2D elemental mapping of micrometeorites via LA-ICP-ToF-MS

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INTRODUCTION

Micrometeorites are tiny extraterrestrial particles, which survived atmospheric entry. They fall to Earth at a rate of 40,000 tons annually, and can be retrieved *e.g.* from the Antarctic. They represent a valuable source of information on the chemical evolution of the Solar System. The microscopic size (50-2000 µm) of micrometeorites requires the use of novel *in situ* mapping techniques of elemental analysis: with high lateral resolution, preferably non-destructive, with multi-element capabilities, and capabilitiy to provide quantitative data. Hyphenated with a low-dispersion laser ablation (LA) system, time of flight ICP-MS (ICP-ToF-MS) allows for 2D mapping with a laser repetition rate of several hundred Hz, with each laser shot recorded as a single pixel, and rapid quasi-simultaneous acquisition of almost the entire periodic table.

AIMS AND GOALS

- Evaluation of the applicability of **LA-ICP-ToF-MS method for 2D element mapping** analysis of 50-2000 µm ø cosmic spherules (CS)
- Development of a **calibration procedure** for fully quantitative mapping (using GeoReM consensus values)
- **Validation using glass reference materials** of natural composition

SAMPLES

- **Melted micrometeorites (cosmic spherules, CS)** larger than ~200µm (glassy, barred olivine, cryptocrystalline, and Ca-Al-Ti rich types)
- Collected from sedimentary traps near the Widerøefjellet (altitude ~2750m), Sør Rondane Mountains, **East Antarctica**
- Casted into epoxy mounts and polished with 4000 grit diamond paste

METHODS

- **icpTOF2R (TOFWERK) Time-of-Flight ICP-MS** unit. Quazi-simultaneous detection (ToF) of a m/z range 23 - 238 ($^{23}Na^+$ to $^{238}U^+$), base integration time 48 µs, m/z = 40 ($^{40}Ar^+$) notch-filtered
- **IRIDIA (Teledyne Photon Machines)** 193 nm ArF* laser ablation system, Cobalt™ ablation chamber, ARIS aerosol rapid introduction system. Mapping speed: 0.3 - 30 $mm^2 \cdot h^{-1}$, spot size 1x1 to 5x5 µm, laser repetition rate 100-300 Hz. Single pulse response duration ~1 ms, fluence: ~2 $J \cdot cm^{-2}$
- **HDIP** processing software for visualization, image calibration and segmentation
- Multi-point calibration using USGS and MPI-DING glass reference materials (GSE-1G, GSD-1G, BCR-2G, NKT-1G, BIR-1G, BHVO-2G, GOR132-G, GOR128-G, ML3B-G, ATHO-G, StHs6/80-G, KL2-G, T1-G)
- **GeoReM consensus values** are relied onto where certified data is missing
- Normalization of the oxides to 100 % to account for ablation yield variations

LA-ICP-ToF-MS METHOD VALIDATION

CALIBRATION

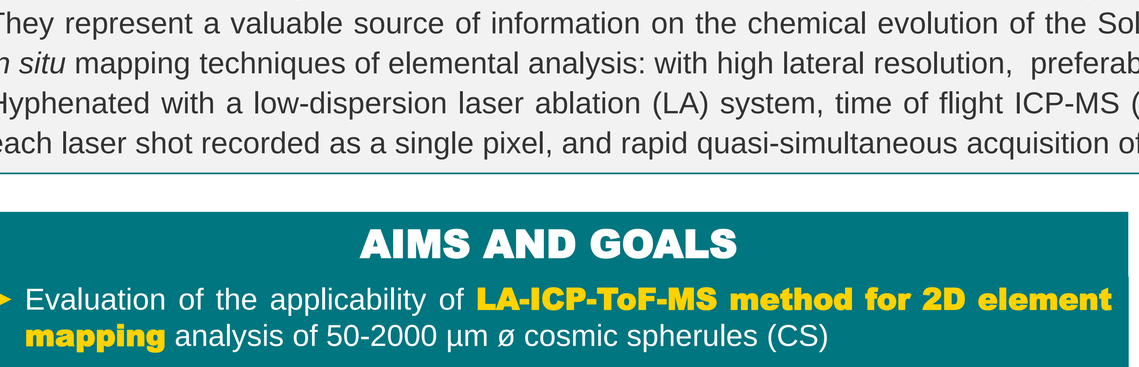


Fig.1. Calibration lines for the selected elements using LA-ICP-ToF-MS mapping

REPRODUCIBILITY

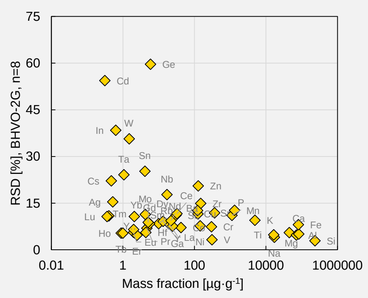


Fig. 2. Intermediate precision of the LA-ICP-ToF-MS mapping (results of USGS BHVO-2G over a period of ~1 year)

