HEMS WOKRSHOP 2013

A miniature LIMS system for accurate isotope composition measurements in situ planetary surfaces

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Introduction
Isotopes in nature

- Isotope abundances are fingerprints of the processes in which isotopes were produced or their ratio modified
  - Isotope compositions of some elements: stellar-thermometers/stellar dosimeters (highlighting the birth of the elements)
  - Short lived radioactive isotopes: illuminators of clouds of SN ejecta
  - Long lived radioactive isotopes: clocks for the time scale of nucleosynthesis
- Variations in stable isotope abundances are due to radioactive decay, nuclear reactions and fractionation
  - Constrain the time of events (radio-isotope chronology)
  - Fractionation: variations of isotope composition help to understand the underlying chemical and physical processes
- **Isotope abundance ratios are much less disturbed than element abundances and are robust tracers of early events that set their values**

Introduction
Isotopes with relevance to space research

- **Radioactive decay: "dating"**
  - radio-isotope chronology methods are considered currently for in situ planetary surfaces application (Rb-Sr, K-Ar; Pb-Pb, U-Pb)
- **Isotope fractionation**: interstellar and planetary processes
  - D/H: presolar conditions
  - ^{14,15}N, ^{16,17,18}O: heterogeneity
  - ^{12,13}C, ^{32,33,34}S: **bio-relevant**
- **Mass spectrometers are required**
  - High accuracy and precision
  - High sensitivity
  - Sufficient high mass resolution
  - Sufficiently high spatial resolution (mineralogical context)

Introduction
Current projects for in situ isotope measurements in planetary solids

- **KArLE**: geochronology by K-Ar dating method
  (Cohen, in 43th Lunar Planet. Sci. Conf., 2012, #1267)
- **LDRIMS**: geochronology by Rb-Sr dating method
  (Anderson et al., IEEE, 2013)
- **LAMS**: element and isotope measurements
  (Brinckerhoff et al., Rev. Sci. Instrum., 2000)
- **LAZMA**: element and isotope measurements
  (Managadze et. al., Sol. Sys. Res., 2010)
- **LMS: elements and isotopes**
  (Rohner et al., Meas. Tech., 2003; A. Riedo et al., J. Mass Spectrom., 2013, 48, 1-15, Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256)

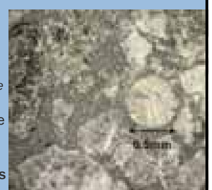
(LAZMA, LMS:)
- Dating (Pb-Pb, U-Pb)
- Fractionations
- Trace elements

Introduction
Capabilities of in situ measurements in space research using LMS

> **In-situ measurements**

— **Complete elemental and isotopic composition measurements (ablation mode)**
- Normative mineralogy (e.g., single grain mineralogy)
- Chemical maps of heterogeneous material surface (e.g., composition of bulk vs. individual surface components) (*Neuland et al., Planet. Space Sci., 2013, accepted*)
- Depth profiling analysis (e.g., weathered surface vs. interior composition)
- **Element and isotope fractionations**
- **Radio-isotope chronology of planetary solids** (e.g. *Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256, Riedo et al., Planet. Space Sci., 2013, in press*)

— **Molecular composition (desorption mode)**

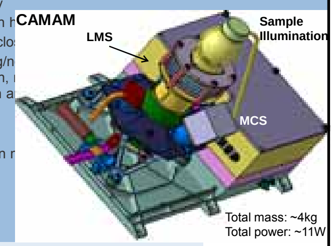


Introduction
LIMS for in-situ measurements

> Advances in last decades (modeling tools, fast electronics and data acquisition, miniaturized laser system)

> Miniaturized laser-ablation mass spectrometer (LA-MS)
- tens of ppb detection sensitivity
- measurements on isotopes with h
- relative sensitivity coefficients clo
- sample consumption in the ~ fg/n
- no sample preparation, no oven,
- straightforward data acquisition a

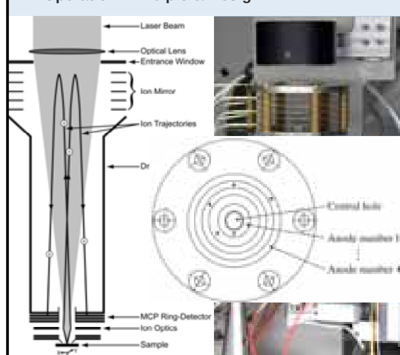
> Current space instruments
- LAZMA (Phobos-Grunt sample return r
- LMS on CAMAM assembly



