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Mass Spectrometric Analysis in Planetary Science: Investigation of the Surface and the Atmosphere[1]

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Abstract—Knowing the chemical, elemental, and isotopic composition of planetary objects allows the study of their origin and evolution within the context of our Solar System. Landed probes are critical to such an investigation. Instruments on a landed platform can answer a different set of scientific questions than can instruments in orbit or on Earth. Composition studies for elemental, isotopic, and chemical analysis are best performed with dedicated mass spectrometer systems. Mass spectrometers have been part of the early lunar missions, and have been successfully employed to investigate the atmospheres of Mars, Venus, Jupiter, Saturn, Titan, and in comet missions. Improved mass spectrometer systems are foreseen for many planetary missions currently in planning or implementation.

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INTRODUCTION

When trying to understand the present state of our solar system with its variety of planetary objects, one is confronted with a few major scientific questions: (i) to understand how the physical and chemical processes determine the characteristics of planetary objects; (ii) to investigate how planetary systems originate and evolve; (iii) to determine how and where life evolved, and in what ways it modifies its planetary habitat; and (iv) to discover how the laws of physics and chemistry can lead to the diverse phenomena observed in the Solar System.

For all these scientific questions knowledge of the chemical composition is an important factor because the composition is a direct result of major Solar System processes: the accretion of interstellar matter into planetesimals and then into planetary bodies; initial heating due to accretion and thermal metamorphism of small planetary bodies; planetary differentiation in both small and large planetary bodies; local geological processes that build or modify planetary surfaces; interaction of solids with liquids (e.g. water); the interaction of the solid surface with the atmosphere, by the present and a past atmosphere; the alteration of the surface by biological activity.

Since the outermost planetary surface is often severely modified due to weathering processes (e.g., cratering, fluids), it is useful to also measure the subsurface material of unaltered planetary material. This approach will help to calibrate the orbital and/or Earth-based spectral observations of the planetary body, since these have only access to the top-most surface (e.g., see discussion in Wurz, et al., 2010). Also, unambiguous answers to scientific questions will commonly require more than one measurement or analytical technique. Especially, when it comes to deriving the mineralogy the mass spectrometric information will have to be complemented by optical spectroscopy in the infrared region.

Because planetary surfaces are the most accessible portion of any of the Solar System's objects they are logical targets of future spacecraft missions and instruments for the investigation of the planetary surface. However, to justify a planetary lander with in situ analyses of surface material the addressed scientific questions should be unresolvable from orbit observations, and should be significantly cheaper than sample return missions, which rely on the much larger measurement capabilities of terrestrial laboratories. Sample return mission have the additional mission risk of bringing the collected sample to Earth, which makes it advantageous to combine a sample return mission with a substantial in situ science package, like is done for the Phobos-Soil mission (Zelenyi, et al., 2010). Bringing a sample from a planetary body to Earth becomes increasingly difficult with distance of this object to the Earth. Whereas bringing samples from the Moon is "fairly easy", bringing samples from Mars poses already significant mission challenges, and bringing a sample from Europa, for example, is highly unlikely. Moreover, some samples may degrade considerably during transport to Earth, e.g. the ice-dust mixture at

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the surface of a comet, or an ice sample from a Galilean moon. Thus, developing highly capable in situ instrumentation is necessary to advance research in planetary science.

In the following sections we will report on the present level of development of mass spectrometry for planetary science in our laboratories, with focus on two areas: (i) investigation of atmospheres and volatiles; and (ii) investigation of solid surfaces and the near-surface soil/regolith.

Mass Spectrometric Investigation of Atmospheres

Neutral gas mass spectrometers on a lander provide a view of the atmosphere from within, which cannot be obtained from orbit. Given the much larger density at the surface, mass spectrometers on a lander allow for the chemical analysis of minor and trace elements, undetectable by remote spectroscopy. Also, from a lander the atmosphere-surface interaction can be studied. Being located on a fixed geographic location, temporal variations of the atmosphere composition (e.g. condensation/sublimation, chemical interaction with the surface), on time scales of diurnal, seasonal, and annual periods, given sufficient operation time of the lander. These analyses are made mostly, but not exclusively, by mass spectrometers.

Understanding the atmospheric composition is a key element in understanding a planet. The atmospheres of most of the terrestrial planets, of Jupiter, of Saturn and its moons Titan and Enceladus have been investigated with mass spectrometry. The elemental, isotopic, and chemical composition including all trace species are of great scientific interest by giving clues to the evolution of the planetary object. Mass spectrometric analysis of an atmosphere is relatively straight forward since the sample to investigate is already in the gas phase. Depending on the atmospheric pressure, the gas inlet needs special attention, also enrichment cells, e.g. for noble gases, might be of advantage to enhance the accuracy of the analysis.

A second area of investigation for neutral gas mass spectrometers in space are the analysis of gases trapped in solids, i.e., the analysis of evolved gases. Usually this involves collection of near-surface samples, the release of volatiles from samples in a furnace (e.g. ten Kate, et al., 2010), or gas release by acid dissolution, or other selective processes. Additionally, gas-chroma-tographic (GC) columns can assist in the separation of the volatile compounds, which is of advantage when analysing complex chemical or biological mixtures. The GC separation technique is widely used in the laboratory and has been used in space for sample preparation beyond the possibilities of an evolved gas analysis (e.g. Swindle, et al., 1995; Goesmann, et al., 2007).

In a detailed study of instrumentation for planetary research (Meyer, et al., 1995) it was concluded thatfor atmospheres one needs to measure the elements H, C, N, O, and the noble gases in the atmosphere with a minimum accuracy of 10%, and the isotope ratios of D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ with an accuracy of at least 1% (COMPLEX report, 1994; Swindle, et al., 1995), and accuracies of 0.1% for the isotope measurements would be desirable. In addition, the measurement of minor and trace species in the atmosphere is needed, but the specifics change with the planetary object under investigation (e.g., CH_4, O_3, HCN, ...). The need to measure the noble gases drives the dynamic range of the instrument, since a useful determination of a noble gas isotope ratio requires an accuracy at least at the percent level, which is complicated by the fact that at least one of the isotopes is of low-abundance, with the noble gases themselves being a minor or trace substance in an atmosphere. The measurement of noble gases may necessitate other instrumental capabilities such as dedicated enrichment cells.

Investigation of the Surface Composition of Planetary Bodies

To study the origin and evolution of a planetary body one needs to learn about the elemental composition of the rocks and the soil on its surface. From the elemental composition one can derive a normative modal mineralogy of the surface. If the sampled spot is commensurate with the grain size of the soil or mineral then a more direct determination of the modal mineralogy may be possible. The use of complementary analytical techniques may be necessary for an unambiguous identification of the mineralogical composition.

Currently, mass spectrometry is the method of choice, which also gives the isotopic composition of elements (i.e., if the mass spectrometer has sufficient mass resolution) that allows the study of the origin and evolution of the material investigated. Probably the single most important measurement would be an absolute age determination, which has never been done with an in situ instrument so far. Acid dissolution K-Ar dating and laser ablation Pb-Pb or U-Pb dating are possible techniques (Treiman and Meyer, 1995). Even the determination of very imprecise ages with accuracies of 25% can be very valuable in same situations (Swindle, et al., 1995). If there is sufficient dynamic range in the mass spectra allowing for element identification at the ppm level, the abundance of trace elements can be determined to provide further information on the nature of planetary differentiation and the geological origin of surface materials (e.g. from rare-earth element fractionation patterns). Trace elements are of relevance to the search for life. Moreover, mass spectrometric investigations can identify potentially toxic elements in the soil, which is relevant for manned missions since the spacesuits will get contaminated with the soil, the soil is thus brought into the habitats, and can be inhaled or ingested by the crew.

Potential toxic elements are for example Be, As, Cd, Tl, and severalother heavy metals.

