EPSC Abstracts Vol. 8, EPSC2013-360, 2013 European Planetary Science Congress 2013 © Author(s) 2013



# Isotopic analysis of planetary solids

M. Tulej, A. Riedo, M. Neuland, S. Meyer, and P. Wurz

Physics Institute, University of Bern, Switzerland (marek.tulej@space.unibe.ch / Fax: +41-31-631 44 05)

### Abstract

Isotopic analysis of planetary surfaces is of considerable interest for planetology. Studies of isotope composition can deliver information on radio-isotope chronology of planetary soil/regolith, an insight to processes that altered planetary surface (space weathering) or on possible biogenic processes that occurred or still occur on the planet. Mass spectrometry is a well-suited method that delivers accurate and precise isotope composition. Among other instruments (LAZMA and LAMS), the miniature laser ablation/ionisation mass analyser, LMS developed in Bern for in situ space research can be used to measure the elemental and isotopic composition of planetary solids. LMS support mass spectrometric investigation with a mass resolution of m/ $\Delta$ m $\approx$ 500-1500, dynamic range of at least 8 decades and detection sensitivity of ~10 ppb. Current studies of various solid materials and standard reference materials show that isotope composition can be conducted with an accuracy and precision at per mill level if the isotope concentration exceeds 10-100 ppm. Implications of the studies for in situ application are discussed.

## **1. Introduction**

Development of sensitive space instrumentation for in situ investigation of elemental and isotopic composition of planetary surface materials are of considerable interest to current space research. Among a few instruments which are developed for specific application such dating of planetary materials via Sr-Rb or K-Ar isotope geochronology, laser ablation/ionisation instruments including LAZMA (space instrument), LAMS, and LMS are to date the only mass spectrometric instrument that can measure sensitively isotope composition of most of chemical elements [4].

Isotopes are robust tracers of element formation processes in stars. Contrary to elemental composition of planetary solids, changes of isotopic ratios are relatively small over the time of planetary evolution. A few processes that can modify isotope composition include natural decay of radiogenic elements, nuclear reactions induced by interaction with Cosmic Rays, and chemical or bio-chemical reactions. Sufficiently accurate and precise isotope compositional analyses of solid samples are often necessary to obtain meaningful results and deliver accurate dating of planetary solids, insights to space weathering or conclude on past or present biological activities on planetary surface [1].

A number of mass spectrometric methods (TIMS, LA-ICP-MS, and SIMS) are applied in laboratory for measuring accurate and precise isotope composition of solid materials. Recent studies show that laser ablation/ionisation mass spectrometry can be also highly competitive to these well-established methods[2, 3]. We will discuss perspectives for the isotope analysis in space and demonstrate current performance of the LMS laser mass spectrometer.

## 2. Experimental

The LMS instrument uses a laser ablation ion source to vaporise, atomise and ionise a solid sample material and a reflectron-type time-of-flight mass spectrometer (R-TOF MS) to perform mass spectrometric analyses [2, 5]. The surface material is removed repeatedly by an intense pulsed laser radiation that is focused to a spot of  $\emptyset$ ~10-40 µm. With repetition rate of laser of 1-10 kHz highly sensitive and accurate elemental and isotope analyses can be performed within 5-50 seconds. High performance ion detector and acquisition system support dynamic range of 10<sup>8</sup> and mass spectra can be measured with a mass resolution (m/ $\Delta$ m) of ~ 600-1500 [2, 5]. The LMS instrument supports routinely highly sensitive analysis with the current detection limits ~10 ppb [2]. Recent studies demonstrate also instrument capabilities for chemical mapping of a surface by LMS [6].

## 3. Isotopic analysis

An appropriate control of experimental conditions (choice and details of operation of laser ablation ion source, ion confinement, mass selection and ion detection) is necessary for obtaining analytical capabilities of LMS instrument. These conditions are established by performing a number of calibrations including measurements of samples of standard reference materials (SRM). The calibration studies

Table 1: Relative sensitivity coefficients (RSC) determined from mass spectrometric analysis. The accuracy of RSC determination does not exceed 15% (SRM 665).

Element (IP[eV])	RSC: ns-laser	RSC: fs-laser
C: 11.26	0.0002	0.90
Si: 8.151	0.02	1.04
P: 10.486	0.03	1.10
S: 10.316	0.05	1.16
V: 6.82	1.40	0.90

yield relative sensitivity factors, RSC (a deviation between measured and quoted element concentration) which are used to correct the measurements of a sample with unknown elemental composition. If



Figure 1: Accuracy of the isotope composition determination as a function of isotope concentration.

The RSCs are close to unity for all elements indicating that efficiency of ion production and detection are optimal for the accurate quantitative analysis and the chemical can be performed without using additional standards. The choice of a laser ablation ion source is of primary importance for achieving stoichiometric ion production and the quantitative performance of the instrument. Our current studies show that a fs-laser ablation ion source is highly preferable over ns-laser sources. An efficiency of ion formation and detection using fs ablation ion source is observed to be similar for most of chemical elements. In contrary, a ns-laser ablation ion source is found to have significantly lower efficiencies for ion formation of non-metallic elements (Table 1) [2, 4]. Also accuracy and precision of isotope analysis can be improved considerably by applying fs-laser ablation ion source. Current studies shows that LMS can be used to deliver highly accurate and precise measurements of isotope composition. For isotope concentration larger than 50-100 ppm, these values can be determined at per mill level (Fig.1). With an increase of the instrumental dynamic range and sensitivity of measurements, also the accuracy and precision of the isotope measurements is expected to improve, accordingly [4].

#### 4. Summary and Conclusions

Instrumental performance of LMS is a subject of continues improvement in our lab. The current studies show that a fs-laser ablation ion source is very promising for further progress regarding elemental and isotopic analysis in space research and the development of standard-less instruments. can be advantageous over sources that use ns-laser. By coupling of this source with LMS an increased number of elements can be now detected with high sensitivity (H, O, N, Cl and other halogenic elements). The current studies show that the instrumental performance is sufficiently high to investigate various isotope fractionation effects (Pb-Pb isotope geochronology, C, S biomarkers, sensitive isotope analysis of upper most surface composition by space weathering).

#### Acknowledgements

Authors gratefully acknowledge the financial support by the Swiss National Science Foundation.

#### References

- Wurz, P. Abplanalp, D. Tulej, M. Iakovleva, Fernandes, V.A. Chumikov, A. Managadze, G., 2012, *Sol. Sys. Res.* 46, 408-422.
- [2] Riedo, A. Bieler, A. Neuland, M. Tulej M. Wurz P., 2013, J. Mass. Spec., 48, i. doi: 10.1002/jms.3157.
- [3] Tulej, M. Iakovleva, M. Leya, I. Wurz, P., 2011, Anal. Bioanal. Chem., 399, 2185–2200,
- [4] Riedo A. et al., Planet. Sp. Sci., 2012, submitted.
- [5] Riedo, A. et al., 2013, JAAS, accepted.
- [6] Neuland, M. et al., 2012, Planet. Sp. Sci., accepted.