

RAMAN INVESTIGATION OF IRON SULFIDES UNDER VARIOUS ENVIRONMENTAL CONDITIONS.

I. Weber¹, U. Böttger², S.G. Pavlov², H.-W. Hübers^{2,3}

¹Institut für Planetologie, Wilhelm-Klemm-Str. 10, WWU Münster, Germany, ²DLR, Institut für Optische Sensortechnik, Rutherfordstr. 2, Berlin, Germany, ³HU Berlin, Berlin, Germany.(sonderm@uni-muenster.de)

Introduction: Missions to bodies of our solar system are coming up and imply new instrumentation to investigate the surface of the planetary body in the best case *in situ*. One of the fundamental aims of space mission is to understand formation conditions and therefore draw conclusions about former processes on Earth as well as on other planets and/or asteroids in our solar system. In the case of such missions it is significant to expect the estimated data in order to support a correct interpretation. This could be done by the investigation of analog material.

Here we present the results of a Raman study on different iron sulfides in various environmental conditions. For this study we chose iron sulfides because it is a well known phase on planetary surfaces and in meteorites [e.g. 1,2]. Iron sulfides are difficult to study while they occur in a large range of possible oxidation states and are difficult to investigate with Raman due to a possible laser-induced alteration and fluorescence [3]. Therefore a proper investigation mode for this kind of minerals should be developed. Additionally, analyses in vacuum at different temperatures with a Raman spectrometer allow a continuous completion of the Raman database for upcoming missions, e.g. the Raman Laser Spectrometer (RLS) onboard of ExoMars [4].

Samples: At the beginning of this investigation we examined pyrite (FeS₂-cubic), marcasite (FeS₂-orthorhombic), chalcopyrite (CuFeS₂), pyrrothine (Fe_{1-x}S), and a declared pyrrothite within the martian meteorite Dar al Gani (DAG) 670 [5].

Sample Preparation and Technique: For Raman spectroscopy due to the size of the vacuum chamber in the cryostat each sample is not larger than 1cm × 1cm × 0.5cm. Based on the natural origin of the iron sulfides and the meteorite sample a proper flat surface must be prepared for Raman investigations. Accurate measurements on the samples are guaranteed by a plane parallel and polished surface. Special attention is paid by using a polishing powder with a known Raman spectrum. In addition, no mineral has a specific crystallographic orientation.

We performed Raman measurements with a confocal Raman microscope Witec alpha300system. 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 develop a well functioning measurement method different laser power and temperatures are chosen. For the investigations each of the samples is fixed in the cryostat and the measurements in the cryostat are as follows:

- in vacuum (<10⁻⁴ mbar) from ~ 10 K with increasing temperature back to room temperature (RT), and
- at room temperature under air at ambient pressure, to show the behavior of iron sulfides on the Raman laser.

Results: The results of the Raman measurements are given in figures 1-5.

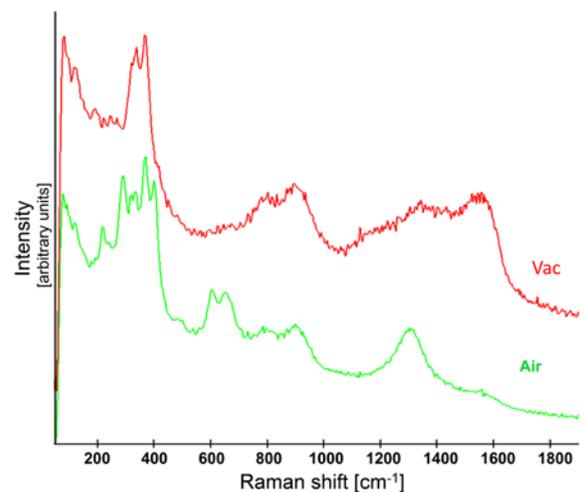


Fig. 1: Raman measurements at RT of pyrrothite with 30mW laser power in vacuum (red) and in air (green).

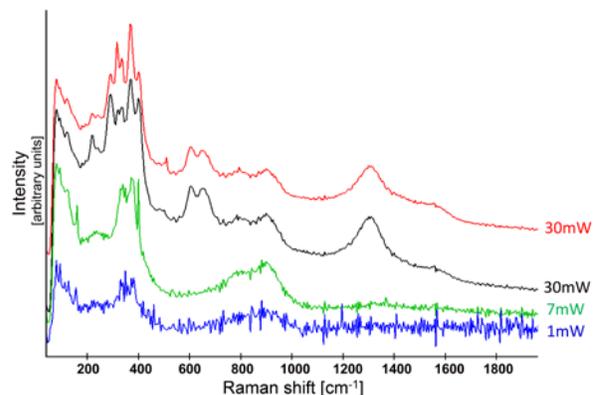


Fig. 2: Raman measurements at RT of pyrrothite with different laser power in air.