In addition, mass spectrometric compositional analysis of the soil also provides context science for the other investigations performed on the landing site. The use of a mass spectrometer with sufficiently high spatial resolution allows one to infer the modal mineralogy of a surface far more directly and with more confidence than from bulk measurements. Furthermore, the spatial resolution allows confident identification of secondary alteration products, e.g. due to weathering by aqueous solutions, such as seen for many martian surface materials, and even on the martian meteorite, ALH 84001 (Shearer, et al., 1996). Thus, the underlying mineralogy allows one to identify the rock type (e.g. basalt, granite, sandstone), and therefore the process responsible for its origin (igneous, plutonic, sedimentary). The nature of any alteration products provides information and constraints on the history of the environment in which these rocks have been e.g. the presence of liquid water, the pH, the nature of trace elements in solution etc. This is particularly important when assessing the significance of any possible biomarkers.

In recent years Laser Mass Spectrometers (LMS) have been developed for space application, which are very well suited for the compositional analysis of solid surfaces (Vertes, et al., 1993). Laser ablation was chosen as a sample introduction technique for space applications principally because of its high spatial resolution and the lack of any need for sample preparation (Becker and Dietze, 2003). Ions for analysis are generated directly from the surface under investigation by short, intense laser pulses. Once a critical power density of approximately 10^9 W/cm^2 is exceeded during the laser pulse the released surface material is atomised and its ionisation is more or less independent of the element, i.e., minimal element fractionation in the ionisation process occurs. If one operates at much lower laser intensities quantitative measurements become more difficult and molecules also appear in the mass spectra. When operating at laser intensities near the threshold of material removal from the surface, in the so called desorption mode, chemical analysis of the surface material can be performed (e.g. Riedo, et al., 2010). If one has the desirable capability to vary the laser intensity over a wide range one can operate the LMS instrument either in the mode of quantitative elemental and isotopic analysis at high laser intensities, or in the mode of chemical analysis at low laser intensities.

Advantages of laser ablation/ionisation include simplicity of the resulting instrument design, speed of measurement, and the ability to do depth profiling (potentially important for a regolith in which mineral grains are coated with impact produced glass). Time-of-Flight mass spectrometers (TOF-MS) are a natural match to the pulsed laser ablation/ionisation because they couple well to a pulsed ion source such as that produced by laser ablation. The produced ions are accelerated into the ion optical system of the TOF-MS, which consists of the ion acceleration, a drift tube, an ion mirror, another drift tube and an ion detector (e.g. Cotter, 1994). TOF-MS are simple, robust instruments that are used more and more frequently in space research. In laboratory instrumentation the detection limit for LMS is normally between 10 ppb and 1 ppm depending on element, and fractionation is less than in the often used spark source mass spectrometry (Dietze and Becker, 1993). Recently, the 1 ppm detection limit has been reached also for a flight prototype (Tulej, et al., 2011).

If one wants to go deeper than the top-most surface, let's say a few meters, then one needs a drill to bring up material to be analysed. Drilling below the surface down to 2 m is planned for the ExoMars mission of ESA (Vargo, et al., 2006) and down to 5 cm for the Mars Science Laboratory mission of NASA (http://mars.jpl.nasa.gov/msl/). For the Russian Phobos-Soil mission it is planned to take samples from the very surface and from not the so deep surface layer (up to 1 cm) with the help of a manipulator (Zelenyi, et al., 2010). Again, a LMS instrument is a good choice for the analysis of samples brought up by a drill. Having a LMS inside the drill bit is currently not feasible because mass spectrometers cannot be accommodated within the small volumes available inside a drill. Typical drill designs for planetary exploration have an outer diameter of about 30 mm, which would need a miniaturisation of our smallest LMS, the rover LMS (see below), by roughly a factor of two.

Before the availability of LMS instruments for planetary research Alpha Proton X-Ray Spectrometers (APXS) were used for elemental analysis.For example, an APXS was part of the scientific payload of the Mars Sojourner rover of NASA's Mars Pathfinder mission (Rieder, et al., 1997) and on the Mars Exploration Rovers (Rieder, et al., 2003). The approach used is to expose material to a radioactive source that produces alpha particles, and to acquire energy spectra of the alpha particles and X-rays returned from the sample. Such an instrument can identify and determine the amounts of many chemical elements. The APXS instrument consists of ^{244}Cm alpha particle sources ($E_\alpha = 5.902$ MeV) and detectors to register back-scattered alpha particles and X-rays. The analytical process is based on two interactions of alpha particles with matter: (i) elastic scattering of alpha particles by nuclei, and (ii) excitation of the electronic structure of atoms by alpha particles, leading to the emission of characteristic X-rays. In addition, hard X-rays emitted by the curium source induce X-ray fluorescence in elements with mostly high atomic number. The X-rays are measured with a solid-state silicon detector. The basis of the alpha mode of the instrument is the dependence of the energy spectrum of alpha particles scattered from a surface on the composition of the surface material (Rutherford backscattering). The method is very sensitive to C and O, however, the resolving power of this mode is limited for other elements (Foley, et al., 2003). H and He cannot be detected because alpha particles are used as a source. The X-ray emission mode works well for light elements ranging from sodium up to nickel, but also for the heavier elements if they are present in sufficient quantities in the investigated sample (Rieder, et al., 2003). The sampling depth is about 10 μm with an element detection threshold of 0.5 to 1% in weight, depending on the element (Rieder, et al., 1997). The resolution of elements obtained by this technique is limited by the energy resolution of the X-ray detector, especially for the Mg/Al/Si group, which are the main rock forming elements. However, with careful calibration of the instrument and elaborate deconvolution of the data a lot of interesting results were obtained (e.g. Rieder, et al., 1997). Unfortunately, an improvement of the energy resolution, and thus of the elemental resolution, requires cryogenically cooled detectors, which is impractical within a planetary mission. Nevertheless, APX spectrometers were useful for elemental composition measurements on landers. A similar technique is used in orbit, in the absence of a X-ray absorbing atmosphere, where X-ray fluorescence induced by solar flares is recorded to establish compositional maps of the surface (e.g. Grande, et al., 2009; Swindyard, et al., 2009).

Laser-Induced Breakdown Spectroscopy (LIBS) is similar to laser ablation mass spectrometry in that it uses a strong laser pulse to ablate material from a sample and create a plasma plume from this material. Contrary to LMS, LIBS registers the emitted photons from the plasma plume, and identifies the different elements in the plasma plume by optical spectroscopy. The main advantage of LIBS is that it can work at considerable distances to the sample of interest, thus many more samples can be investigated from a planetary lander or rover than by in situ analysis. The main disadvantage of LIBS is that the elemental information is distributed over many optical lines (compared to elemental lines in a mass spectrometer), which significantly complicates the analysis. In particular with the limited spectral resolution of space-born instruments quantitative measurements are difficult and identification of trace elements is limited to the permil level (Lanza, et al., 2010). Isotopic analysis is not possible with a LIBS system. Nevertheless, identification of rocks and minerals is possible. The Mars Science Laboratory mission will bring ChemCam, a LIBS instrument that can investigate a rock to a distance up to 7 m away, onto Mars in 2012 (Maurice, et al., 2005).

Mass Spectrometric Investigation of Icy Surfaces

Many planetary objects in the outer Solar System, i.e., beyond Jupiter have considerable amounts of ice, and have icy surfaces. Investigating the surface and the sub-surface has also been discussed for icy planetary surfaces, like the Martian polar caps or for the surface of Europa. In the case of an icy surface, access to the interior can be accomplished via a melting probe (Zimmerman, et al., 2001), rather than a mechanical drill. The realistic goal is to penetrate at least below the radiation altered layer of Europa's surface (a few meters) but more ambitious investigations aim at going through Europa's entire ice shell into the putative ocean. In any case, a mass spectrometer for a payload of a melting probe needs a special design. The Membrane Inlet Mass Spectrometer is a possible design for such an application, as has been proposed recently (Wurz, et al., 2009).

