



Probing the Allende meteorite with a miniature laser-ablation mass analyser for space application

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ABSTRACT

We measured the elemental composition on a sample of Allende meteorite with a miniature laser ablation mass spectrometer. This laser mass spectrometer (LMS) has been designed and built at the University of Bern in the Department of Space Research and Planetary Sciences with the objective of using such an instrument on a space mission. Utilising the meteorite Allende as the test sample in this study, it is demonstrated that the instrument allows the in situ determination of the elemental composition and thus mineralogy and petrology of untreated rocky samples, particularly on planetary surfaces.

In total, 138 measurements of elemental compositions have been carried out on an Allende sample. The mass spectrometric data are evaluated and correlated with an optical image. It is demonstrated that by illustrating the measured elements in the form of mineralogical maps, LMS can serve as an element imaging instrument with a very high spatial resolution of μm scale. The detailed analysis also includes a mineralogical evaluation and an investigation of the volatile element content of Allende. All findings are in good agreement with published data and underline the high sensitivity, accuracy and capability of LMS as a mass analyser for space exploration.

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1. Introduction

The knowledge of the chemical composition of planetary bodies, moons, comets and asteroids is a key issue to understand their origin and evolution. In particular, the chemical analysis of their surfaces is of great importance on every space mission to such a celestial object, where the investigation can be conducted only remotely (McSween et al., 2011). In turn, laboratory studies of extraterrestrial material and samples returned from space were also greatly conducive to the fields of planetology and cosmochemistry (Zinner et al., 2011). In the laboratory, a variety of analytical techniques can serve to investigate in detail the samples that were returned from solar system objects (Brucato et al., 2009; Barucci et al., 2011, 2012).

For cosmochemistry, the elemental and isotopic composition of the surface material is an essential information to investigate origin, differentiation and evolution processes of the body and therefore the history of our Solar System (McSween and Huss, 2010; Wurz et al., 2009). In particular, the elemental composition, resulting in the surface modal mineralogy, gives unambiguous

information about rock and soil constituents. In addition, rocks store the record of processes acting on the planetary materials (Tulej et al., in preparation). Measurements of the abundances of radiogenic isotopes provide age information on mineral and rock formation and the processes involved in their evolution. Isotope and elemental abundances provide information on planetary differentiation, geology, thermal metamorphism, volcanism, aqueous alteration and weathering processes. Such investigations may also reveal biosignatures, which makes them relevant to the search for past and present life (Wurz et al., 2009).

So far, several space missions to planets and their moons were carrying mostly orbit-based optical spectrometers for elemental analyses with limited sensitivity in element detection and spatial resolution. Spectroscopic instruments deployed on planet- or moon-orbiting spacecrafts provided data of the surface chemical composition, mostly for a few elements only and generally on a global scale (Tulej et al., in preparation). Analyses with the gamma-ray spectrometer (GRS) onboard Mars Odyssey made it possible, e.g., to compile a map of Fe, Th and K on the Martian surface (Taylor et al., 2006). Lunar Prospector's GRS and neutron spectrometer was used to infer a map of the hydrogen-abundance and the abundances of some other elements on the Lunar surface (McSween et al., 2011; Moskalenko and Porter, 2007). One pixel on the map from the Lunar Prospector's GRS data corresponds to an area of 150 km^2 and contains about 140 single spectra, which

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needed in total about 75 min to be recorded (Lawrence et al., 1998). Improvements of detected elements and spatial resolution have been made by employing the alpha-particle X-ray spectrometer (APXS) onboard the Pathfinder and Mars Exploration Rovers (MER) Spirit and Opportunity on the surface of Mars. These instruments enabled an extension of the former Martian surface studies by measurements of rocks and soils on the planetary surface. With a spatial resolution of a few cm and an instrument sensitivity at the per mill level, more elements could be analysed in the Martian surface. Nevertheless, environmental conditions and the long acquisition time for single measurements in the range of several hours up to days limited the efficiency of these investigations (Rieder et al., 2003).

Current and near future space missions with landers and rovers offer new possibilities for the implementation of instruments that apply in situ measurement techniques for chemical composition measurements on planetary, moon or asteroid surfaces. NASA's Mars Science Laboratory (MSL) mission, landed on Mars in early August 2012, is carrying a laser spectrometer for in situ sample analysis on Mars, applying the Laser Induced Breakdown Ionization Spectroscopy (LIBS) method, an optical spectroscopic approach. The instrument points an intense laser beam onto the sample that ablates surface material and generates a plasma plume. The emission lines of the excited atoms in the laser plasma are interpreted by spectroscopic analysis (Kim et al., 2006). Using LIBS, several elements can be measured, down to the sub per mill level. As an alternative to LIBS, lightweight mass spectrometers with high instrument performance become highly attractive for space research (Rohner et al., 2003, 2004; Managadze et al., 2010). Compared to spectroscopic methods, the mass spectrometric technique has the better analytic potential because of its much higher elemental sensitivity and the capability to detect all elements (Wurz et al., 2012). Because of the use of a focused laser beam, a high lateral and vertical resolution of chemical composition measurements is possible and this offers the opportunity of single grain investigations and therefore allows for the investigation of the heterogeneity of rocks on spatial scales of grain-size as well as studies of alteration processes on planetary surface material (Bazalgette Courrèges-Lacoste et al., 2007).

