EPSC Abstracts
Vol. 7 EPSC2012-156 2012
European Planetary Science Congress 2012

Raman spectra of olivine measured in different planetary environments.

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1. Introduction

Missions to bodies of our solar system are coming up and imply new instrumentation to be applied remotely and in situ. In ESA's ExoMars mission the Raman Laser Spectrometer (RLS) will identify minerals and organic compounds in Martian surface rocks and soils. Here we present the results of a Raman study of different olivines with variable Fo and Fa contents. We chose olivine because it is a rock forming mineral and is found as an abundant mineral in Martian meteorites. We determined the Raman spectra in different environmental conditions that include vacuum, 8mbar CO_2 atmosphere and temperatures between room temperature and 10K. These environmental conditions resemble those on asteroids as well as on Mars and Moon. Thus our study investigates the influence of these varying conditions on the position and band width of the Raman lines, which is to be known when such investigations are performed in future space missions.

2. Samples

In total we measured five olivine samples. Two of them were provided by the Institute for Geosciences in Jena and three were available within the mineral collection at DLR, Berlin.
Four of these olivines are forsterites, including the San Carlos olivine, and one is fayalite. As also other rock forming minerals are investigated an internal serial number is chosen to subdivide all minerals. For this study we measured Olivine 21, 36, 61, 62, 63 (Table 1).

2.1 Sample preparation

All minerals are prepared properly for microscopy as well as for Raman investigations:
Based on the natural origin of the selected olivines, we made a thin section of each sample in order to do all required mineralogical (chemical composition, mineral zoning, inclusions etc.) analyses. For Raman spectroscopy each sample was not more than 1cm × 1cm × 0.5cm in size. Special attention is payed by using one side of olivines for Raman measurements, and opposite side for thin section preparation, respectively. Accurate measurements on the samples are guaranteed by a plane parallel and polished surface. In addition, no mineral has a specific crystallographic orientation.

Table 1: Size and origin of the investigated olivines

No.	size / habitus	origin
21	9 mm × 3 mm / single crystal	Dreiser Weiher, Germany
36	7 mm × 7 mm / single crystal	Feldstein, TH, Germany
61	10 mm × 10 mm / single crystal	San Carlos Reser-vation, Arizona, USA
62	1 mm × 1 mm / multi-crystal	Dreiser Weiher, Germany
63	10 mm × 5 mm / single cracked crystal	Billiton, Sumatra, Indonesia

3. Methods

For the initial characterization of the olivines we used light optical microscopy with transmitted light as well as the polarization unit. Subsequently we produced with a JEOL JSM-6610LV SEM an overview and proper image of all minerals. In addition, element mappings and first analyses are made on the coated thin sections. Detailed quantitative analyses of all olivines are made with a JEOL JXA-8900 Superprobe EPMA.
We performed Raman measurements with a confocal Raman microscope Witec alpha300 R system. The laser excitation wavelength is 532 nm; the resolution of the spectrometer is 4-5 cm^{-1}. A Nikon 10 x objective is used with a spot size on the sample in focus of about 1.5 µm. To represent the RLS instrument on ExoMars a laser power of 1 mW on the sample is chosen. For the investigations each of the samples is fixed in the cryostat and the sequence of measurements in the cryostat is as follows:

- at room temperature under air at ambient pressure

- in vaccum (<10-4 mbar) from 300 K and 200 K and, to verify low-temperature behavior, ~ 4 K
- in CO_2-atmosphere of 6 – 8 mbar at 300 K and 200 K (Mars-like conditions)
- finally, laboratory conditions again to check for irreversible changes of the minerals that might have led to changes of the Raman signals

4. Results

4.1 Mineralogical results

Olivine 21: This crystal is homogeneously forsteritic (Fo90.5) without zoning. One small inclusion (200 µm × 10 µm) containing FeO and plagioclase is visible.
Olivine 36: This crystal is also a homogeneous forsterite (Fo90.8) without zoning. One small inclusion (150 µm × 10 µm) containing chromite, plagioclase, and pyroxene is visible.
Olivine 61: The San Carlos olivine is a homogeneous crystal and only some crack fillings in a small, up to 15 µm width crack is visible. As usual for a San Carlos olivine [1] the Fo content is 90.2.
Olivine 62: Although this olivine has the same origin as No. 21 it has a Fo content of 91.3. As it is a multi-crystal sample it contains crack fillings like garnet, pyroxene, chromite, and FeO. In addition, single crystals of enstatite are found. Therefore, we selected one pure single forsterite crystal for our study.
Olivine 63: This fayalite (Fa98.4) has a high Mn content of 0.11 mole%. This crystal shows abundant fractures filled with FeO and/or pyroxene.

4.2 Raman results

The typical position and band width of the Raman lines of olivine are shifted in dependence on temperature (Table 2). The magnitude of these shifts depends on the olivine type and its orientation.

Table 2: Raman shifts of the main peaks from room temperature to ~ 4 K

No	wavenumber (cm^{-1}) (room temp.)	shift (~ 4 K)
21	827 // 862	+ 3 cm^{-1} // +2 cm^{-1}
36	828 // 859	+3 cm^{-1} // +3 cm^{-1}
61	828 // 859	+ 1 cm^{-1} // + 1 cm^{-1}
62	828 // 860 // 885	+1 cm^{-1} // +1 cm^{-1} // +2 cm^{-1}
63	819	+ 6 cm^{-1}

All four forsterites show only slight temperature dependent shifts of the Raman spectra, while fayalite is characterized by major shifts. We detected no variation of the Raman signals with the pressure or the composition of atmosphere. In addition, no irreversible changes of the olivines were detected.

5. Discussion

As is apparent from the results all major peaks in all olivines reveal temperature related shifts from lower wavenumber at room temperature to higher wavenumber at low temperature. This is consistent with the results of [2] who investigated the behavior of olivines from room temperature to higher temperatures. Furthermore, also some minor peaks show this effect. The temperature dependence might be an effect of dynamic field splitting. In addition, in fayalite magnetic interactions can occur that may be responsible for more significant temperature dependent Raman shifts [3].
Although four of the olivines are forsterites with similar compositions, the relative intensity of the main Raman peaks is different. This is attributed to different and accordingly random orientation of the crystals in natural samples.
In summary, the results demonstrate that natural non orientated minerals produce Raman spectra that differ from sample to sample despite chemical and mineralogical similarity. This will be the case in all Raman instruments employed in space missions and has to be considered in the interpretation of space born Raman spectra.

References

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Acknowledgements

Thanks go to Prof. Dr. F. Langenhorst from the University in Jena, Institute for Geosciences (Germany) for providing two olivine samples.
This work is supported by a grant 50 QX 0602 from the Deutsches Zentrum für Luft- und Raumfahrt to E.K. Jessberger.