Miniaturised LIMS (LMS)
Instrumental Overview

(*Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256; A. Riedo et al., J. Mass Spectrom., 2013, 48, 1-15*)

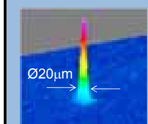
Miniaturised LIMS (LMS)
Operation Principle & Design



- 160mm x 60mm
- Flight model ~ 1.5kg
  Power consumption: ~4W
- Voltages:
  Ion optics/Detector: ~2 kV
- Design based on Simion-simulations
- Ring-anode detector
- 2 x 8-bit high speed digitizer with on-board processing ADC cards, each with 2 channels

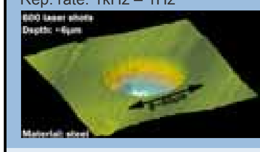
Laser ablation / ionisation source Reflectron-type TOF analyser

Ion source: laser



ns-laser
Nd:YAG, λ=266nm
Pulse duration: 3ns
Rep. rate: 20Hz
< ~1GW/cm^2

fs-laser: λ=775nm; pulse length: 190fs;
Rep. rate: 1kHz – 1Hz



R-TOF characteristics

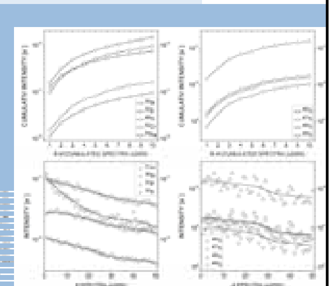
- Mass calibration: $m(t) = k_0(t-t_0)^2$
- Mass calibration accuracy: Δm/m ~10^{-4}
- Spectra collected within ~13 µs
- Mass resolution: 500-1000
- Dynamic range: 10^6/channel and > 10^8 by combined detection with various rings (channels at different gains)
- Metallic and non-metallic elements down to 10ppb can be detected

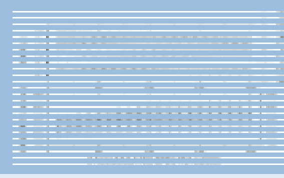
(*Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256; Riedo et al., J. Mass Spectrom., 2013, 48, 1-15*)

Quantitative elemental analysis (temporal control)

Temporal control

- Individual spectra analysis
- Cumulative analysis / relative
- Mass resolution (m/Δm)
- SNR
- etc.

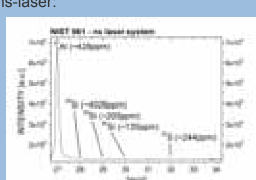




(*Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256*)

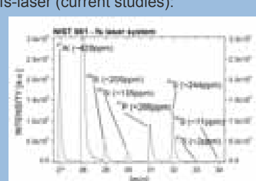
Quantitative elemental analysis (ns-laser vs fs-laser)

NIST vs. LMS measurements
ns-laser:



RSC in the range ~ 10^{-4} - 10
e.g. C(2·10^{-4}), Si(2·10^{-2}), P(2.5·10^{-2}), S(4.5·10^{-2}), Ti(2)
N = 60'000 waveforms accumulated
I ~0.5 GW/cm^2
Accuracy: <10%

NIST vs. LMS measurements
fs-laser (current studies):



RSC close to one
→ C(0.90), Si(1.04), P(1.10), S(1.16), Ti(0.92)
N = 100'000 waveforms accumulated
I ~ 2230 GW/cm^2

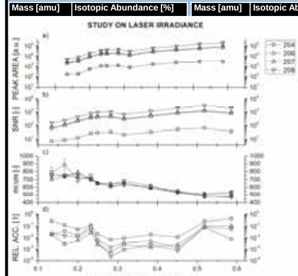
(*Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256*)

Isotope measurements and accuracy (ns)
Case study Pb

> NIST SRM 981 (standard lead sample)

Mass [amu]	Isotopic Abundance [%]	Mass [amu]	Isotopic Abundance [%]	Accuracy [%]
			352 ± 0.0033	0.68
			092 ± 0.0308	0.15
			959 ± 0.0289	0.06
			597 ± 0.0743	0.02

abs(Ref. – Meas.)/Ref.