INSTRUMENTATION

Instrumentation for Mass Spectrometric Investigation of Atmospheres

Many different mass spectrometer types have been used in the past, with magnetic sector instrument and quadrupol analysers being used most often so far (e.g. Niemann, et al., 2002; Waite, et al., 2004). A review of possible instruments has been given by Swindle, et al. (1995) and more recently by Wüest, et al. (2007). Probably the mass spectrometer with the highest resolving power ever flown in space is the Double Focussing Mass Spectrometer (DFMS) on the Rosetta mission of ESA to investigate the comet Churyumov-Gerasimenko (Balsiger, et al., 2007). Mass resolutions around $m/\Delta m = 9000$ have been achieved, which allows for the separation of many mass interferences. The sensitivity of this instrument is more than sufficient to analyse the faint gaseous envelope arising from outgassing of the Rosetta spacecraft even after 6 years in space (Schläppi, et al., 2010).

Time-of-flight (TOF) systems are in use for plasma composition measurements since the early 1970s (e.g. Gloeckler and Hsieh, 1979; Stüdemann and Wilken, 1982), featuring high detection sensitivity albeit with lower mass resolution than needed for atmospheric research. Because of the increasing availability of fast electronics the time-of-flight technique became feasible also mass spectrometers for gas analysis. Compared to other systems, TOF analysers have the advantage of a large mass scale, larger mass resolution, and larger sensitivity. The latter in part because TOF systems do not need to perform a mass scan, but measure the whole mass spectrum at once. For future planetary missions the TOF mass analyser will be clearly the systems of choice. In particular, when the object of interest can only be studied in a flyby mission scenario taking whole mass spectra at a high cadence is a big advantage. Recently, high performance time-of-flight systems became available, which was developed for cometary research (Scherer, et al., 2006; Balsiger, et al., 2007). Mass resolutions around $m/\Delta m = 5000$ have been achieved, with a mass range in excess of 500 amu (Scherer, et al., 2006). Because the available resources are very limited on many spacecraft we developed a

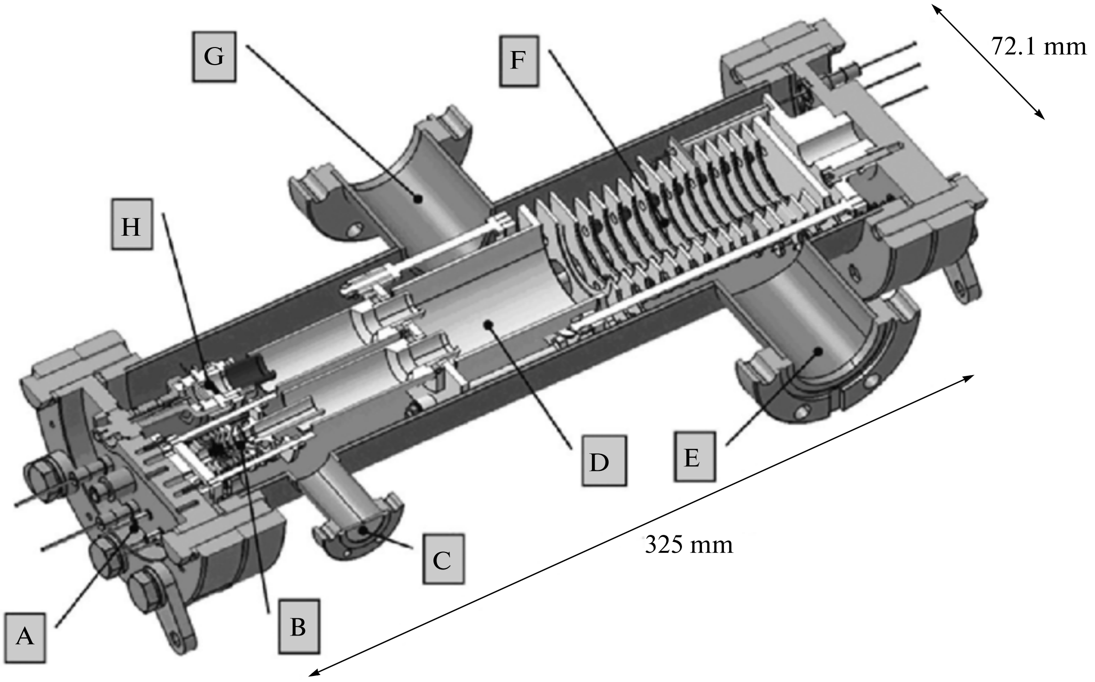

Fig. 1. Engineering drawing of the mass spectrometer. A—flange with ion source and detector, and corresponding electrical feedthroughs, B—ion source with acceleration electrodes, C—sampling gas inlet, D—drift region, E—flange for external turbomolecular pump, F—ion reflectron, G—flange for ion getter pump, H—ion pulse detector (from Abplanalp, et al., 2009).

miniaturised TOF mass spectrometer for neutral gas analysis, which will be discussed in detail below.

THE P-BACE INSTRUMENT

The P-BACE instrument (Abplanalp, et al., 2009) is a time-of-flight mass spectrometer with an ion mirror (like ROSINA/RTOF on the Rosetta mission by the European Space Agency). However, the P-BACE design is about one third in size and one fourth in mass than RTOF, since resources for a RTOF size instrument will likely not be available on future missions. A first prototype of this instrument was built, the Edel Gas Time-of-Flight (EGT) instrument, which is currently in use for noble gas analysis of meteorites in our institute.

Ions to be mass analysed are either generated from gas in a storage ion source in the neutral mode (Abplanalp, et al., 2010) with the gas from the ambient atmosphere, or volatiles released from soil material in a furnace, from the output of the gas-chromatography column. Alternatively, ions are collected from the ambient plasma in the ion mode. With the pulsed ion optics of the ion source ion packets are produced, accelerated, shaped and sent into the TOF structure. After passing the first leg of a field-free drift path, ions are reflected by the ion mirror, which allows for energy and spatial focussing of ions, and directed onto a fast micro-channel plate detector. The charge signal versus time is recorded on the detector and converted into a mass spectrum. A design drawing of a possible realisation of the Ion and Neutral Gas Mass spectrometer (INMS) is shown in Fig. 1.

Figure 2 shows two results from the calibration campaign of the P-BACE instrument. Shown in the left panel of Fig. 2 is a residual gas mass spectrum, recorded in 1 minute where mass lines at the 10^{-14} mbar pressure level can be clearly identified, which corresponds to a particle density of about 200 particles/cm^3. At this instrument sensitivity the measurement is limited by the spacecraft outgasing, because even after years in space the total pressure near the spacecraft is in the 10^{-11} mbar range (Schläppi, et al., 2010). The mass range of P-BACE extends to about 1000 amu, although not shown here. Figure 2, right panel, shows a section of a mass spectrum where Kr was introduced at a pressure of 2×10^{-9} mbar, demonstrating a mass resolution of $m/\Delta m = 1100$ for the Kr isotopes. The mass resolution is constant at higher masses, but decreases below about 30 amu. At mass 3 amu the mass resolution is about 400. Current instrument optimisation is focussed on improvements of the mass resolution at low masses, to reach $m/\Delta m \geq 700$ at mass 3 amu, so that ^{3}He–HD can be resolved.

