RAMAN SPECTROSCOPY OF MARS RELEVANT MINERALS FOR PLANETARY EXPLORATION.

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Introduction: ExoMars, launch in 2018, is the first mission in ESA's Exploration Program Aurora. In the scope of the ExoMars mission Raman measurements will be performed with the Raman Laser Spectrometer (RLS). The RLS onboard ExoMars will achieve measurements to identify mineral products and organic compounds in Martian surface rocks and soils. In preparation for these analyses we investigate Mars relevant minerals as well as Martian meteorites and analogue materials with a Raman instrument working under "realistic" conditions. Therefore, the analysis is performed in vacuum, and with pressure, temperature, and atmospheric composition corresponding to environmental conditions on Mars, but, for comparison, also with terrestrial conditions.

Samples: In the first instance the minerals gypsum ($CaSO_4 \cdot 2H_2O$) and its anhydrous equivalent anhydrite ($CaSO_4$), phlogopite ($KMg_3(Si_3AlO_{10})$ $(F,OH)_2$), tremolite ($Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$), and carnallite ($KMgCl_3 \cdot 6H_2O$) have been chosen for this study as they have an OH group in their formula and O-H vibrations are known from other minerals as a function of variable temperature [1]. Furthermore they are (1) known as weathering or sedimentary products on Earth and some of them have already been detected on Mars, (2) easy to prepare for Raman measurements and available in larger amounts, and (3) are perfect indicator minerals for Raman spectra shifts due to changes of ambient conditions [2-4]. Additionally, we study different rock forming silicates, initially olivines, because the temperature dependence of fayalite in Raman spectra is already proven by [5].

Preparation: All sample types are properly prepared:

Due to the fact that only natural minerals were used for this study a thin section of each sample is made in order to do the mineralogical (chemical compostition, mineral zoning, inclusions etc.) work on the minerals. Furthermore, for Raman spectroscopy each mineral sample is cut in a piece of roughly 1cm × 1cm × 0.5cm in size, in particular for the work in the cryostat. Accurate measurements on the sample are guaranteed by a plane parallel and polished surface. Special attention is payed by using the opposite side of the mineral for Raman measurements than for the thin section preparation, respectively (Fig. 1). No mineral has a specific orientation.

Measurements: Light microscopy is performed using transmitted and reflected light as well as a polarization microscope. For an overview and proper image of all minerals a JEOL JSM-6610LV SEM was used. In addition element mappings and first analyses are made on the coated thin sections. Detailed analyses of all samples (minerals and meteorites) are and will be applied with a JEOL JXA-8900 Superprobe EPMA.

The Raman measurements are performed with a confocal Raman microscope Witec alpha300 R system. The Raman laser excitation wavelength is 532 nm. The spectral resolution of the spectrometer is 4-5 cm-1. A Nikon 10x objective is used. The spot size on the sample in focus is about 1.5 μm. The laser power of 1 mW on the sample is chosen to represent the RLS instrument on ExoMars. The sequence of measurement 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, down to 4 K
- in CO_2-atmosphere of 6 – 8 mbar at 300 K and 200 K (Mars-like conditions)
- finally: laboratory conditions again to exclude irreversible changes in the minerals

Results and discussion: In the following, Raman spectra unter Martian conditions are compared to those obtained under laboratory conditions (LC).

The Raman spectra of the so far investigated minerals show no detectable shifts due to the CO_2 atmosphere or any change pressure from ambient down to a few mbar. However, depending on the mineral (its structure and symmetrie) temperature related shifta are observed for all samples.

Gypsum (hydrous sulfate): The strongest Raman shift of gypsym is visible in the translational modes H_2O-Ca at 316 cm^{-1}. Minor shifts are visible for the stretching vibration mode of water at the characteristic band of 3941 cm^{-1} and at the ν_2 symmetric bending of the SO_4-tetrahedra at 494 cm^{-1} [6,1].

Anhydrite (sulfate): The spectra of anhydrite presents the strongest shift at the weakest band at 234 cm^{-1}, which belongs to the vibrational mode of Ca-O bonding. Further shifts are visible at 1017 cm^{-1} (sulfate tetrahedra ν_1 vibration mode) and 675 cm^{-1} as well as 1129 cm^{-1} (sulfate tetrahedra ν_4 and ν_3 vibration mode) [6].

Phlogopite (mica): The spectrum of phlogopite shows a very large shift at the 93 cm^{-1} in a CO_2 atmosphere and 200 K. This is calculated [7] to appear from a (F,OH) in x($\|$a)-transition + z-transition of the octrahedral site 1 (M1) + x($\|$a) z-transition of the octrahedral site 2 (M2) + the non-bridging O-atom in y($\|$b) transition. A weaker shift (683 cm^{-1}) belongs to a octrahedral-tetrahedral-octrahedral bending (with a bridging and non-bridging O atom).

Carnallite (halegonide): As gypsum, carnallite exhibits a shift within the stretching vibration mode of water at the band of 3427 cm^{-1}. For this mineral it is the strongest shift; however, two more shifts are visible at the 121 cm^{-1} and 654 cm^{-1} band. Further identification on these shifts are needed (Fig. 2).

