



Mineralogical and Raman spectroscopy studies of natural olivines exposed to different planetary environments



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ABSTRACT

New lander missions to bodies of our solar system are coming up and thus new techniques are desirable for the in-situ investigation of planetary surface and near surface materials. During the last decade Raman spectroscopy has been developed to become an excellent laboratory tool for fast petrological and mineralogical investigation of terrestrial and extraterrestrial rocks. Consequently, Raman spectroscopy has successfully been proposed for operation on planetary surfaces. In the joint ESA and Roscosmos mission ExoMars a Raman Laser Spectrometer (RLS) will for the first time be applied in space to identify minerals and organic compounds in Martian surface rocks and soils. The present study aims to investigate the possible response of various environmental conditions to Raman spectra in preparation for the ExoMars mission, as well as other space missions in future. For our study we selected five natural olivines with different forsterite (Mg₂SiO₄) and fayalite (Fe₂SiO₄) compositions. Olivine as an important rock forming mineral of the Earth upper mantle and an abundant mineral in Martian meteorites is one of the key planetary mineral. The spectra were taken in various environmental conditions that include vacuum down to 10⁻⁶ mbar, 8 mbar CO₂ atmosphere, and temperatures ranging between room temperature and ~8 K resembling those on Mars as well as on the Moon and on asteroids. We have found that forsterite shows only small temperature-related shifts in Raman spectra at very low temperatures indicating relatively weak changes in the lattice modes. Fayalite demonstrates, in addition to temperature dependent changes in the lattice modes found for forsterite, modification of Raman spectra at low Stokes frequencies. This is an effect in the SiO₄ internal modes that most probably is caused by the high amount of iron in the mineral structure, which triggers antiferromagnetic transition at low temperatures. No influence of a CO₂ atmosphere on Raman spectra for the investigated rock-forming minerals has been observed at any pressure from ambient 1 bar down to a few mbar.

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1. Introduction

One of the fundamental aims to study minerals under different temperature and pressure conditions is to understand their formation conditions to draw conclusions about former processes on Earth as well as on other planets and/or asteroids in our solar system. In the case of space missions it is important to anticipate the expected data beforehand in order to enable proper interpretation and to optimize the instrumentation during its development.

Chemical and bond structure of minerals determined by elemental composition and atomic order in lattice can be probed by phonon spectroscopies, such as infrared absorption and

inelastic light scattering. Raman spectroscopy is well known as a powerful non-destructive technique for the investigation of mineral phases and organic matter, and does not require a special sample preparation. It allows, with detailed μm-scale mappings, to catch very small particles and characterize them. A Raman instrument does not require vacuum or valves and almost no moving parts. Therefore, it appears to be an excellent analytical instrument for the in-situ exploration of planetary surface materials.

For the years 2016 and 2018 ESA will perform two missions to the Mars called ExoMars in collaboration with the Russian Federal Space Agency (Roscosmos) (Vago et al. 2012; The ExoMars Programme 2016–2018). The first ExoMars launch in 2016 is an orbiter with a trace gas analyser and, most importantly, an entry, descent and lander demonstrator module. The second launch in 2018 will contain an European rover and a Russian surface platform. This second ExoMars mission will visually and spectrally

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characterize the surface of Mars. The particular goal of the mission is, besides the investigation of the Martian rocks and soils, to search for indications of present and previous life signatures. One of the on board Pasteur Payload instruments of the ExoMars Rover is the Raman Laser Spectrometer (RLS) (Rull et al., 2011). This will be the first time that a Raman spectrometer will be flown on a planetary mission. The rover is equipped with a sampling drill capable of drilling up to 2 m depth. The sampled material will then be crushed into fine powder (average grain size is 0.15 mm) before being analysed first by RLS and then by other instruments. To distinguish the rocks and soils from possible life forms it is necessary that all mineral phases in the drilled powder are assigned securely in advance, ideally in a RLS database.

The objective of our present study is to extend the existing database of Raman spectroscopy by adding data of a mineral kit measured especially under Martian conditions as well as other planetary conditions for future missions. A dependence of Raman shifts on environmental measurement conditions is known from literature (e.g. Kolesov and Geiger, 2004b). Here we present the investigation of five olivines measured under different environmental conditions, including Martian conditions. Olivines, are chosen because they belong to the rock forming minerals on Earth and especially forsterites are in addition a widespread mineral in Martian meteorites and thus – by inference – on the surface on Mars. Furthermore, results from other space missions (e.g. Viking, Observer, Global Surveyor, Pathfinder, Spirit, Opportunity, Express etc.) strongly suggest that olivine is present on Mars.

Olivine has an orthorhombic crystal system (space group Pbnm) with isolated silicate tetrahedra. It has $4 M_2^{2+} SiO_4$ formula units per crystal unit cell, in where the M represents two different metal sites (M1 and M2), filled with Mg^{2+} and Fe^{2+} within the natural olivine solid solution Fo–Fa (Birle et al., 1968). The SiO_4 tetrahedra have four internal Raman active modes (ν_1 : symmetric stretching, ν_2 : symmetric bending, ν_3 : asymmetric stretching, ν_4 : asymmetric bending), a lattice rotation, and a lattice translation mode (Williams, 1995). In addition, within these structure the isolated SiO_4 tetrahedra are linked with octahedral coordinated M^{2+} cations, which have two different sizes (M1: smaller, M2: larger). The smaller one, which shares only three edges with neighboring polyhedron and one with a SiO_4 tetrahedra, is Raman active (e.g. Iishi, 1978; Rao et al., 1988).