Investigations on:

- Number of accumulated waveforms (crater depths, mass resolution)
- Analysis method (fit models or direct integration)
- Laser fluence dependency

(*Riedo et al., Planet. Space Sci., 2013, in press*)

Isotope measurements and accuracy (ns)

LMS accuracy referenced to TIMS data

- Galena samples from different mines!

Kengere, Katagne, Belgian Congo

Mass [amu]	Isotopic Abundance [%]	Accuracy [%]
204	1.3768 ± 0.006	0.24
206	24.965 ± 0.011	0.43
207	21.568 ± 0.010	0.19
208	52.090 ± 0.027	0.12

Dilia Mine, Kilo Moto, Belgian Congo

Mass [amu]	Isotopic Abundance [%]	Accuracy [%]
204	1.4946± 0.0006	0.52
206	23.1899 ± 0.0075	0.66
207	22.9223 ± 0.0086	0.53
208	52.393 ± 0.018	0.22

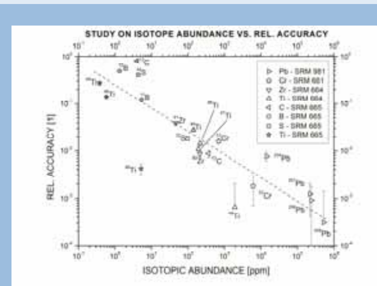
Ambatofangehana, District Ambositra, Madagascar

Mass [amu]	Isotopic Abundance [%]	Accuracy [%]
204	1.4154 ± 0.0005	0.13
206	24.4297 ± 0.0086	0.20
207	22.2584 ± 0.0093	0.18
208	51.897 ± 0.0620	0.02

- Estimated accuracy for isotope concentration of 100 ppm: ~10 ‰

(*Riedo et al., Planet. Space Sci., 2013, in press*)

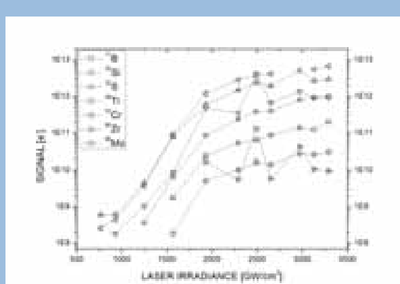
Accuracy and precision of isotope ratio measurements vs. concentration (ns)



(*Riedo et al., Planet. Space Sci., 2013, in press*)

Isotope measurements and accuracy (fs)

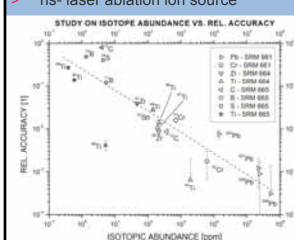
- NIST SRM 661/664/665 samples (terrestrial isotopic ratios assumed)



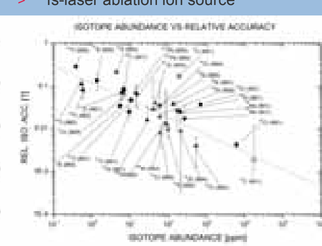
 (*Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256*)

Accuracy and precision of isotope ratio measurements vs. concentration

- ns- laser ablation ion source
- fs-laser ablation ion source



(*Riedo et al., Planet. Space Sci., 2013, in press*)



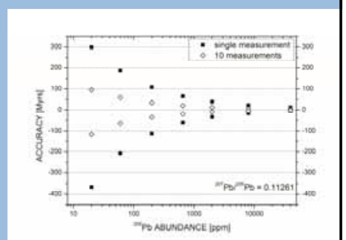
(*Riedo et al., J. Anal. At. Spectrom., 2013, 28, 1256*)

Pb-Pb radio-isotope chronology (ns)

> $^{207}Pb/^{206}Pb$ in monazite grains (Willigers et al., Geochim. Cosmochim. Acta, 66, 1051—1066, 2002)

→ **accuracy of ± 25 millions of years**

> Lunar KREEP/ zircon grains: high abundant in Pb (Nemchin et al., 2008)



(*Riedo et al., Planet. Space Sci., 2013, in press*)