Although the P-BACE instrument, a prototype instrument for planetary research, has not been optimised for isotopic studies, the Kr isotopic abundances come out fairly well, the accuracy is a few per-mil for the larger Kr peaks, and rises to a few percent for the small peaks. With integration times exceeding

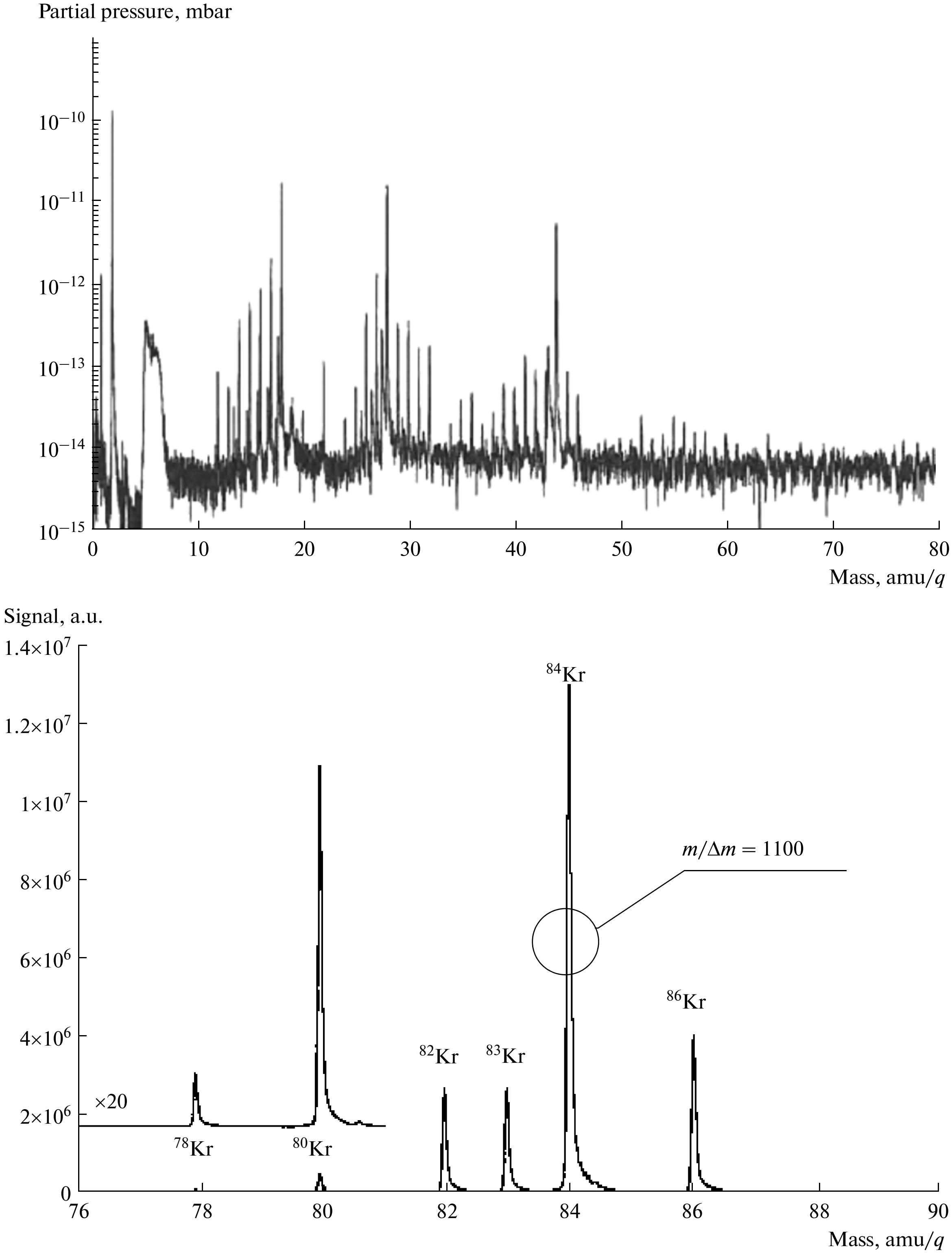

Fig. 2. Left panel: Mass spectrum recorded with the P-BACE instrument for the stratospheric balloon mission. Total pressure is 6×10^{-10} mbar with an integration period of 65 seconds. Right panel: Figure shows a section of a mass spectrum recorded at a total pressure of 2×10^{-9} mbar when Krypton gas was introduced into the chamber.

Analysis of 100 P-BACE mass spectra from the stratosphere, 2008-07-01 18:50–20:40 UT. S_{tot} gives the total signal of the stratosphere. Literature values are from http://nssdc.gsfc.nasa.gov/ and http://cdiac.ornl.gov/

Species	Measurement	Meas. Error, %	Literature value	Remarks
$^{36}Ar/^{38}Ar$	5.313	7	5.35	
$^{36}Ar/S_{tot}$	28×10^{-6}	7	32×10^{-6}	
$^{36}Ar/^{40}Ar$	7.2×10^{-4}	–	3.38×10^{-3}	Calibration problem in the data acquisition electronics
$^{21}Ne/S_{tot}$	0.053×10^{-6}	21	0.049×10^{-6}	Possible interference with H_2F^+
$^{20}Ne/^{22}Ne$	40	80	9.782	Interferences with $^{40}Ar^{++}$ and CO_2^{++}
$^{78}Kr/^{84}Kr$	0.010	50	0.006	
$^{80}Kr/^{84}Kr$	0.040	50	0.040	
$^{82}Kr/^{84}Kr$	0.200	11	0.203	
$^{83}Kr/^{84}Kr$	0.200	11	0.202	
$^{86}Kr/^{84}Kr$	0.300	7	0.304	
Kr_{tot}/S_{tot}	1.15×10^{-6}	6	1.14×10^{-6}	
$^{129}Xe/^{132}Xe$	0.9615	14	0.9833	
$^{131}Xe/^{132}Xe$	0.8846	14	0.7877	
$^{134}Xe/^{132}Xe$	0.3462	22	0.3882	
$^{136}Xe/^{132}Xe$	0.3077	22	0.3299	
Xe_{tot}/S_{tot}	0.08×10^{-6}	16	0.087×10^{-6}	Consideration of the large cross section for Xe
$^{196}Hg/^{202}Hg$	0.020	82	0.005	
$^{198}Hg/^{202}Hg$	0.367	14	0.334	
$^{199}Hg/^{202}Hg$	0.600	14	0.565	
$^{200}Hg/^{202}Hg$	0.800	14	0.774	
$^{201}Hg/^{202}Hg$	0.467	14	0.441	
$^{204}Hg/^{202}Hg$	0.233	14	0.230	
Hg_{tot}/S_{tot}	1.72×10^{-6}	6	—	Source unknown, gondola
O_3/S_{tot}	0.59×10^{-6}	21	8×10^{-6}	Pronounced fragmentation
$^{1}H/^{2}D$	8800	14	8694	From H_2/HD
$^{23}Na^+/S_{tot}$	0.99×10^{-6}	11	?	Probably from oceanic NaCl
$^{40}Ca^{16}O_2^+/S_{tot}$	0.07×10^{-6}	21	?	Contamination from spacecraft or meteorite material

the 1-minute spectra better accuracies will also be obtained for the small mass lines.

The P-BACE instrument was part of the scientific payload of the MEAP stratospheric balloon. During June of 2008 MEAP flew from Kiruna (northern Sweden) to Umingmaktok (northern Canada) at an altitude of almost 40 km making use of the circumpolar wind pattern during this season (Wieser, et al., 2009; Abplanalp, et al., 2009). During a five-day flight about 4500 mass spectra of the terrestrial stratosphere were recorded with P-BACE.

Table 1 shows a preliminary analysis of some of the mass spectra. Of special interest is the analysis of the noble gases in the stratosphere. Although no enrichment of the noble gases with respect to the other stratospheric gases has been performed in these investigations the noble gases Ne, Ar, Kr, and Xe can be identified in the mass spectra despite their very low abundance. Quantitative measurements, where the mass line is free from mass interference, show reasonable agreement with the literature values. Even the determination of isotope ratios is possible, again with reasonable agreement with the literature values, although the accuracy is limited at present. Enrichment of the noble gases to partial pressures in the 10^{-9} mbar range, e.g. with cryotraps, will improve the accuracy of the isotope measurement to a level that is commensurate with the requirements in planetary research, which we established in the calibration (see Fig. 2).

