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Raman study of the role of pressure and temperature on potential Martian mineralogy

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Abstract

Water is potentially the key to understanding the geological and biological evolution of Mars. Here, we analyses the structure of selected hydrated minerals such as phyllosilicates, hydrated sulphates, carbonates and mafic minerals with Raman spectroscopy in a Mars atmospheric simulation chamber (MASC) between +40 and -40°C and a dominantly CO_2 atmosphere between 0.1–30 mbar. Temperature is shown to have a significant influence on Raman spectra emphasizing that quantitative analysis of mineralogy under ambient P-T conditions is needed prior to the use of the Raman techniques on planetary bodies.

1. Introduction

Univocal evidence of past or present life on Mars is the principal objective of ESA's first mission of the Aurora programme, ExoMars. Due to its essential role in supporting all types of known life forms there is a huge scientific effort to search for evidence of water on Mars. Detection and quantification of the amount and form of water is therefore a key requirement of instrumentation on ExoMars. A combined Raman-laser induced breakdown spectroscopy (LIBS) was initially chosen to be the pivotal first contact part of the rover Pasteur instrument package of ExoMars. Raman spectrometry would characterize mineralogy and organic compounds and simultaneously the LIBS determine multi-elemental compositions. Descoping of ExoMars means that only a Raman system will now be flown but the innovative RLS instrument remains under consideration for future missions to Moon and Mars. The principal goal of the work reported here was to set up a versatile Mars atmosphere simulation chamber (MASC), which can allow comprehensive testing of components and entire instruments under the variable but extreme conditions characteristic of Mars. Our initial focus is to determine how Raman analyses of selected "Martian" minerals are influenced by parameters such as temperature, $p$$CO_2$.

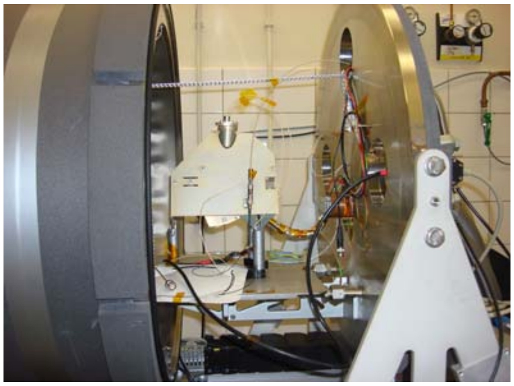
2. MASC System Design and control

MASC was designed to allow large prototype instruments to be tested under Martian conditions. The chamber is optimised to provide stable atmospheric conditions and minimal thermal gradients so that the influence of these parameters on analytical techniques can be rigorously assessed (Table 1). The cylindrical chamber is 1000 mm in length with an internal diameter of 440 mm. Independently cooled mounting plates are attached to the end doors meaning that instruments and samples can be maintained at different temperatures if required. In addition, independent cooling can be applied to detectors if required (e.g., CCD kept at low temperature).

Operating Pressure	0.1 – 50 mbar
Background vacuum	$<10^{-4}$ mbar
Leak tightness	$<10^{-9}$ scc/sec
Atmospheric composition	Carbon dioxide ~100%
Water content	0.05%
Temperature	-40 to +40 °C
Cool-down / warm-up time	One night (16 hours)

Table 1: Operating conditions of MASC

The outer chamber wall has an isolation vacuum over its full length. Freon is used as the cooling fluid via contact with a heat exchanger containing silicon fluid. Internal temperature variation is monitored by 20 sensors. The atmosphere can be operated in static mode or continually flushed with CO_2. Numerous electronic feed throughs as well as optical ports are built into the end doors to provide the versatility required to test different instrumentation. In fig.1, one side of MAS chamber with electronic feed throughs and optical ports is shown. In this figure the spectrometer with CCD detector are mounted on one of the cooled support plates. This chamber is available for use to outside users as part of the trans-national access programme (TNA-2) of the Europlanet-RI initiative.



3. Results

Production and control of various but stable temperatures throughout the chambers is a challenging aspect of any Mars chamber design. We have shown that MASC is able to produce and maintain uniform temperatures throughout the chamber volume and also has the flexibility to temperature for some devices sensitive at low temperature such as CCD detectors.

Initial work examined the behaviour of Raman vibration bonds in silicate and sulphate minerals with a particular emphasis on hydrated minerals (e.g., jarosite and amphibole) at Martian conditions compared to terrestrial measurements. As implied previously (1) low temperature has a significant influence on some Raman spectroscopic bands. Raman spectra in some samples show better resolved peaks with the appearance of new bands. Work is underway to fully quantify the temperature dependence of shifts in Raman bands, i.e., a simple correlation with temperature or significant shifts due to bond re-configurations. Subsequent work will also characterise variations in LIBS spectra in typical Martian minerals with changing temperature and pCO_2.

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References

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