Summary
Performance overview

> Isotope composition studies were performed for standard materials and natural samples
- fs-laser ion source is preferred over ns-laser ion source
  - nearly stoichiometric ion production for all elements
  - Increase sensitivity for nonmetallic elements
- Accuracy and precision of the measurements increase linearly with an increase of isotope concentrations; for isotope concentrations >100 ppm the accuracy lies in ‰ and sub-‰ range.
- Pb isotope analysis shows that the age determination by the Pb-Pb chronology can be made with accuracies ±25 My; these analyses are currently underway.
- High sensitivity in detection of elements supports isotope analysis; all light elements and their isotope including H/D, Li, B, C, N, O, Mg, Al, Si, P, S can be well studied by means of light isotope ratio fractionation.

Outlook

> fs-laser studies (parametric studies, e.g. wave length, pulse width, etc.)
> Design of a miniature fs-system for space research (fiber laser system)
> Analysis of high spatial resolution studies are currently undertaken (Ø3.5 µm, spatial resolution 30 µm)

Outlook – 2d chemical finger printing

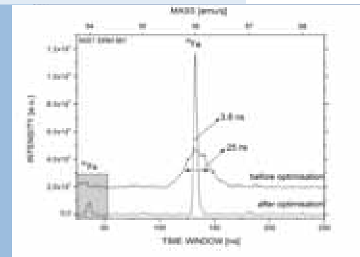
> Area of 1.5 x 1.5 mm^2 → 2’500 measured positions
> 60 k laser shots on one single surface position
> ~50h on time

Thank you for your attention!

Computer-controlled performance optimiser (voltage settings on ion optics, sample positioning (crater diameter), laser fluence)

- Performance optimizer is based on a adaptive particle swarm algorithm (APSA)
- Minimization of fitness function defined by user, e.g., -A/FWHM
- LMS: mass resolution, ion transmission, sample position, laser fluence

(A. Riedo et al., J. Mass Spectrom., 2013; A. Bieler et al., J. Mass Spectrom., 2011; T. Beck al., App. Therm. Eng., 2012)



- Mass resolution had increased from m/Δm = 122 to 743, factor of ~ 4.5!
- Intensity decreased ~ 30%

Isotope measurements and accuracy (ns)

> Galena samples (Kengere, Katagne, Belgian Congo; Dilia Mine, Kilo Moto, Belgian Congo; Ambatofangehana, District Ambositra, Madagascar)

Mass [amu]	Isotopic Abundance [%]	Accuracy [%]	Mass [amu]	Isotopic Abundance [%]	Accuracy [%]	Mass [amu]	Isotopic Abundance [%]	Accuracy [%]
204	1.3763 ± 0.0019	0.36	204	1.4947 ± 0.0019	0.40	204	1.4154 ± 0.0018	0.01
206	24.969 ± 0.035	0.40	206	23.192 ± 0.023	0.11	206	24.435 ± 0.031	0.23
207	21.571 ± 0.030	0.19	207	22.921 ± 0.025	0.52	207	22.257 ± 0.031	0.16
208	52.083 ± 0.076	0.10	208	52.392 ± 0.059	0.19	208	51.892 ± 0.064	0.04

Reference: TIMS measurements

> Allende: homogenized sample (few examples!)

Mass [amu]	Isotopic Abundance [%]	Accuracy [%]	Mass [amu]	Isotopic Abundance [%]	Accuracy [%]	Mass [amu]	Isotopic Abundance [%]	Accuracy [%]
^{24}Mg	79.15 ± 0.12	0.2	^{32}S	94.92 ± 0.82	0.1	^{52}Cr	83.73 ± 0.31	0.1
^{25}Mg	9.91 ± 0.02	0.9	^{34}S	4.32 ± 0.50	1.6	^{23}Cr	9.56 ± 0.24	0.6
^{26}Mg	10.94 ± 0.02	0.6						

Reference: I.N. Tolstikhin and J.D. Kramers, 2008; H.Y. McSween and G.R. Huss, 2010.