Of course, there are many species in the stratosphere other than the noble gases, which are identified in the P-BACE mass spectra (see Abplanalp, 2009), which goes beyond the scope of this paper. Here we will give a few examples. Hydrogen is measured by the P-BACE instrument well and the derived the isotopic abundance agrees with the established values. Ozone is also present in the mass spectra, as expected considering that these measurements were taken at about 40 km altitude. However, the quantification of the ozone abundance suffers from severe fragmentation of the ozone molecule in the ion source and also from chemical decomposition in the atmosphere inlet system. For the quantitative measurement of ozone dedicated inlet systems and ion sources have to be used. We also identified Na in the P-BACE mass spectra, which is likely from NaCl from the ocean. Also debris from meteoritic infall is observed in the mass spectra, for example we identified CaO_2 in the mass spectra. Finally, also mercury is detected with its distinct isotope pattern. The Hg must be released from a non-identified source within the balloon gondola; a stratospheric source of atomic Hg can be excluded at this abundance level.

A space-flight version of P-BACE with a mass of 4 kg, and a volume of about $350 \times 70 \times 100$ mm^3 fits inside the payload resources of many future planetary missions, e.g. the Europa Jupiter System Mission (EJSM), of ESA and NASA. This mass spectrometer has been selected for the gas-chromatography mass spectrometer (GC-MS) complex on the Luna-Resurs and Luna-Glob missions of Roskosmos. The GC-MS will analyse the volatiles released from the lunar soil that will be sampled near the lunar poles.

Instrumentation for Direct Mass Spectrometric Investigation of Surface Material on Planetary Bodies

Direct analysis of soil samples with laser-based mass spectrometric (LMS) systems has been proposed as spacecraft instrumentation previously (Sagdeev, et al., 1985; Sagdeev, et al., 1993; DeYoung and Situ, 1994), and one such instrument, LIMA-D (Managadze, et al., 1987), was included in the previous Phobos missions (Sagdeev and Zakharov, 1990). LIMA-D was a time-of-flight mass spectrometer designed to study the surface composition of Phobos from a hovering distance of 30–80 m. However, these instruments were rather heavy, mainly due to the mass of the laser system. Modern laser systems are much smaller and allow for compact instruments.

In recent years highly miniaturised laser mass spectrometers for direct compositional investigation of planetary surfaces have been developed by several groups for various planetary missions (Managadze and Shutyaev, 1993; Brinckerhoff, et al., 2000; Rohner, et al., 2003, 2004). These instruments are based on high intensity pulsed lasers removing material from a rock (or other solid), atomising and ionising the material and identification of the ions by time-of-flight analysis.

A compact LMS prototype based on an earlier Russian design (Managadze and Shutyaev, 1993) has demonstrated its capabilities for mineralogical studies of meteorites (Brinkerhoff, et al., 2000). An adapted version of this instrument, the LASMA instrument, which will be discussed below, is part of the lander payload of the Russian Phobos-Soil mission (Managadze, et al., 2010). The major scientific goal of the Phobos-Soil mission is to collect a sample of Phobos' soil and bring it to the Earth for detailed analysis. In addition, there will be in situ investigations of the regolith to learn about Phobos' origin and evolution (Zelenyi, et al., 2010), to which the LASMA instrument will contribute with composition analysis.

One of the scientific goals of the BepiColombo mission of ESA to Mercury is to understand the formation and evolution of the planet (Balogh, et al., 2000). To address this scientific goal two highly miniaturised laser ablation time-of-flight mass spectrometers (LMS) were developed and built, for in situ measurements of the elemental and isotopic composition of the surface of airless planetary bodies (Rohner, et al., 2003; 2004). These instruments were designed to determine major, minor, and trace element abundances in minerals on a spatial scale of 10 μm. These instrument also have sufficient dynamic range and mass resolution to perform useful isotopic measurements in favourable cases, i.e., no isobaric interferences and isotope ratios larger than about 10^{-3} (e.g. iron isotopes). In the following section we will discuss the LMS instrument for the Phobos-Soil mission, and the two LMS instruments developed for the BepiColombo mission. We will distinguish between Lander-LMS and Rover-LMS, with the former being accommodated on a stationary landing spacecraft and the latter on a planetary rover, which has an impact on available resources and instrument capabilities.

LANDER LMS

The LMS for the landing spacecraft (the lander LMS) is intended to be installed on a spacecraft landing on a planetary surface, and mounted either on a fixed position or on an articulated arm. The total dimension of the instrument is 120 mm × 60 mm (length × diameter). A flight instrument would be somewhat longer since the laser electronics would be accommodated in a compartment above the ion mirror. The anticipated weight of the flight unit would be about 500 g including all electronics (Rohner, et al., 2003).

Samples are taken directly from the vicinity of the landing site, or brought to the instrument by an articulated arm from places within its reach. The arm may be equipped with in situ instrumentation (e.g. a camera) that assists in the sample selection. The advantage of being on a lander is that larger resources are available on a lander compared to a rover; the disadvantage is that the choice of samples might be limited depending on landing location.

The lander LMS is a simple TOF instrument using a grid-less reflectron as ion mirror. For the laser, commercially available Nd:YAG microchip lasers were used operating either at $\lambda = 1064$ nm or at $\lambda = 532$ nm. These microchip lasers provided sub-nanosecond pulses of about 10 μJ at a repetition rate of 10 kHz, which can be focused to spot sizes of less than 20 diameter. Each laser pulse results in a mass spectrum, and typically 10^3 to 10^5 spectra are accumulated for a large dynamic range (Rohner, et al., 2003; Tulej, et al., 2011; 2012). The ions removed from the sample surface by the laser pulse are accelerated electrostatically into the mass spectrometer through a small hole by a strong electric field and are focussed through a narrow tunnel in the centre of the detector toward the reflectron. The ions pass through the time-of-flight tube and are reflected by the ion mirror back onto the MCP detector. Mass resolution is typically $m/\Delta m$ = 600 FWHM. With this instrument Cr and Fe isotope ratios were measured at the per-mil level for a NBS stainless steel sample (Rohner, et al., 2003). The mass resolution can be changed by adjusting the ion-optical settings; a higher mass resolution can be set at the expense of ion-optical transmission and vice-versa.

The initial configuration of the laser system of this instrument has been changed such that the laser beam is co-linear with the ion-optical axis of the mass spectrometer (Tulej, et al., 2011). Initial tests of this new optical setup with a laboratory Nd:YAG lasers at λ = 1064 nm (because the micro-chip lasers have a limited life span) were performed to assess the dynamic range and the capability for quantitative measurement of elemental abundances. Figure 3 shows the comparison between the measurements of the lander LMS and the values for NIST standard sample for two stainless steel samples (SRM 661 and SRM 664). For the quantitative abundance measurements calibration factors for each element have to be established, typically in the range of 0.5 to 2 for most elements, and with factors of the order of 10 for elements with high first ionisation potential (Tulej, et al., 2011; 2012). The latter is a result of the long laser wavelength ($\lambda = 1064$ nm) used in this study. In this first study we find the calibration factors for each element being not the same for the two reference samples. We found that this problem can be mitigated by assuring accurate and reproducible laser irradiation conditions. To prepare for actual measurements in a planetary environment steel reference samples are not the optimal choice to establish precise calibration factors, and measurements with mineral standards, possibly NIST glass standards, will be performed in the future. Preliminary results with shorter laser wavelengths, especially in the UV range, show that these calibration factors are closer to 1 in that case.

With the elemental abundance measurements shown in Fig. 3a dynamic range in excess of 6 decades is demonstrated for our lander LMS instrument. Therefore, for minerals where Pb is in the ppm range in situ age determination via ^{207}Pb/^{206}Pb system, albeit with limited accuracy, becomes possible with such an instrument, which nevertheless is of great value in planetary science(Swindle, et al., 1995).In a recent study with the LMS instrument using Pb bearing samples we found that the Pb isotope rations can be established with an accuracy between 0.1 and 10%, for a Pb abundance in the sample between 100% and few ppm, respectively (Riedo, et al., 2012). In addition to the LMS capability of an accurate Pb isotopic measurement one will need a microscopic system to identify the uranium-rich phase of the mineral for the age determination.