DETECTION LIMITS

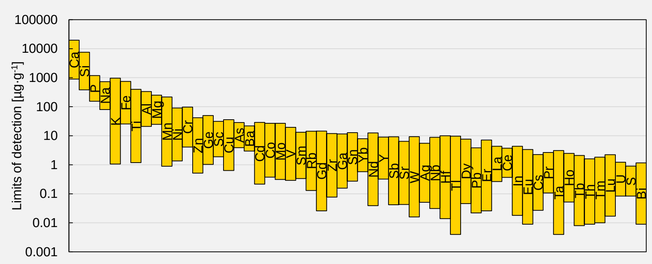


Fig. 3. Limits of detection of the LA-ICP-ToF-MS mapping for integrated areas according to the equation of Pettke *et al.*, 2012 (3x3 µm min-max range over a period of ~1 year)

ACCURACY

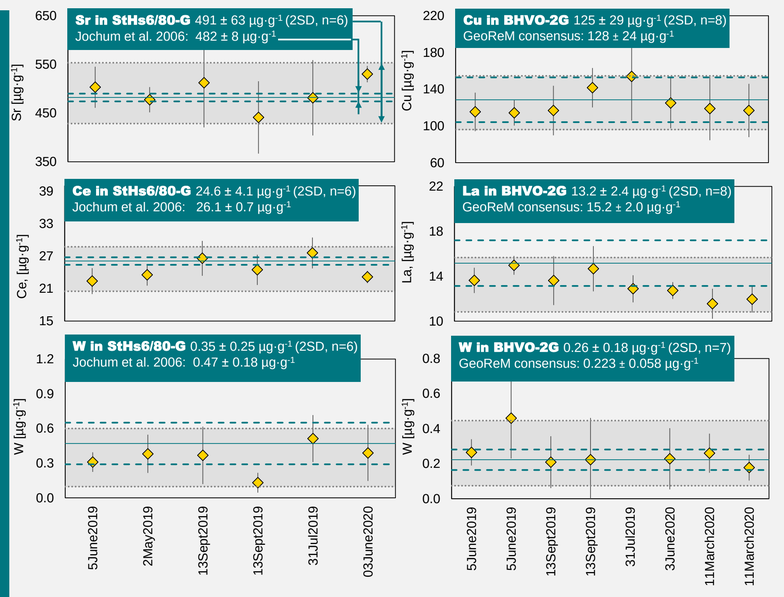


Fig.4. LA-ICP-ToF-MS mapping of glass RMs shows no bias and decent intermediate precision