Tremolite (amphibole): Tremolite presents also only one large shift at 548 cm^{-1}, which belongs to a Al–O deformation mode. The very small shift only in vacuum at the 674 cm^{-1} band fits to the symmetrical Si–O–Si and Si–O vibrations [8] (Fig 3).

Olivine (Silicate): The investigated olivine is a Fo-rich olivine. As in [5] no shift in the two major peaks (813 cm^{-1} and 845 cm^{-1}, which belong to the SiO_4-streching mode) are visible. But, as reported for fayalite, a change of the intensity of these bands is found. This might be also a result from iron in olivine whereby magnetic interactions can take place. Further results will be presented at the meeting.

Conclusions: This work demonstrates that it is very important to study the temperature effects on Raman measurements of all probable Martian minerals for the upcoming ExoMars Mission. Although our minerals are natural and therefore they had no specific orientation during the measurements nearly each mineral shows a Raman shift in at least one band. Certainly, some of the minerals exhibit shifts in minor characteristic bands, which may be neglected. But this should be reviewed especially for all rock forming minerals, which are not yet investigated with Raman at different temperatures, and ideally with natural samples in different orientations. In addition, if Fe^{2+} is present in the formula, possible magnetic interactions at various temperatures should be kept in mind.

References: [1] Sobron P. et al. (2011) LPS *XXXXII* Abstract #1580, [2] Gooding J. L. (1978) *Icarus* 33, 483 – 513, [3] Bandfield J. L. (2002) *Journal Geophys. Res.*, 107, E6, 9-1 - 9-20, [4] Chevrier V. (2004) *Geology* 32, 1033 – 1036, [5] Kolesov B.A. & Geiger C.A. (2004) *Phys. Chem. Minerals* 31, 155 – 161, [6] Buzgar N. et al. (2009) Analele Ştiin. Univers. *Geologie* 1, [7] McKeown D.A. et al. (1999) *Am. Mineral.* 84, 970 – 976, [8] Kloprogge J.T. et al. (2001) *Mineral. Mag.* 65, 775 – 785.
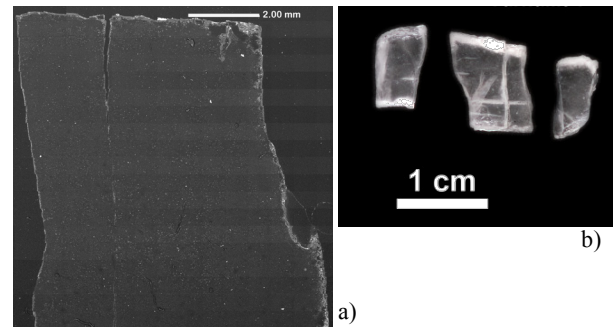

Fig. 1: a) Backscattered electron image of the polished thin section of carnallite.
b) Image of the carnallite samples prepared for Raman (the center piece was used).
The images show that for both preparations and therefore measurements the same sample was used.
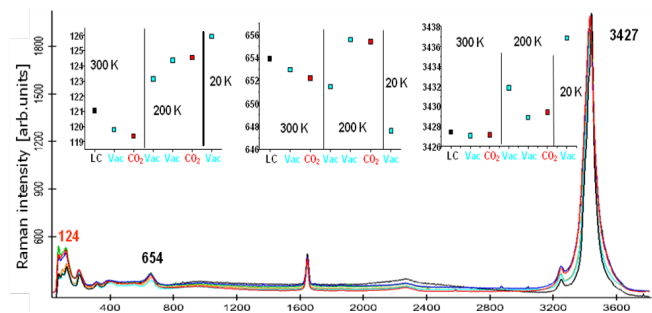

Fig. 2: Raman spectra of carnallite in 0 – 3800 cm^{-1}. The different measurement conditions are coloured. Black: LC, Blue: Vacuum with different temperatures, Red: CO_2-atmosphere with different temperatures.
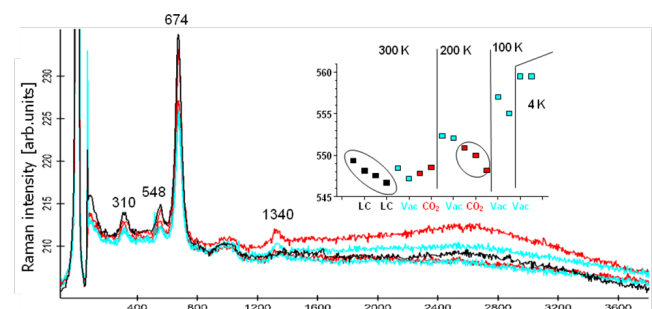The inserts indicate the shifts at different bands for the sequence of measurements.

Fig. 3: Raman spectra of tremolite in 0 – 3800 cm^{-1}. The different measurement conditions are coloured. Black: LC, Blue: Vacuum with different temperatures, Red: CO_2-atmosphere with different temperatures.
The insert indicate the shift at the 548 cm^{-1} band for the sequence of measurements.