ROVER LMS

The instrument for the rover (the rover LMS) has the advantage that the mobility of the rover possibly gives access to a larger variety of samples. Since resources are typically much smaller on a rover compared to a lander, a rover LMS needs to be much more economic in using resources.

The rover LMS is also a TOF-type instrument, uses also a microchip laser system, but is of substantially smaller size. We estimate that a flight instrument would have a mass of 280 g (including laser and all electronics) and a total volume of $70 \times 40 \times 30$ mm^3 including all electronics. For full operation only 3 W power will be needed making use of local energy storage to accommodate the short-term power needs of the laser system.

Because of the limited space available, a novel combination of an electrostatic analyser and grid-less reflectron was used to fold the time-of-flight path two times to make it long enough for sufficient mass analysis (Rohner, et al., 2004). The prototype instrument has demonstrated a mass resolution $m/\Delta m$ in excess of 180 (FWHM) and a predicted dynamic range of better than five orders of magnitude. The ion-optical system itself has a mass resolution of 400, as determined from single shot mass spectra, which is in good agreement with the ion-optical design. Again, the major Cr and Fe isotope ratios were measured with this instrument and accuracies at the % level were achieved (Rohner, et al., 2004). As with all time-of-flight instruments, covering a large mass range is not a problem here and elements from hydrogen up uranium have been detected with this instrument. When aiming for the detection of chemical compounds of higher mass we have to improve the mass resolution during routine

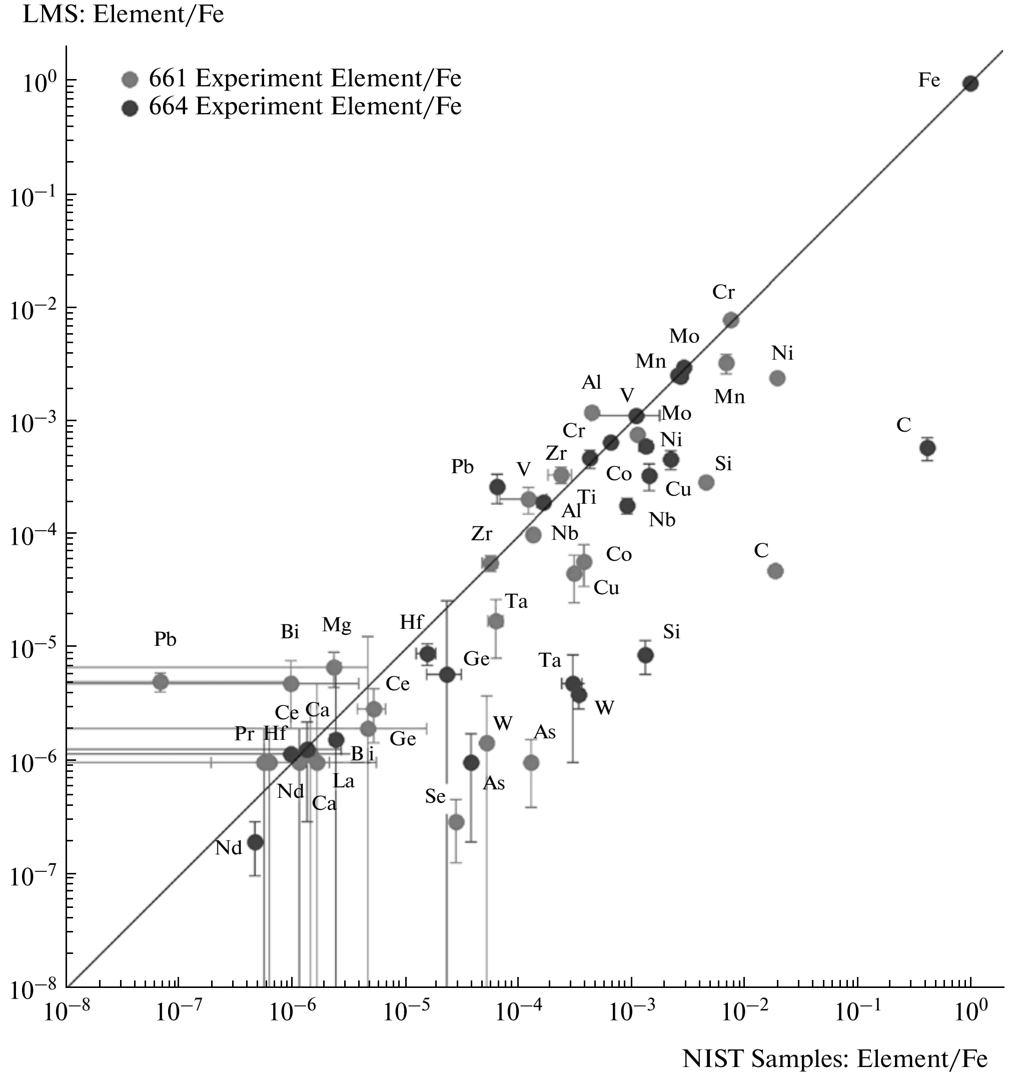

Fig. 3. Comparison of the elemental abundances measured with the LMS instrument with the abundances given by NIST for two stainless steel samples SRM 661 and SRM 664.

operations to the single-shot value, which is close to the theoretical limit of an instrument of that size.

Figure 4 shows the prototype of the rover LMS consisting of three printed circuit boards (PCB). The top board contains the actual mass spectrometer and laser system. The entrance to the LMS is the small hole in the vertical plate of the ion optics, which is also where the laser comes out. The sample is placed directly in front of this hole. The middle PCB contains the laser electronics, and the bottom board the high voltage power supplies.

THE LASMA INSTRUMENT

The LASMA instrument is a laser ablation mass spectrometer for planetary research, and its most recent realisations is for the Phobos-Soil mission(Managadze, et al., 2010), which is scheduled for launch in November 2011 (Zelenyi, et al., 2010). LASMA is a typical lander LMS and is based on an earlier development (Managadze, 1992; Managadze and Managadze, 1999). In this instrument a 7 ns laser pulse with 16 mJ power from a flash-lamp pumped Nd:YAG laser (wavelength 1064 nm) is used, which is focussed to a spot of ∅50 μm on the sample surface. Since the laser repetition rate has to be kept very low (maximum repetition rate of 0.1 Hz) to stay within the power limits of the Phobos-Soil spacecraft, spectra are recorded with a high-dynamic range detector and matching signal acquisition system. For each individual laser shot the recorded spectrum is transmitted to Earth. The flight instrument has overall dimensions of 220 × 110 × 260 mm^3, weighs about 2.6 kg, and is mounted on the outside wall of the lander. A picture of the integrated LASMA instrument is shown in Fig. 5. An articulated arm will collect surface soil samples