SINGLE PULSE RESPONSE PROFILE

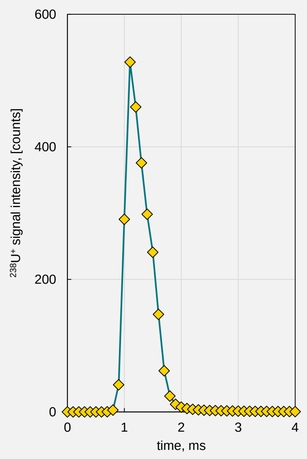
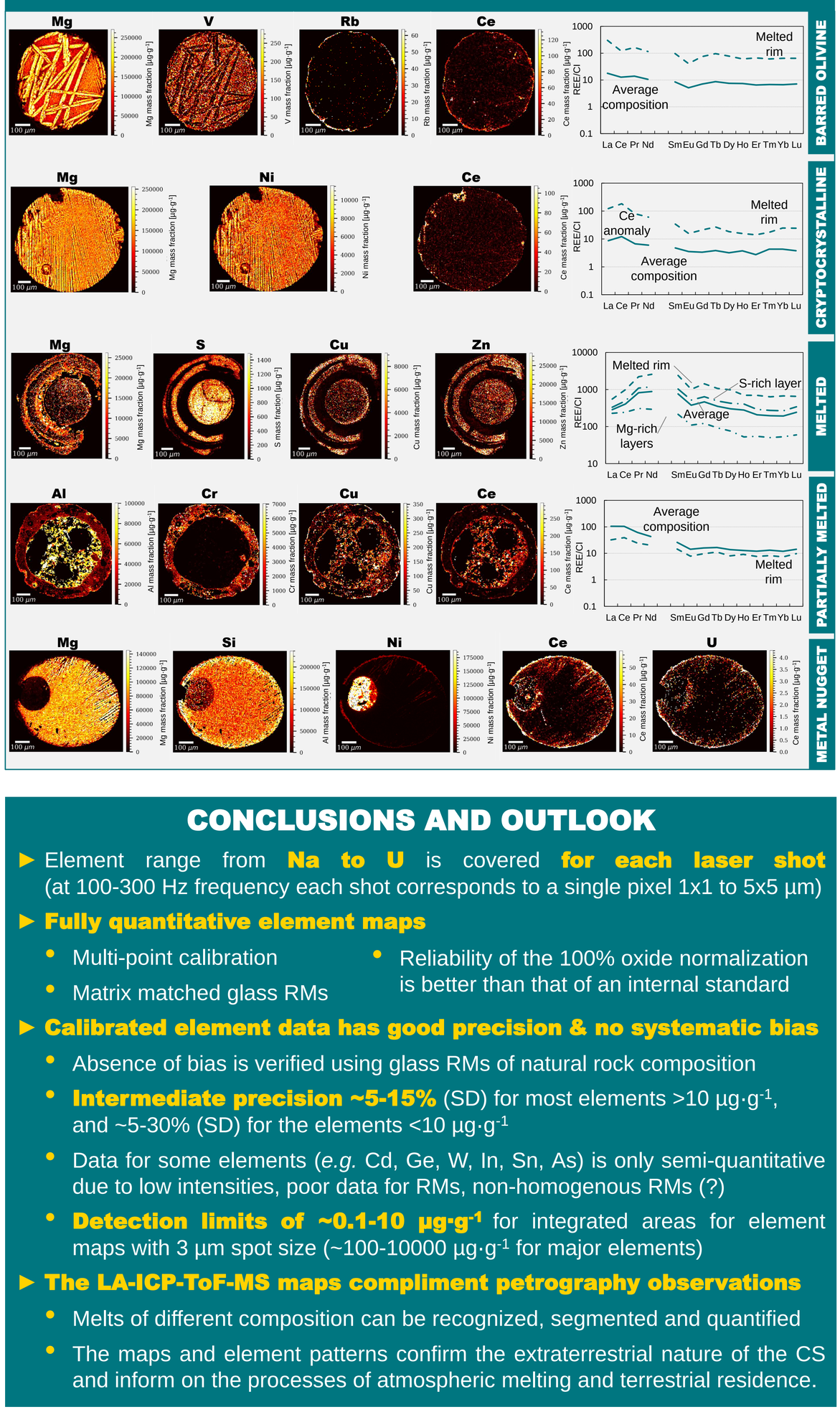


Fig. 5. Single pulse response profile of the LA-ICP-ToF-MS setup

MAPS OF THE ELEMENT MASS FRACTIONS



CONCLUSIONS AND OUTLOOK

- Element range from **Na to U** is covered **for each laser shot** (at 100-300 Hz frequency each shot corresponds to a single pixel 1x1 to 5x5 µm)
- **Fully quantitative element maps**
  - Multi-point calibration
  - Matrix matched glass RMs
  - Reliability of the 100% oxide normalization is better than that of an internal standard
- **Calibrated element data has good precision & no systematic bias**
  - Absence of bias is verified using glass RMs of natural rock composition
  - **Intermediate precision ~5-15%** (SD) for most elements >10 $\mu g \cdot g^{-1}$, and ~5-30% (SD) for the elements <10 $\mu g \cdot g^{-1}$
  - Data for some elements (*e.g.* Cd, Ge, W, In, Sn, As) is only semi-quantitative due to low intensities, poor data for RMs, non-homogenous RMs (?)
  - **Detection limits of ~0.1-10 µg·g⁻¹** for integrated areas for element maps with 3 µm spot size (~100-10000 $\mu g \cdot g^{-1}$ for major elements)
- **The LA-ICP-ToF-MS maps compliment petrography observations**
  - Melts of different composition can be recognized, segmented and quantified
  - The maps and element patterns confirm the extraterrestrial nature of the CS and inform on the processes of atmospheric melting and terrestrial residence.

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