increasing shock pressure) are not detected in olivine of these polycrystalline samples.

The formation of a high pressure phase or diaplectic olivine glass was not evident in any of the Raman spectra for the progressively shocked Åheim samples. Band broadening with increasing shock pressure was detected for the 824 and 856 cm^{-1} bands from 45 to 59 GPa. In comparison, olivine of 66 to 99 mole % forsterite from the Cold Bokkeveld C1 carbonaceous chondrite showed much wider variation of FWHM, and the FWHM of the shock calibrated olivine samples of this study could not be applied as a suitable shock indicator for this meteoritic olivine. These differences in FWHM are probably due to the differences in chemical composition between the meteoritic and the experimentally shocked dunite olivine.

Extra bands at 650 cm^{-1} were identified in the Åheim dunite shocked to pressures of 5, 29.3 and 59 GPa, and in the unshocked Mooihoek olivine (40 mole% fayalite). This band is therefore not characteristic for shocked samples or iron-rich samples.

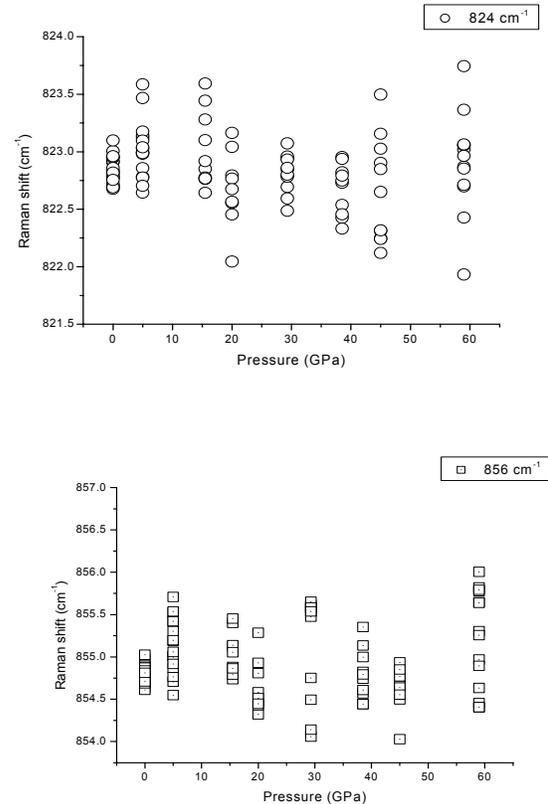


Fig1: (a) Shift of Raman band at 824 cm^{-1} and (b) at 856 cm^{-1} versus shock pressure for Åheim dunite progressively shocked from 0-59 GPa.

The cause of the extra band at 696 cm^{-1} identified in all the spectra of the sample shock loaded to 59 GPa is not known.

References: [1] Reimold W.U. and Stöffler D. (1978) Proc. Lunar Planet. Sci. Conf. 9th, 2805-2824. [2] Heymann D. and Cellucci T.A. (1988) Meteoritics., 23, 353-357. [3] Stöffler D. (1972). Fortschr. Mineral. 49, 50-113. [4] Bauer J.F. (1979) Proc. Lunar Planet. Sci. Conf. 10th, 2573-2596. [5] Stöffler D. et al. (1991) Geochim. Cosmochim. Acta, 55, 3845-3867. [6] Bischoff A. and Stöffler D. (1992) Eur. J. Mineral., 4, 97-106. [7] Reimold W.U. (1977) MSc Thesis, Westf. Wilh.-Univ., Münster, Germany, 132 pp.. [8] Besson J.M., Pinceaux J.P., Anastopoulos C. and Velde B. (1982) Geophys. Res., 87, 773-775. [9] Durben D.J., McMillan P.F. and George H.W. (1993) Amer. Min., 78, 1143-1148. [10] Miyamoto M. and Ohsumi K. (1995) Geophys. Res. Lett., 22, 437-440. [11] Shinno I. (2002) J. Min. Pet. Sci., 97. No. 4, 153-160.