Determination of the Ni isotope fractionation in microfossils embedded in the aragonite phase

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Introduction 1

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- Microbial remnants that are preserved and fossilised are likely to remain on the planetary surface as endoliths and epilithswell preserved, embedded in veins or vesicle filling mineral phases, e.g., carbonates or quartz.

- Advanced analytical instruments and methods are needed for planetary and space exploration that are capable of the detection of life signatures at micrometre scale. Among others biosignatures, the chemical composition indicating metabolic processes and bioorigin of the material is of paramount importance

- We describe a method for accurate isotope ratio measurements using our laser ablation ionisation time-of-flight mass spectrometer (LIMS) that is designed for in situ planetary research. The method is based on chemical depth profiling a spectrum cleaning procedure and isotope peak intensity correlations.

Chemical analysis using laser ablation / ionisation

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- Elements: host rock and fossil chemical composition
  Isotopes: possible fractionation processes

  [Riedo et al. 2013, JMS 48]
  [Riedo et al. 2013, JAAS 28]
  [Riedo et al. 2013, PSS 87]

- Chemical mapping of rock surface
  → quantitative analysis of the element redistribution/mineralogy with µm- resolution

  [Neuland et al. 2014, PSS 101]

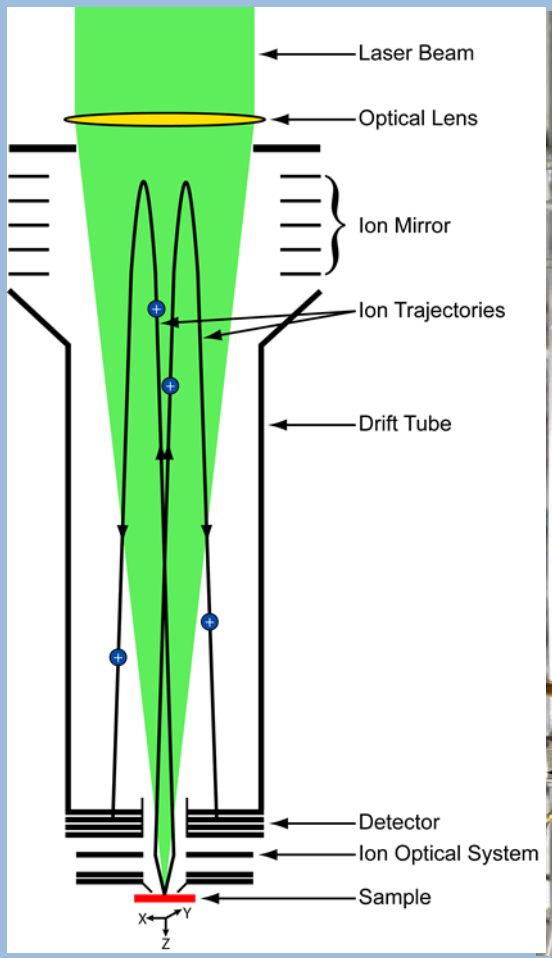
- Depth profiling
  → quantitative analysis of redistribution of elements across the surface thickness with nm-resolution

  [Grimaudo et al., 2015; Anal. Chem. 87]

- Mass spectrometry (LMS) combined with optical microscopy: CAMAM
  → surface morphology
  → microstructure, texture

  [Tulej et al, 2014; GGR 38]

LMS in Bern



Mass spectrometer: grid-less R-TOF

→ Size: 160 mm x Ø60 mm
→ MCP ion detector + multianode
→ 3 x 8-bit high speed digitizer with on-board processing

fs-laser ablation / desorption ion source

spot size ..... ~15 µm
laser pulse duration ..... 190 fs
energy/pulse ..... < 1 mJ
repetition rate ..... < 1 kHz
→ duration of single measurement ..... ~ s

[Rohner et al. 2003, Meas. Sci. Technol. 14]
[Tulej et al. 2011, Anal. Bioanal, Chem. 399]
[Riedo et al. 2013, JAAS 28]
[Riedo et al. 2013, JMS 48]

Samples: NIST981 (Ni_isotopes), Ni bearing mineral and filaments in aragonite phase