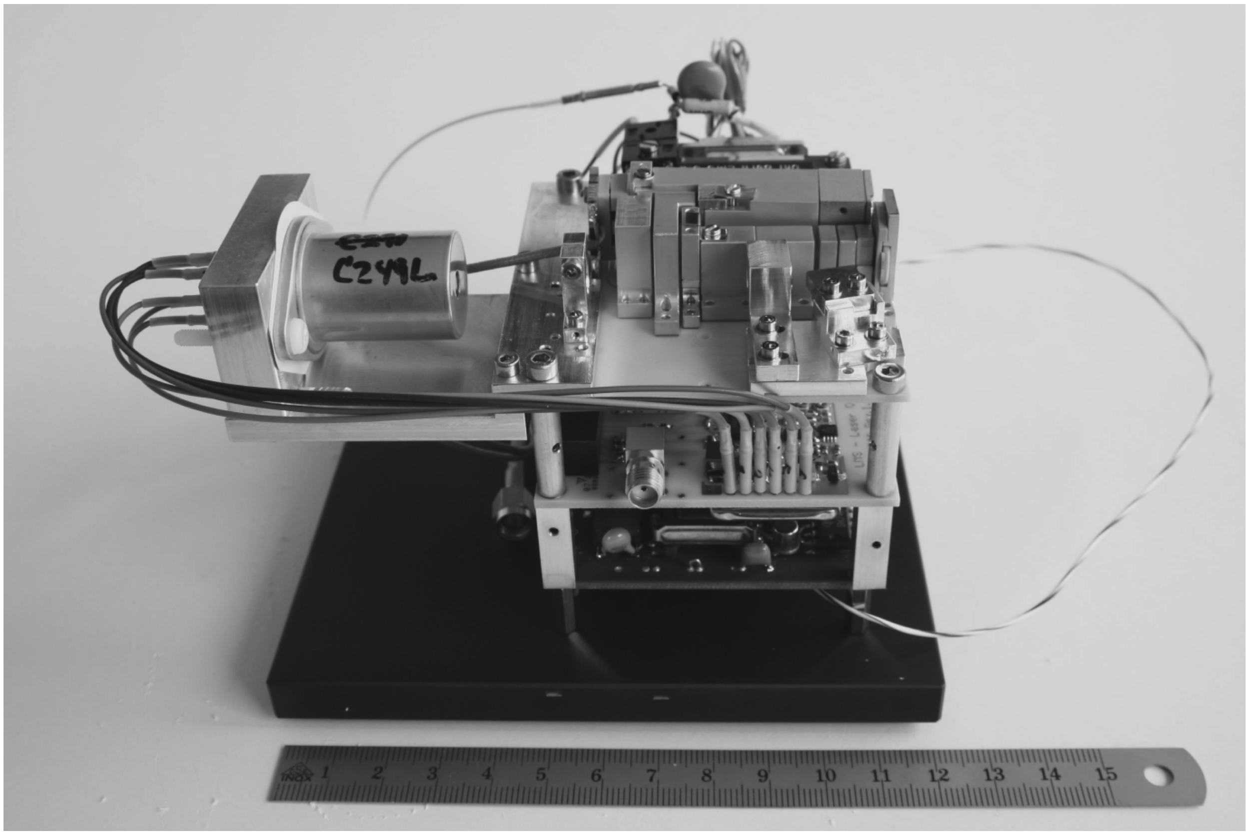

Fig. 4. Rover-LMS prototype instrument (Rohner et al., 2004) built onto a printed circuit board (top board), together with laser and temperature control board (middle board) and the high-voltage supply board (bottom board). The sample inlet is a small hole on the centre of the entrance electrode (vertical golden plate at the right edge) of the TOF structure, which is on the top board. The micro-chip laser is on the right, with the laser optics in the foreground of the top board.

from the vicinity of the landing site and deliver these to the sample carousel of LASMA, which can accommodate up to 14 samples.

LASMA can record mass spectra in the mass range from 1 to 250 amu, with mass resolutions of $m/\Delta m \approx 380$ (FWHM). Figure 6 shows a mass spectrum from the early testing of the LASMA flight model (FM) instrument before instrument optimisation took place. The mass spectrum is from a Ti-W alloy sample that is intended for the calibration of the mass scale of the instrument, and which is also used as reference sample in the LASMA instrument to evaluate the in-flight performance. As can be seen from Figure 6 the mass scale can be established with good accuracy over the whole mass range of LASMA. The Ti-W alloy sample is a mechanically robust sample with selected elements to cover most of the LASMA mass range and which will not degrade upon prolonged laser irradiation. Themass spectrumshown in Figure 6 is recorded for a single laser shot, however, for routine elemental and isotopic analysis several mass spectra of the same sample will be co-added in increase signal-to noise ratio and dynamic range, and to reduce shot-to-shot variations. Individual elements are easily identified in the single-shot spectrum, and isotope patterns are resolved for the major elements (see inserts in Figure 6 showing Ti and W isotope patters). The detection efficiency for the elements is reasonably constant allowing for quantitative elemental analysis of solid surfaces. However, the elemental abundances in these samples cannot directly be read off the recorded mass spectra, but have to be corrected by Relative Sensitivity Coefficients (RSC) to derive a quantitative elemental analysis of the investigated sample (e.g. Dietze and Becker, 1993; Becker and Dietze, 1998; Tulej, et al., 2011; 2012). Elements such as alkali metals or earth-alkaline metals give larger signals (i.e., low RSC values); elements like oxygen or carbon give rather low signals (i.e, large RSC values) using infra-red lasers (Tulej, et al., 2011). Although the oxygen detection efficiency is rather low in such laser ablation instruments, the oxygen content in a mineral sample is quite large, thus oxygen can be measured without problems in such samples (Tulej, et al., 2011; 2012), but cannot be detected by X-ray fluorescence (Foley, et al., 2003). The RSCs for LASMA will be derived from many such mass spectra for different sample classes. Based on earlier realisation of this instrument (Managadze, et al., 2010) it is expected that an accuracy of elemental composition measurement of about 10% will be

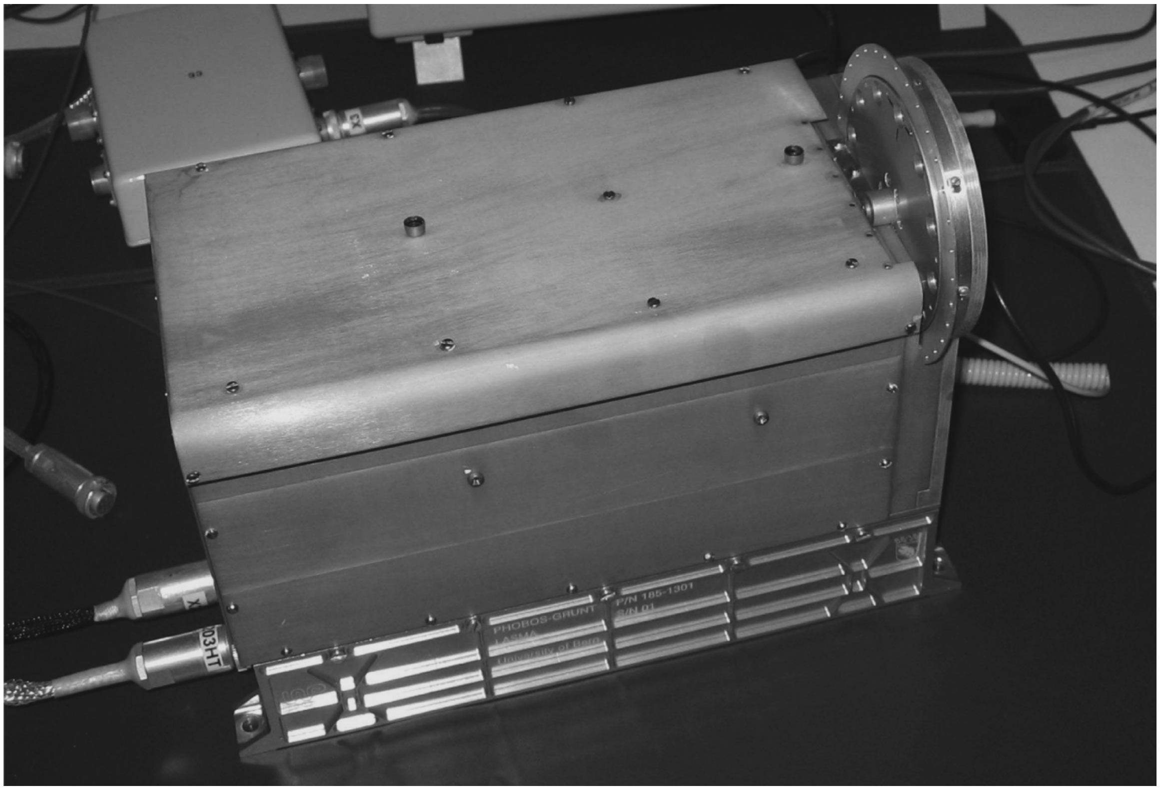

Fig. 5. Integrated LASMA instrument. The analyser is the yellowish structure on top, with the sample carousel on the right; the electronic box is the silvery structure on the bottom with the connectors to the spacecraft (power and digital) on the left (Managadze et al., 2010).

achieved, and the accuracy of the isotope measurement is expected to be about 1%. The LASMA instrument has been selected for the scientific payload of the Luna-Resurs and Luna-Glob missions of Roskosmos. LASMA will analyse the composition of the lunar soil that will be sampled in the vicinity of the lunar poles.

