



How Do Minerals Affect the Search for Organics and Biosignatures on Mars by the Exomars-2020 Rover? Case Study on Magnetite and Gypsum

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HOW DO MINERALS AFFECT THE SEARCH FOR ORGANICS AND BIOSIGNATURES ON MARS BY THE EXOMARS-2020 ROVER? CASE STUDY ON MAGNETITE AND GYPSUM. W. Goetz¹, M. Oehlke¹, X. Li^{2,3}, R. M. Danell⁴, A. Grubisic^{2,5}, R. Arevalo Jr.⁵, S. Siljeström⁶, W. B. Brinckerhoff², S. A. Getty², F. Goesmann¹, H. Mißbach¹, F. Raulin⁷, M. Reinhardt¹, F. Stalport⁷, C. Szopa^{8,9}, F. H. W. van Amerom¹⁰, and the MOMA Science Team, ¹MPS, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany (goetz@mps.mpg.de), ²NASA GSFC, Greenbelt, Maryland, USA, ³University of Maryland, Baltimore County, Maryland, USA, ⁴Danell Consulting, Winterville, North Carolina, USA, ⁵University of Maryland, College Park, Maryland, USA, ⁶RISE Research Institutes of Sweden, Stockholm, Sweden, ⁷LISA, U. Paris-Est, Creteil, U. Paris Diderot, Paris, CNRS, France, ⁸LATMOS/IPSL, Guyancourt, France, ⁹Institut Universitaire de France, Paris, France, ¹⁰Mini-Mass Consulting, Hyattsville, Maryland, USA.

Introduction: The MOMA instrument (Mars Organic Molecular Analyzer) onboard ESA's ExoMars rover (to launch in July 2020) is designed to characterize and identify organic compounds in Martian sediments [1, 2, 3]. MOMA will achieve this goal in 2 ways: (i) by heating surface samples and crushed drill cores in ovens and analyzing emitted volatiles by Gas Chromatography – Mass Spectrometry (GC-MS) and (ii) by analyzing Laser-Desorbed and Ionized molecular fragments by Mass Spectrometry (LDI-MS). This work is an update to previous work [4, 5] investigating the sensitivity of MOMA/LDI-MS to inorganic (mineral) compounds. More specifically, the goal of this study is to catalogue potential LDI mass peaks for certain key minerals (common on Mars) and to explore MOMA's potential capability to distinguish between different such minerals. If discrete mineral-diagnostic mass peaks cannot be found then it shall be assessed if such minerals as a result of laser ablation can contribute specific noise components or noise patterns. Careful characterization of LDI noise should enhance MOMA's overall detection limit of organic compounds. Ideally, this study will help characterize the mineral (or mineraloid) phase that detected organics may be associated with on a spatial scale much smaller than the LDI footprint (~300 µm). The latter information will be important for understanding the origin of organic compounds on Mars.

Samples: Here we focus on powders and thin sections of specific mineral samples (magnetite and gypsum, Table 1). Element compositions as well as spatial homogeneity of these compositions were determined by EDX/WDX electron microprobe and controlled by Raman spectroscopy and polarization microscopy (Table 1) [4]. MOMA-LDI may provide only very rough information on chemical composition, but (most likely) no structural information. Therefore, the present case study focusses on two minerals that do not have any overlap in terms of chemical composition (see Table 1). All samples were analyzed by MOMA-LDI both in powder state (as on Mars during ExoMars/MOMA operations in 2021) and as petrographic thin sections. In order to improve LDI laser coupling, thin sections

were first polished and thereafter (slightly) roughened with P600 sandpaper. A difference in LDI-spectra of powders and thin sections is not expected *a priori*, but can neither be ruled out due to different sample processing. Obviously, thin sections are needed to determine the mineral composition (Table 1) and have the advantage that a given point can be found again and re-analyzed by LDI or other *in situ* microbeam techniques. All results reported here are consistent with and have been inferred from both powder and thin-section experiments.

mineral	stoichiometry (WDX)
magnetite 'IM', Ishpeming, Michigan, USA	Fe ₃ O ₄ (traces of Al & Mg detected)
gypsum 'R', Red River Floodway, Winnipeg, MB, Canada	CaSO ₄ (no other elements detected)

Table 1 Minerals used for this work. The gypsum sample was actually analyzed by LDI-MS in the water-free state (as anhydrite). Therefore the crystal water is omitted in the stoichiometric formula.

Experimental setup: Experimental data presented here have been acquired by the ETU LDI-MS setup (Engineering Test Unit). This setup has been described previously [4]. Briefly, bursts of laser pulses ($\lambda = 266$ nm, $\tau \sim 1.3$ ns) of variable energy (30-120 µJ) hit the sample (powder or thin section) at an incident angle of 45°, thereby desorbing molecular fragments to be detected by the MS. All experiments are performed at room temperature in a Mars-like atmosphere (~8 mbar 96% CO₂, 1.9% N₂, 1.9% Ar, 0.15% O₂). Therefore, gypsum transforms quickly to anhydrite (or the hemihydrate) while residing in the ETU test chamber. To ensure a clean/fresh sample surface for compositional analysis the samples (powders or thin sections) have been irradiated by typically 500 or 1000 laser shots before acquiring the actual LDI spectra. Decontamination works better on thin sections than on powders due to laser-impact-induced dislocation of powder grains.

