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RAMAN SPECTROSCOPY OF MINERALS AT SIMULATED PLANETARY CONDITIONS FOR SPACE EXPLORATION

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Introduction:

New exploration tasks for space missions to solar system bodies demand new techniques and instrumentation for remote and *in situ* analysis. Inelastic light scattering (Raman) spectroscopy is considered as a powerful tool for mineralogical and organic matter *in situ* surface investigation for the future missions to Mars and the Moon [1,2]. On the ExoMars mission the Raman Laser Spectrometer (RLS) shall identify minerals produced by water related processes, igneous minerals and their alteration products, as well as organic compounds in the Martian surface rocks and soils. Environmental conditions influence Raman spectra [3-5] and result in spectra different to those in conventional mineral databases measured at laboratory ambient conditions.

The goal of this study is to investigate the influence of planetary conditions on the positions and bandwidths of the characteristic Raman lines prior to the future space missions. We determined the Raman spectra in environmental conditions varying from Earth-like (ambient 1 bar atmosphere, room temperature) through Martian-like (8 mbar CO₂ atmosphere, 220 K) to Moon-like (vacuum below 10⁻⁴ mbar, mean 130 K on the pole) or asteroid like (vacuum and < 10 K) conditions. The results of a Raman spectroscopic study of different rock forming and water bearing minerals and the minerals found in the Martian meteorite Dar al Gani 670 (DAG670) are presented. The investigated minerals include the sylvite (KCl), anhydrite (CaSO₄), gypsum (CaSO₄·2H₂O), phlogopite (KMg₃[AlSi₃O₁₀(OH,F)₂]), tremolite (Ca₂Mg₅[Si₄O₁₁(OH)₂]), carnallite (KMgCl₃·6H₂O), five olivine samples (four forsterites (Mg₂SiO₄), including the San Carlos olivine, and one fayalite (Fe₂SiO₄)). The Martian meteorite DAG670 is classified as a shergottite and consists of pyroxene, olivine and a feldspathic glass groundmass with minor inclusions of chromite (FeCr₂O₄) and sulphide as well as calcite (CaCO₃), a terrestrial weathering product. The minerals chosen for this study are (1) known as weathering or sedimentary products on the Earth and some of them have already been detected on Mars [6-8], (2) easy to prepare for Raman measurements and available in large amounts, and (3) good indicators for spectral line shifts in Raman spectra due to changes of ambient conditions [4,9].

Measurement Details:

Initial images of the minerals have been taken by light optical microscope with transmitted light and a polarization unit. Detailed images and elemental mappings on the coated thin sections of the minerals have been obtained with a scanning electron microscope (SEM) JEOL JSM-6610LV. Quantitative analysis of most of the minerals have been made with an electron probe micro-analyzer (EPMA) JEOL JXA-8900 Superprobe. For the DAG 670 meteorite, eight selected areas were marked by laser ablation for subsequent detailed studies by SEM and Raman spectroscopy on the uncoated sample, and finally, EPMA on the coated section. We performed Raman measurements with a confocal Raman microscope Witec alpha300 R. The laser excitation wavelength is 532 nm; the resolution of the spectrometer is 4-5 cm⁻¹. A Nikon 10x objective was 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 was chosen. The samples were fixed to the cold finger in the Oxford cryostat MicrostatH-iResII with their polished side towards incident laser beam. The excitation laser has been focused on the sample surface. The scattered light has been collected through a crystalline quartz glass window in the cryostat.

Results and Discussion:

As a rule, there are no detectable frequency shifts of Stokes lines in the Raman spectra for the investigated minerals due to the presence of a CO₂ atmosphere or due to the pressure variation from ambient down to 10⁻⁴ mbar at a fixed temperature. However, different temperature related frequency shifts of Raman lines have been observed for different atmospheric conditions, such as vacuum and carbon dioxide. Some of the minerals show Stokes lines that undergo detectable temperature related frequency

shifts, but often with no systematic gradients of different sign and strength.

Raman bands for O-H stretching modes (between 3200 and 3600 cm⁻¹) in hydrated minerals (gypsum, carnallite) show no distinct frequency shifts due to change of environment atmosphere but vary in their line intensities. The O-H stretching band in carnallite shows specific line structure becoming resolved with decreasing temperature. This can be explained with a sharpening of the individual OH – stretching lines possibly due to increased ordering of the water molecules in the crystal lattice by its cooling [9,10]. Low-frequency (100-400 cm⁻¹) translational modes exhibit the largest temperature related frequency shifts, up to about 10 cm⁻¹ (at 10 K) in comparison with room temperature. Some minerals, such as tremolite, exhibit detectable variations of positions of Raman lines with temperature only below 100 K.

For the olivine mineral group, both the Raman line widths and their frequencies, are affected by temperature. The magnitude of the frequency shifts depends on the olivine type and its orientation relative to the incident light. All four forsterites show only slight temperature dependent shifts of the Stokes lines (up to 3 cm⁻¹), while fayalite is characterized by shifts up to 6 cm⁻¹. The temperature dependence might be an effect of dynamic field splitting. In addition, magnetic interactions can occur in fayalite that may be responsible for more significant temperature dependent Raman shifts [11]. No change in the Raman spectra of the olivines with the atmospheric composition or its pressure has been observed. Although the forsterites have a similar composition, 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. No irreversible changes in the Raman spectra of the olivines were detected.

The Raman measurements on the Martian meteorite DAG670 are sensitive to mineral zonings in pyroxene by Raman shifts in two bands and possible grain orientation effects are visible in the change of the relative peak intensity. The position and bandwidth of the Raman lines are slightly shifting with temperature. The direction of the shift depends on the mineral type. The influence of pressure and kind of atmosphere is negligible. Raman measurements enable high spatial resolution with detection of the particles in micrometer size range. Special attention must be paid to the analysis of FeS in meteorites because a mineral transformation can take place under certain power of exciting laser and under certain specific environmental conditions.

In summary, temperature variations have been found as the only factor that caused significant shifts of the some lines in Raman spectra of minerals in Martian analogs and in the Martian meteorite. Typically observed variations are about few cm⁻¹ per 100 K that can be neglected in classification of minerals based on positions of major characteristic bands in Raman spectra, but must be considered for identification of minerals. The chosen experimental conditions will contribute to interpretation of the forthcoming RLS data from the ExoMars space mission. More analyses on minerals relevant for Mars are necessary to evaluate the expected data prior the mission.

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