CONCLUSIONS

Exploration plans in planetary research of several space agencies consider landing spacecraft for future missions, because instruments operating on a planetary surface can answer complementary and ground-truth set of scientific questions than can instruments in orbit. There have been successful landings of spacecraft in the past, and more landers are foreseen for the Moon, for Mars and its moons, Venus, asteroids, and possibly even for some of the Jovian moons.

Naturally, it is considered also to bring samples to Earth for detailed investigations in highly specialised laboratories. A mass spectrometer on a landed spacecraft can assist in the sample selection in a sample-return mission, and it can provide the mineralogical context of the sample collection site. In addition to in situ composition investigations of surface material, a sensitive mass spectrometer can identify possible toxic soils on Mars for manned Mars exploration.

Bringing a sample to Earth is still is a major technological challenge, with high mission risks particularly in the entry of the return spacecraft in the Earth's atmosphere. It is unlikely to be realised for planetary objects at and beyond Jupiter's orbit. More realistically, in situ instrumentation is the only means to study the surfaces of far away planetary objects. Given the resources available on landed spacecraft mass spectrometers, as well as any other instrument, will have to be highly miniaturised.

The P-BACE type mass spectrometer presented here has a significantly better performance (mass resolution, mass range, sensitivity) and uses lower resources than the Ion and Neutral Gas Mass spectrometer (INMS) flown on Cassini (Waite, et al., 2004), which is based on a much earlier design (Kasprzak, et al., 1996).

The LASMA instrument on Phobos-Soil is the first instrument miniaturised laser mass spectrometer to be used on a landed spacecraft, which will operate on the surface of a planetary body. The LASMA instrument is also foreseen for the Luna-Resurs and Luna-Glob missions to investigate the composition of soils at the lunar poles. A laser desorption mass spectrometer is considered to be part of the Martian Organic Molecule Analyser (MOMA) to be part of the ExoMars Pasteur payload (Neumann, et al., 2009). Once these

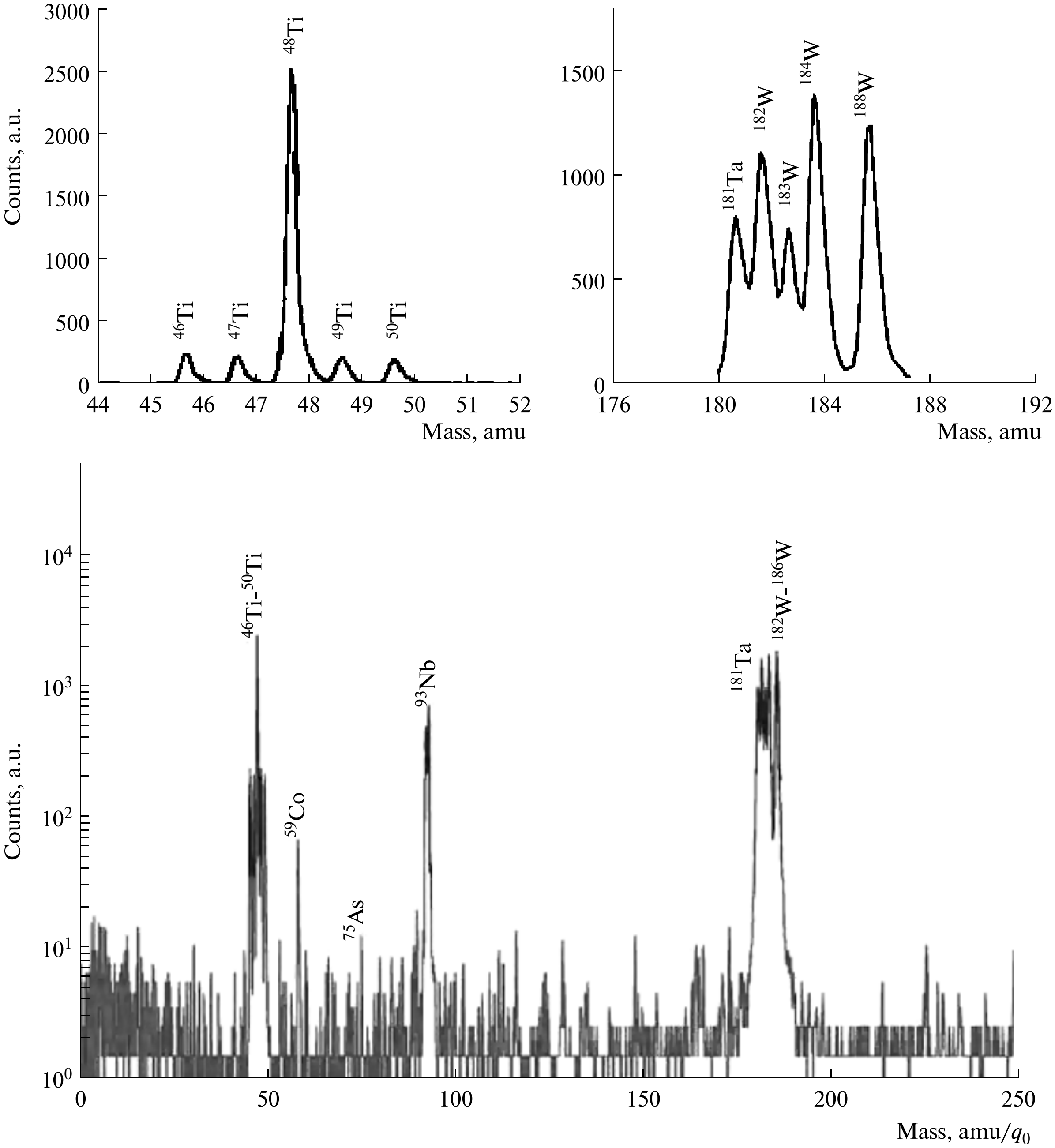

Fig. 6. Mass spectrum from the calibration campaign of the LASMA FM model. Main panel: Mass spectrum from a Ti-W alloy used as in-flight calibration sample; Inserts: Details of the spectrum showing isotopes of Ti and isotopes of Ta/W group.

instruments are in operation on the surface of the intended planetary object, we will have access to much better data sets of surface composition than are available at present.

The present capabilities of the newest generation of LMS instruments, like the lander LMS discussed above, allow for trace element detection at the ppm level and below, and further improvements are expected. This detection level allows for the crude determination of surface ages by Pb/Pb or U/Pb measurements. Even if the uncertainty in the age determinations is 10–20%, it would be significant scientific improvement. Alternatively, or in addition, also in situ K/Ar dating might become feasible in planetary science, by combining measurements from an evolved gas instrument and a LMS instrument, i.e., performing the Ar isotope measurements with the GC-MS and inferring the ^{40}K abundance from ^{39}K and ^{41}K measurements of the LMS instrument. K-Ar dating has been discussed in detail for in situ dating on the Martian surface (Bogard, 2009). For comparison, absolute chronologies of Mars surface elements based on the lunar cratering flux gives ages that vary by as much as 2×10^9 years for some surfaces (Strom, et al., 1992; Tanaka, et al., 1992), thus even crude in situ surface age determinations will improve our knowledge of the absolute chronology of Moon, Mars and other planetary bodies.

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