Results: LDI mass spectra for powder and thin section are shown in Figs. 1 and 2 for magnetite and gypsum, respectively. Individual LDI spectra were selected

such that their Total Ion Counts (TIC) are around 2000 (and strictly <4000) trapped ions (usually accumulated after a burst of 5 laser shots) [2]. The sum of these spectra were then plotted in Figs. 1-2. By systematic comparison of many spectra of these two (and other Mars-relevant) minerals, it became possible to separate mineral signals from other (unidentified) mass peaks (for simplicity hereafter referred to as *contaminants*, see Table 2). This task is difficult due to two reasons: (i) MOMA-LDI being a surface-analysis technique and analyzing surface-bound molecules almost “one by one” the spectra can be easily dominated by contaminants. (ii) So far it was not yet possible to assign the observed mass peaks (either contaminant or mineral-diagnostic) to specific molecules or clusters. By virtue of versatile MS operational modes (Stored Waveform Inverse Fourier Transform (SWIFT), MS/MS [2]) MOMA has the possibility to achieve these goals, but this can be difficult, as the parameters controlling the LIT (Linear Ion Trap) must be optimized to each individual case. Nevertheless, Table 2 provides some plausible assignments.

	Diagnostic mass peaks [Da]
magnetite	168.0 (Fe ₃ , 167.6), 174.9 (Fe ₂ O ₄ , 175.7), 199.9 (Fe ₃ O ₂ , 199.6), 215.9 (Fe ₃ O ₃ , 215.6), 231.8 (Fe₃O₄, 231.6) , 254.8 (Fe ₄ O ₂ , 255.4)
gypsum	135.9 [not shown in Fig. 2] (CaSO ₄ ?, 136.1), 199.8 (Ca ₅ , 200.4), 254.8 (NaCa ₅ O ₂ ?, 255.4), 271.7 (NaCa ₅ O ₃ ?, 271.4), 287.7 (NaCa₅O₄?, 287.4) , 327.7 (NaCa ₆ O ₄ ?, 327.5), 343.6?
unknown species	150-154, 166-168, 172, 180-181, 210-213, 225-226, 242-244

Table 2 LDI mass peaks in MOMA-ETU spectra of mineral powders. Unknown (organic) species tend to show up as narrow bands (rather than discrete lines due to loss of one or several H-atoms): Only the most pertinent unidentified mass peaks are listed. Mass peaks considered to be particularly important are highlighted in bold-face.

Conclusions: The experiments show that MOMA-LDI indeed has the intrinsic capability to discriminate between different minerals. They experiments also emphasize MOMA-LDI's huge sensitivity to surface compounds and therefore to contaminants, - a problem that only exists for the ETU setup (caused by analyzing extensive Mars analog sample suites over several years), - not for the MOMA FM whose building, assembly and even test procedures have been subject to a stringent Contamination Control (CC) protocol.

A straight-forward next step in the current project are LDI-MS experiments on other mineral phases relevant to the designated ExoMars landing site [6] (e.g. pyroxenes, hematite, clay minerals) and experiments on appropriate thin sections are currently being planned or

have already being performed. By these experiments it shall be determined if MOMA can only return rudimentary information on elementary (inorganic) composition or if it can also return some structural/stoichiometric information (e.g. distinction between olivines and pyroxenes).

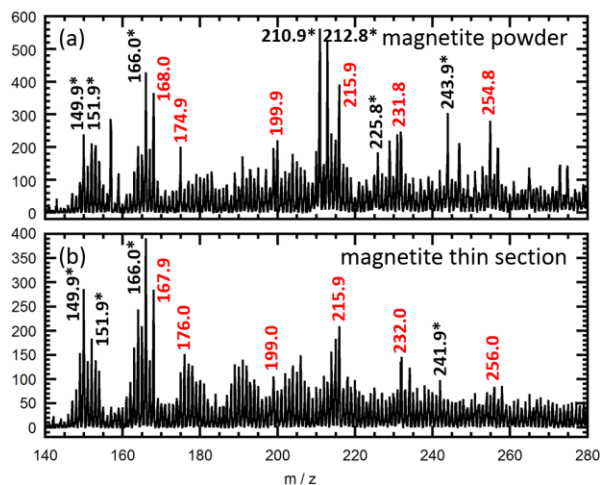


Fig. 1 LDI spectra for magnetite. (a) Powder [Test ID TID8381, 125-202 with Total Ion Count TIC<4000] and (b) thin-section spectra [TID8381, 68-121 with TIC~2000] look different at first glance, but share a fair amount of lines (black with asterisk: contaminants, red: peaks thought to be diagnostic of magnetite, see Table 2).

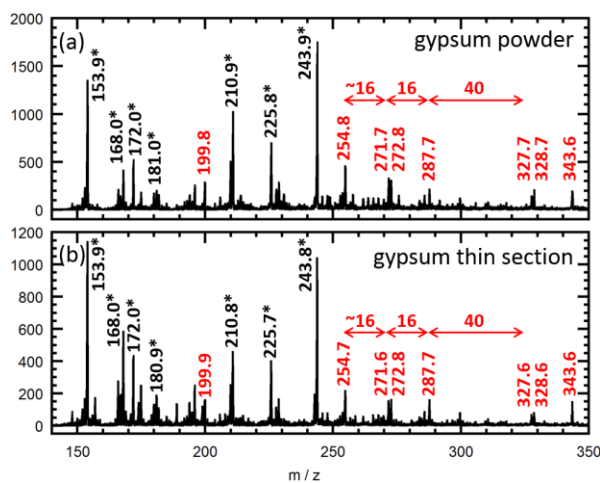


Fig. 2 LDI spectra for gypsum/anhydrite: (a) Powder [TID8381, 482-548 with TIC~2000] and (b) thin-section [TID8381, 587-722 with TIC~2000]. Legend as in Fig. 1.

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