The progress in the development of miniaturised mass analysers, laser technology and fast electronics, over the last two decades, led to new opportunities for design and construction of mass spectrometers using a laser beam for ionisation of the sample material (Tulej et al., 2012). Methods like Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA ICP MS) or Laser Ionisation Mass Spectrometry (LIMS) are used frequently for measurements of trace elements at and below the ppm abundance level. Compared to LA ICP MS, LIMS offers several advantages, including simplicity of construction and operation, and the robustness of the hardware (Tulej et al., submitted for publication). The miniaturised laser mass spectrometer (LMS), developed and built in house at the University of Bern, is a LIMS instrument coupled with a time-of-flight (TOF) mass analyser. The sample material is ablated by an UV-laser pulse from a spot with a diameter of a few μm , a plasma plume is formed, and the ionised atoms are subsequently mass-analysed in a reflectron type TOF analyser. With one laser shot a complete mass spectrum can be recorded. Laser ablation TOF mass spectrometers are also part of the scientific payload of the future Russian missions Luna-Resurs and Luna-Glob to investigate the chemical composition of the lunar surface (Khartov et al., 2011).

In Bern, two prototypes LMS v1 and v2, designed for a planetary lander and rover, have been built (Rohner et al., 2003, 2004). These instruments were part of the early concept of the BepiColombo mission (Balogh et al., 2000). To build a light weight LIMS instrument, microchip lasers can be used. Their application has been tested already with these prototypes (Rohner et al., 2004).

The LAZMA instrument is the only laser ablation/ionisation mass spectrometer that was flown so far in space research. This instrument was part of the Phobos-Grunt payload (Managadze et al., 2010). Unfortunately, the mission failed due to a booster stage failure (Astronomy and Geophysics, 2012). A difference between LMS and LAZMA lies in details of ion confining and detection (Rohner et al., 2003).

Design studies revealed that an LMS flight instrument including the setup, laser system, readout card and electronics and a sample transfer system would have an average power consumption of ~ 8 W and would weigh ~ 1500 g. Assuming an ambient surface pressure of 10^{-6} mbar or higher on the target planet or moon, a vacuum system would be needed for operation of the LMS instrument, increasing the LMS power consumption to about ~ 24 W and the weight to ~ 1650 g (Riedo et al., 2012). For transfer of untreated rock-samples from the planetary surface to the analyser, a sample receiving unit, similar to the one designed for LAZMA (Managadze et al., 2010) would be feasible. In this design, a collecting unit places surface samples in holes on a disc, which can rotate underneath the analyser.

Recently, a combined design of the LMS instrument together with a microscopic imaging system (UV, visible and infrared) and a sample collection stage was proposed for the MarcoPolo-R mission to an asteroid (Tulej et al., submitted for publication).

For a mass spectrometer that is designed as a flight instrument for a space mission to help to answer important questions for planetary sciences, meteorites offer an excellent opportunity for evaluating its performance in the laboratory (McSween and Huss, 2010). To demonstrate the performance of LMS, element analyses on a sample of the meteorite Allende were carried out that serves as an analogue for investigations on a planetary surface in this study. Chondritic meteorites contain information about the conditions in the early solar system (Bonafant et al., 2006) when they formed within the solar nebula by accretion of solid particles more than 4.5×10^9 years ago (McSween and Huss, 2010). Chondrites, in particular members of the CI group, are primitive rocks thought to originate from the outer regions of the Asteroid Belt (MacPherson and Thiemens, 2011) and represent fragments of early formed planetesimals. The Allende meteorite is a chondritic meteorite of the class CV3, possessing a complex heterogeneous structure (McSween and Huss, 2010). It consists of a mixture of accreted components, which have formed under different conditions, including a fine-grained matrix, chondrules, calcium–aluminium-rich refractory inclusions (CAIs), amoeboid olivine aggregates, metals and sulphides (Norton, 2002).

Thus investigation of this material can be challenging, but we will show that using our miniature LMS, a quantitative chemical analysis of Allende meteorite can be performed with high spatial resolution. The mass spectrometer can be used for spatially resolved chemical mapping and from these analyses the mineralogy and chemical differentiation of the material can be deduced. These performance studies offer new great possibilities for the in situ chemical analyses on planetary surfaces.

2. Experiments

2.1. Experimental setup

The LMS instrument is a miniature Laser Ablation Mass Spectrometer combined with a time-of-flight (TOF) mass analyser, developed for a planetary lander. The spectrometer has been fully designed and built at the University of Bern in the division of Space Research and Planetary Sciences. LMS has been designed to be flown on a space mission for investigation of the elemental and isotopic composition of material on the surface, e.g. regolith or

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