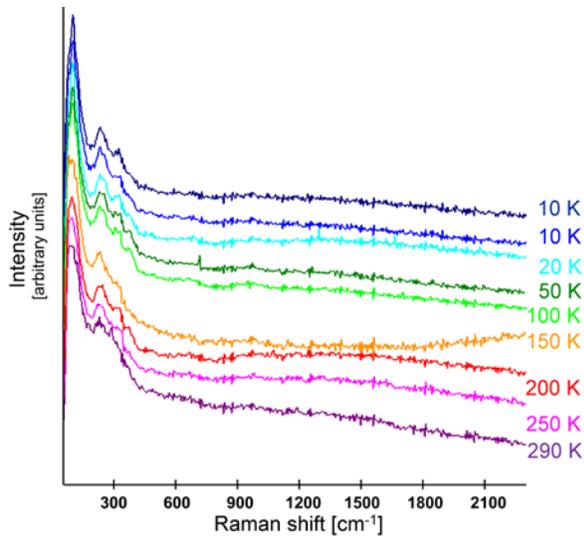


Fig. 3: Raman measurements of the iron sulfide in DAG 670 at different temperatures and in vacuum with a laser power of 7mW.

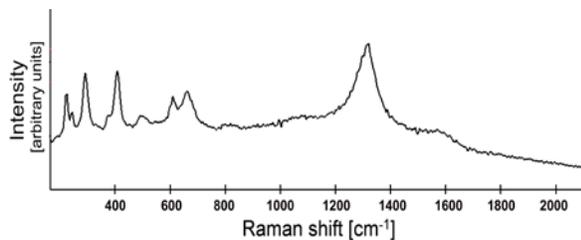


Fig. 4.: Raman measurement at the same position analysed in Fig. 3 in air and at RT showing conversion into a spectrum for hematite.

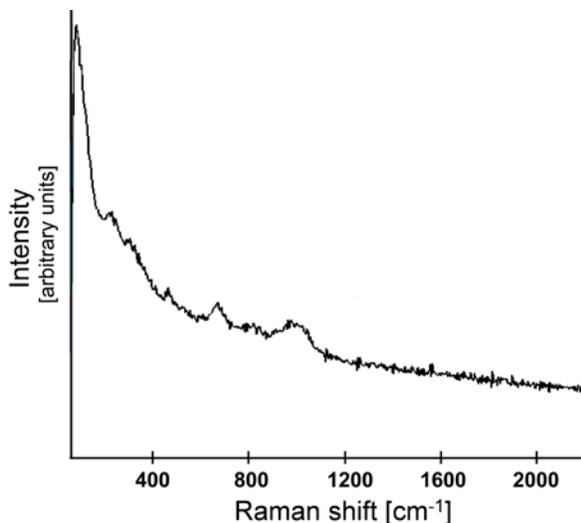


Fig. 5: Raman measurement on another iron sulfide in DAG 670 in air and at RT shows the transformation to another phase.

The Raman peak positions of pyrrhothite (Fig. 1) measured in air and in vacuum, respectively, are clearly different from each other. Investigations of pyrrhothite in air with different laser power (Fig. 2) show a significant relation between the used laser power and the Raman peak position. By using less power (1mW) the peaks are similar but shallow compared to those obtained in vacuum, whereas with increasing power new peaks start to grow representing a new phase.

Iron sulfides within the DAG 670 meteorite analysed in vacuum and at different temperatures show no significant variation in the Raman spectra (Fig. 3). However, by measuring the same sample in air hematite can clearly be identified (Fig. 4) demonstrating a mineral reaction due to laser irradiation on the sample. Figure 5 shows that iron sulfide in the same meteorite measured in air exhibits a change of the Raman shift position.

Discussion: Our investigations show that the iron sulfides with a double sulfur in the stoichiometric formula are very stable minerals concerning Raman spectroscopy. Raman spectra in vacuum at different temperatures show no variation compared with Raman spectra at RT in ambient air [6]. On the other hand iron sulfides with only one sulfur or no fixed value of sulfur in the stoichiometric formula are sensitive to ambient atmosphere during Raman measurement. These sulfides exhibit a clear trend to react with O or OH of the ambient air by building new minerals like e.g. magnetite or hematite. Laser-induced heating serves apparently as an accelerator of these chemical reactions. With measurements in vacuum it is possible to suppress this reaction.

Future plans: Future work includes a systematic study of iron sulfides in different meteorites and other sulfides.

References:

- [1] Morris R.V. et al., (2008) Vol. 113, E12. [2] Avril et al. (2013) Meteor. Planet. Sci, 8, 1415-1426. [3] White S.N. (2009) Chem. Geology, 259, 240 – 252. [4] Vago et al. 2012, Mars Concepts 2012, Houston TX. [5] Grossman J.N. (2000) Meteor. Planet. Sci. 84, A199-A225. [6] Downs R.T. (2006) 19th Gen. Meeting Intern. Min. Assoc., Kobe, Japan, O03-13.

Acknowledgement: Thanks U. Heitmann for sample preparation. Special thanks to the Deutsches Zentrum für Luft- und Raumfahrt e.V. who allows to buy the meteorite DAG 670 within the grant 50 QX 0602.