The Raman active vibrational modes of olivine are between 150 cm^{-1} and 1100 cm^{-1} . The most characteristic peak of olivine is a double peak (DP) between $\sim 815\text{ cm}^{-1}$ and $\sim 860\text{ cm}^{-1}$ for Fe–Mg–olivines. The DP appears because the two SiO_4 -stretching (ν_1 and ν_3) modes are active. In contrast to Forsterite with two clear distinguishable (spectrally resolved) peaks, the second line in DP of Fayalite is in most cases more like a shoulder peak. This lack of the second clear DP in Fayalite is an effect of the amount of Mg^{2+} and/or Fe^{2+} within the structure, which modify the vibration frequencies of Si–O bonds (Kuebler et al. 2006). On the basis of this characteristic it is easy to separate between a magnesium rich and iron rich olivine at the first glance (Kuebler et al., 2006). All Raman active modes in olivine can be subdivided in three spectral regions (Iishi, 1978; Guyot et al., 1986; Price et al., 1986). Peaks below 400 cm^{-1} are attributed to the lattice modes (translational and rotational movements). Peaks between 400 cm^{-1} and 700 cm^{-1} can be connected with the internal bending of the SiO_4 tetrahedron (ν_2 and ν_4) and Si and Mg displacements. And, finally, peaks between 700 cm^{-1} and 1100 cm^{-1} , including the DPs, are associated with the internal stretching of the SiO_4 tetrahedron (ν_1 and ν_3).

Raman measurements were carried out in the Stokes range from 50 cm^{-1} to 1150 cm^{-1} on polished solid samples, which are prepared with the method explained below. All spectra were obtained with the same special measurement sequence and procedure described in Section 2.3.

Investigations of olivines concerning the structure, buildings conditions, dissolution reactions, as well as its behavior under high pressure and high temperature are well known (e.g. Kolesov and Geiger, 2004a; Wang et al., 1993). Additionally, many authors interpret Raman spectra from different olivines with a variety of compositions, with different orientations, and at high pressures (e.g. Ishibashi et al., 2008; Mouri and Enami, 2008; Liu and Mernagh, 1993). Nevertheless, except of a short report by Sharma and Cooney (1990), there is a lack in measurements of Raman spectra under very low temperature and under Martian environmental conditions especially for forsterites. Kolesov and Geiger (2004b) investigated the lattice dynamic behavior of fayalite by cooling it down to $\sim 10\text{ K}$, but these authors worked with a 632.8 nm line of a He–Ne laser and 50 mW output power. In addition, Motamedi et al. (2013) measured forsterites with different compositions under Martian atmosphere, but they did it only down to $-20\text{ }^\circ\text{C}$ and a 659 nm wavelength laser. Thus, combined Raman measurements at low temperature in Martian atmosphere and in vacuum are not known so far. In the present study we attempt to fill this gap. In the present study we investigated essentially forsterites. One fayalite was involved in the investigation kit to underline the measurements done by Kolesov and Geiger (2004b) carried out with a 632.8 nm laser, now with a 532 nm laser. In addition, fayalites are neither expected in high amounts on Mars nor in deep space regions.

2. Samples, preparation, and methods

2.1. Samples

In total we selected five olivine samples in this study. 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 a fayalite. For the preparation of the ExoMars mission we investigate also other rock forming minerals. Therefore we choose an internal serial number for identification of the minerals. In the present study we analysed the olivines (OI) with internal numbers: 21, 36, 61, 62, and 63.

2.2. Sample preparation

Here we present the results of the mineralogical, chemical, and Raman spectroscopic analyses of these five natural olivines. Based on the natural origin of the selected olivines, we paid special attention during preparation. The minerals were properly prepared for microscopy as well as for Raman investigations as follows:

For Raman measurements one plane parallel polished surface of an olivine grain was used whereas the exact opposite side of this parallel polished surface of the olivine grain was applied for thin section preparation, in order to do all required mineralogical (chemical composition, mineral zoning, inclusions etc.) analyses. On the basis of this preparation method (piece and counterpart) we can select one area during mineralogical investigations on the thin section for further Raman measurements on this particular area.

Because of the given dimension of the Raman vacuum chamber (Fig. 1) the maximum sample size is $10\text{ mm} \times 10\text{ mm} \times 5\text{ mm}$. Thin sections have the same square size but with a thickness of $30\text{ }\mu\text{m}$ instead of 5 mm. Since the original geometry of the samples was kept, no surface has a specific crystallographic orientation in a particular main crystallographic axis.

2.3. Methods

First overview images of the samples were obtained with the KEYENCE Digital Microscope VHX-500F. For the initial characterization

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