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On the possible in situ elemental analysis of small bodies with laser ablation TOF-MS

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Abstract

An analysis is presented of the potential application of laser ablation time-of-flight mass spectrometry (LA-TOF-MS) to the study of small bodies on in situ and sample return missions. LA-TOF-MS provides the significant advantages of high-quality, low-ambiguity data, no requirement of sample contact or preparation, rapid analysis, and local probe capability. The ability to address particular scientific goals on a given mission depends strongly on obtaining reproducible instrument- and sample-dependent fractionation factors for heterogeneous samples in various operating conditions. LA-TOF-MS analyses of basalt and mineral separate standards, in both powdered and compressed forms, have been used to establish an understanding of elemental fractionation in the mass range from C to Zn and selected higher-mass elements. Results of a preliminary calibration applied to the bulk analysis of carbonaceous meteorites suggests that sufficient precision is obtained from replicate averaging of spectra to differentiate among some sub-classes. Complementary point-by-point LA analyses of such samples could also provide powerful diagnostic information for mineralogy.

Keywords: Mass spectrometry; Small bodies; Asteroids; Comets; Time-of-flight; Laser ablation; In situ; Elemental composition; Chemical analysis; Ionization; Meteorities; Allende; ALH83100; Planetary moons

1. Introduction

The study of small bodies, including asteroids, comets, planetary satellites, etc., is of immense importance to planetary science. While the planets themselves comprise the vast majority of solid matter orbiting the Sun, small bodies hold critical clues to understanding the origin and evolution of that matter, clues which may not be available through study of the planets alone. Many small bodies remain to a large extent unchanged since the very early stages of the solar system. Asteroids and comets represent matter that was not incorporated into planets during condensation of the nebula, and as such they are prime targets for the study of this period. Early solar system processes, such as differentiation, chemical fractionation, thermal metamorphism, aqueous alteration, and impact processing, were either significant, cut short, or even nonexistent on various small bodies. Analyzing the compositions of both primitive and differentiated small bodies helps elucidate the effect of these processes on early planetary evolution in general. Small bodies are also the dominant source of Earth impactors. During heavy bombardment, asteroid impacts helped set the basic geochemistry and geology of Earth by delivering materials and impact processing the crust. The composition of near-Earth objects may therefore assist our search for how Earth has been affected, even defined, by their presence, and also for how Mars and Venus have evolved differently despite forming in a similar small body environment.

Enormous advances in small body research have resulted from studies of meteorites and interplanetary

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dust particles (IDPs), remote spectroscopy, and reconnaissance-type space missions (e.g., Binzel et al., 1989; Huebner, 1990; Veverka et al., 1994; Russell, 1997; Thomas et al., 1997; Bottke et al., 2002). A number of key facts have emerged: (1) meteorites derive originally from main belt asteroids undergoing impacts and delivering fragments into Earth-crossing orbits fairly quickly, (2) differentiation, so characteristic of planets and their larger satellites, may only have occurred globally on a tiny minority of asteroids, limited by the scales over which heating by decay of radiogenic isotopes such as ^{26}Al could occur, (3) the space environment, marked by unending solar wind, dust, and micrometeorite impact fluxes, has a strong effect on the spectral properties of small bodies, possibly disguising the true extent of their compositional heterogeneity, (4) our only present source of cometary material may be the influx of IDPs, and that these suggest a kinship between comets and the outermost low-albedo asteroidal bodies. These discoveries have led to additional questions that will require in situ and sample return missions, such as: what is the relationship between spectroscopic and meteoritic types? Where are the mantle fragments of differentiated but long-disrupted parent bodies? What is the internal structure of primitive, low-density asteroids? What balance of volatile and refractory compounds characterizes cometary nuclei?

In situ elemental analyses of small bodies could directly address these questions. Simple "presence or absence" data, spatially resolved and measured to low levels of detection (LODs), may indicate differentiation, space weathering, or other processing; provide complementary or verification data for probes of mineralogy; and suggest locations for more detailed analyses such as searches for trace organic compounds. More quantitative elemental compositions, particularly with the same spatial resolution and LOD capabilities, would begin to address the "ground truth" requirements of current research. These include interpreting observational data on the body in question, generalizing the results to reflectance or emission spectra of whole classes of bodies, and possibly linking those bodies to meteorites and IDPs (Burbine et al., 2002). Identifying asteroidal parent bodies of well-studied meteorites is a particularly constructive direction. It helps calibrate and generalize remote sensing data, which may exhibit only subtle variations in measured composition from body to body due to observational constraints. It also helps clarify the situations when an observed asteroid is not represented in the finely graded meteorite taxonomy, which is biased by delivery, survival, and recovery effects.

Here we present a study of one technique, laser ablation time-of-flight mass spectrometry (LA-TOF-MS), that could potentially contribute to future in situ small body missions through its ability to analyze chemical composition in a wide variety of materials. Mass spectrometers are highly desirable on science payloads in general because of their broad-band and high sensitivity detection capabilities, valuable for surveying unknown samples. Mass spectrometers have been included on a wide range of small body missions such as VeGa, Giotto, Phobos, Stardust, CONTOUR, and Rosetta. A number of these are of the time-of-flight (TOF) type (PUMA, PIA, LIMA-D, CIDA, Rosina, COSIMA, and COSAC), which can rapidly detect elements and molecules out to quite high mass-to-charge (m/z) ratios. TOF-MS instruments can be miniaturized to a remarkable degree, as compared to the sizes of typical laboratory mass spectrometers, while maintaining high sensitivity and mass resolution (Cotter, 1997). The use of pulsed lasers to create the gas phase ions required by mass spectrometers is a well-known sample introduction technique for biochemical and geochemical analysis. For application in situ, pulsed lasers offer a powerful capability for local analysis of solid surfaces with no sample contact or preparation. In the high to ultra-high vacuum conditions on the surfaces of small bodies, undisturbed samples may be laser-evaporated from a stand-off position, with the prompt ions travelling unhindered into the mass spectrometer (De Young and Situ, 1994a,b, 1995; Managadze and Shutyaev, 1993). This type of pulsed, pristine sampling couples naturally to a TOF-MS, which measures the masses of ions by the time it takes for them to travel from the surface to the detector. It also reduces risks associated with mechanically acquiring and preparing samples, and allows the mass spectrometer to be positioned at multiple samples of interest if there is an articulated robot arm or similar facility.

This article focuses on a particular LA-TOF-MS that has been optimized for elemental and isotopic analyses on airless bodies (Brinckerhoff et al., 2000). Variations of this type of instrument (Cornish et al., 2000), as well as new multi-MS instrument suite designs (Brinckerhoff et al. 2003a; Mahaffy et al., 2004), that permit both organic/molecular and geochemical analyses, are also under development in parallel. Such enhanced or hybrid designs are of particular interest for use at Mars, where long-duration surface operations and sophisticated sample preparation systems are likely to be available (Brinckerhoff et al., 2003a). A somewhat similar, miniaturized LA-TOF-MS device has also recently been developed for a potential rover at Mercury or Mars (Rohner et al., 2003, 2004). The present instrument and its analytical protocols are reviewed in the next section, followed by a summary of elemental analysis data on a number of sample types. The application of the technique to likely in situ objectives is then discussed in the context of its performance on standard and meteorite samples.