A. Riedo et al., PSS, 2012, sent.

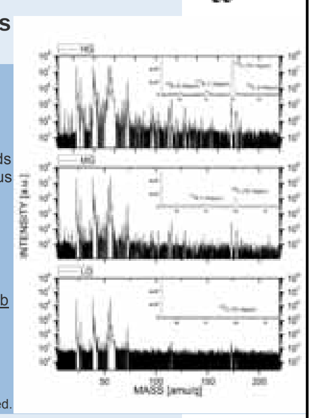
Mass spectrometric results

Dynamic Range & Sensitivity

> Spectra are acquired from three of four anode rings: LG, MG, and HG (low, medium and high gain signals)

> Dedicated measurement procedure yields dynamic range ≥10^8 by combining various channels; the most intense mass peaks are saturated in MG, HG spectra

> The sensitivity of measurements is high non-metallic elements (B, C, S, Si) can be detected down to ~ hundredths of ppb



A. Riedo et al., J. Mass Spectrom., 2012, submitted.

Measurement Results (LMS)
Elemental Measurements

> Standard samples to calibrate the system
(Semi-quantitativ analysis possible without standards at very high fluences)

> RSC (relative sensitivity coefficients) factors for unknown samples, e.g., lunar samples, meteorites, etc.

$$RSC = \frac{measured\ \ abundance}{quoted\ \ abundance}$$

> High dependency on laser fluence (< ~GW/cm^2), sample form (powder, solids), wavelength

LMS
Instrumental Overview

Laser ablation mode

- Laser irradiance: ~ 0.1–8 GW/cm^2 (hot plasma conditions)
- Singly charged elements dominate
- Abundances measured should be similar to specified

(Tulej et al., ABC, 2011)

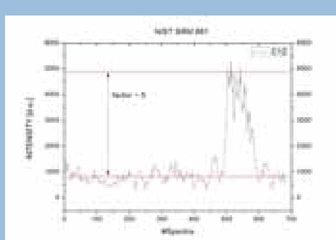
Laser desorption mode

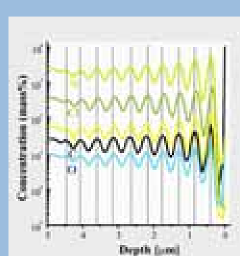
- Laser irradiance: ~ < 100 MW/cm^2
- Large molecules can be desorbed from the surface at reduced fragmentation effects

(Riedo et. al., J. Appl. Physics, 2010)

Outlook
Depth profiling

Depth profiling

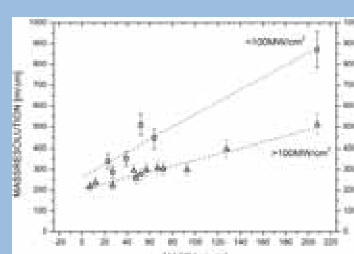




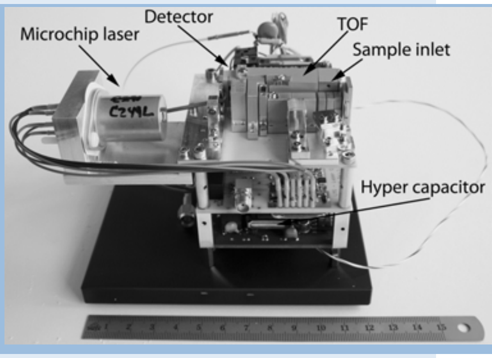
Peter Brockmann (Chem. Dep.)

Mass Resolution (ns)
Laser irradiance dependency

> A mass resolution m/Δm in the range of 500 to 900 is possible (at Pb).



LA-MS for Rover for BepicColombo



Introduction
Extraterrestrial material and in-situ measurements

> Extraterrestrial material:
- major/minor and trace elements -> origin and evolution solar system
- bio-relevant trace elements (C, S, P, …) -> astrobiology
- **isotopes (radio-isotope chronology, alteration, surface processes, etc.)**

> In-situ measurements, why?
- Complete elemental and isotopic composition
  - Normative mineralogy (e.g., grain mineralogy)
  - Chemical mapping of heterogeneous materials
  - Fractionation by major/minor/trace elements
  - Isotopic fractionation: radio-isotope chronology, bio-markers
- Molecular composition

> Currently used Instruments in space research are based typically on **remote sensing techniques** (dedicated mass range, low detection sensitivity in per mill level, lateral resolution, no isotopic composition)