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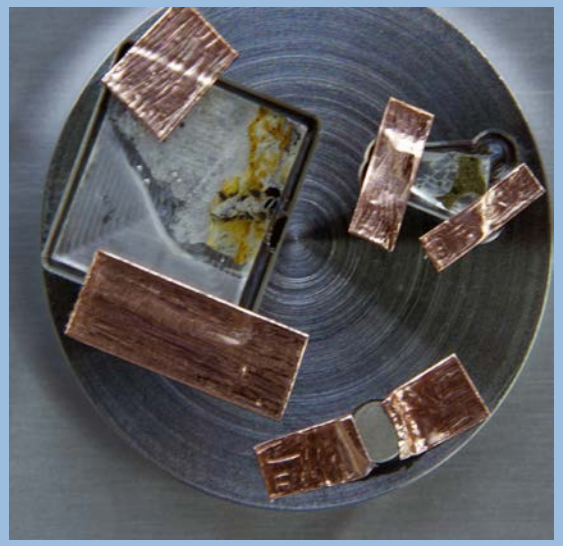
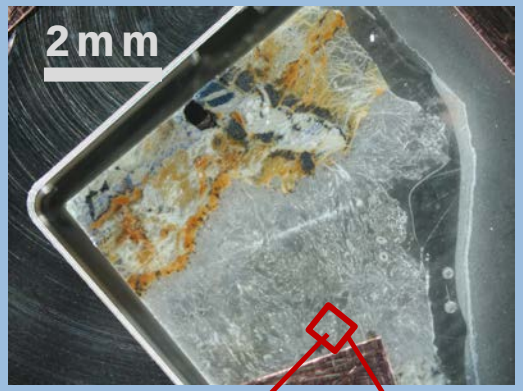
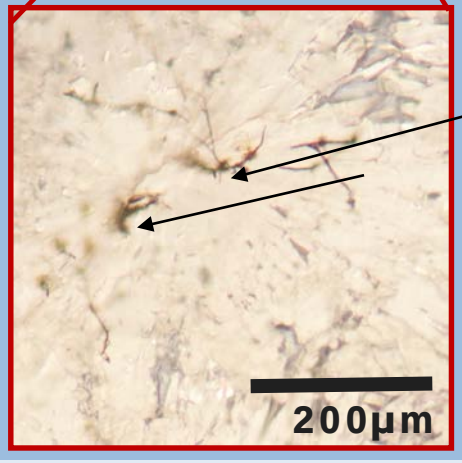


Samples are placed on a stainless-steel holder, in cavities, and stabilized by a cooper tape for UHV.

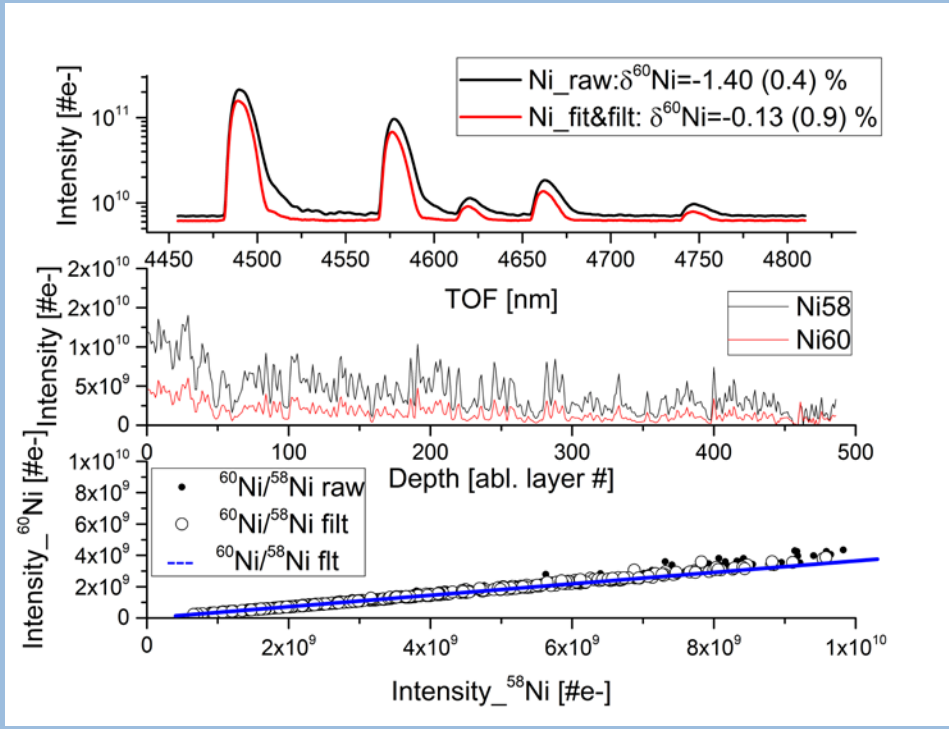




Aragonite veins hosted in serpentinised harzburgite is found in the aragonite vein formed during the last 130 kyrs within the uplifted serpentinized peridotites in Mid-Atlantic ridge area **[Bach et al. 2011]**

Dark filamentous micrometre-structures at the interface between aragonite and the harzburgite host rock

Principles of the isotope analysis applied in this study



(e.g., Wiesendanger, M. Journal of Chemometrics, 33 (2018) 1-10)

- A raw mass spectrum is a summ of 500 mass spectra collected on one sample location.
- The integration of the relevant isotope mass peaks yield isotope abundance, isotope ratio and delta isotope values
- Several effects can affect the isotope values including:

- mass peak shape distorsions (plasma instabilities, surface and space charge effects

- detection inefficiencies (detector saturation, noise and isobaric interferences)

Spectra filtering, isotope mass peak intensity linear correlation and signal isolation using depth profile are used to improve isotope analysis.

Depth profile and Ni isotope peaks correlations

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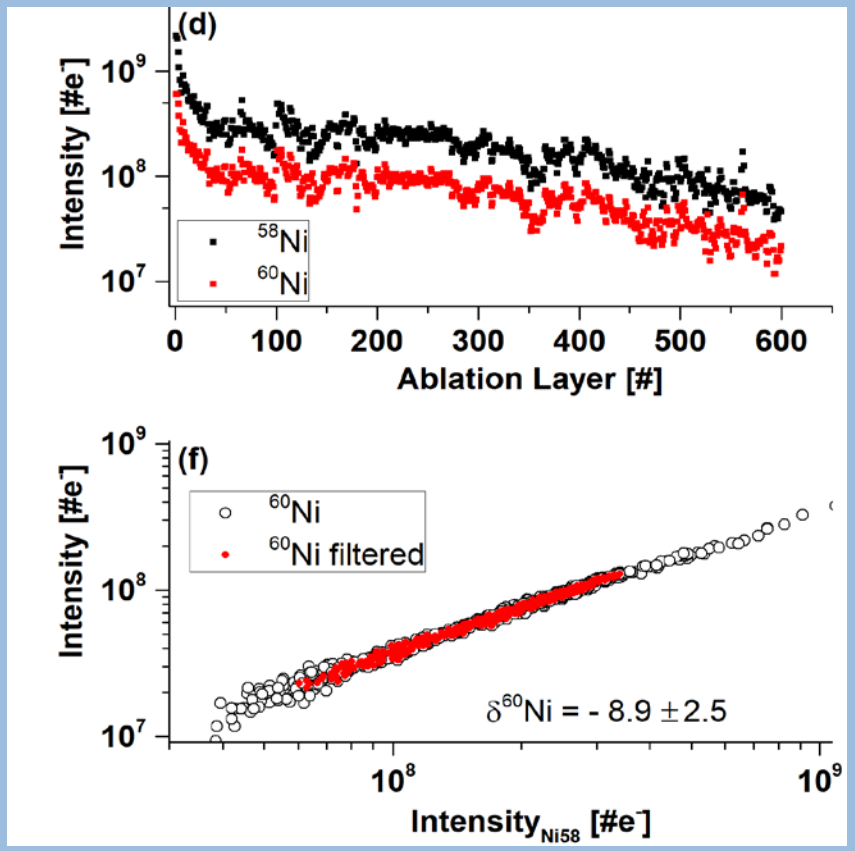
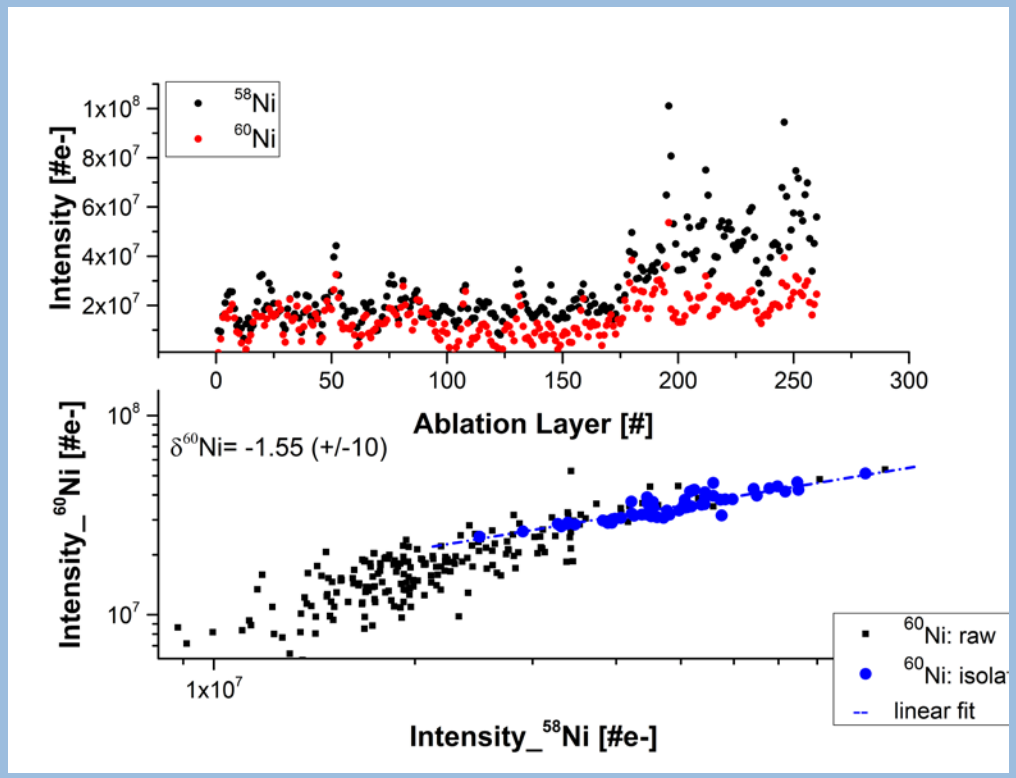
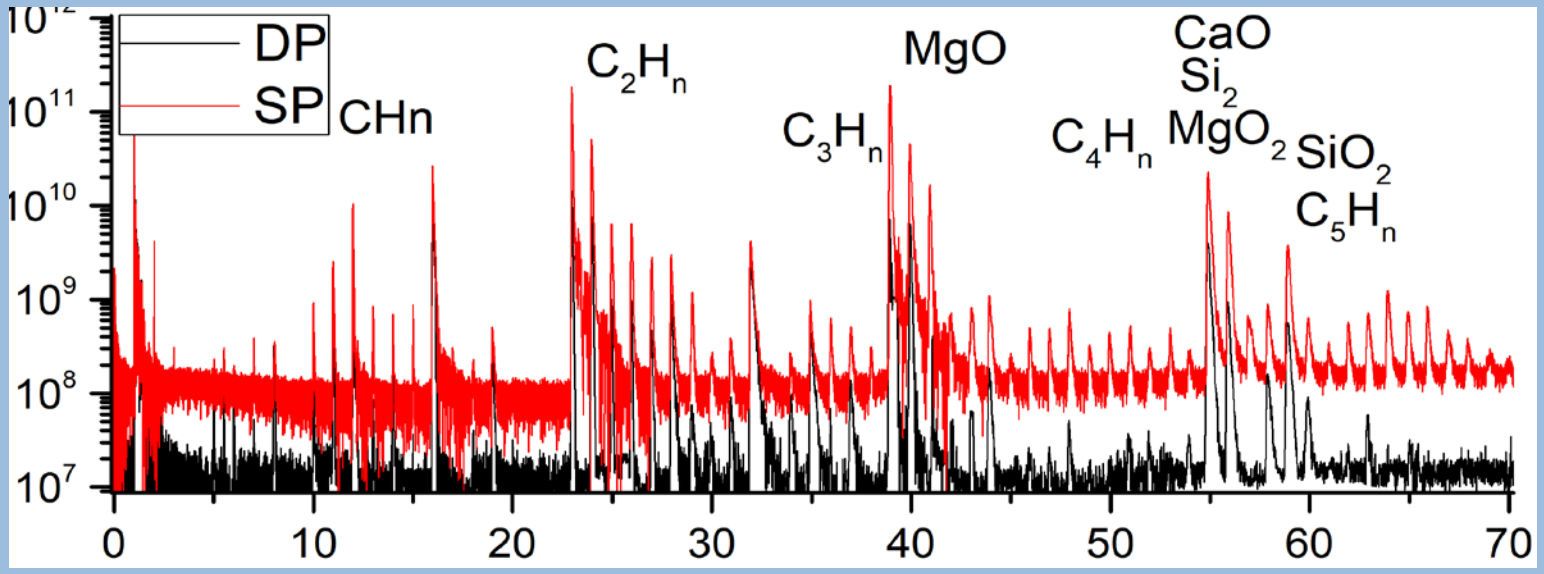
Ni-bearing mineral



Ni in micrometre-sized filament



Effect of isobaric clusters: Single pulse (SP) vs. Double pulse (DP) laser ablation ion source



The TOF MS mass spectrum obtained by double and single pulse laser ablation ion sources:

-Cluster abundances can be reduced significantly

- cluster isobaric interference are reduced but not entirely eliminated

Tulej, et al, J Anal Atom Spectrom, 33 (2018) 1292-1303.

Conclusions

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- LMS delivers highly sensitive chemical analysis with high spatial resolution of host rock and microsized samples that are embedded in the host rock
- Analysis can be conducted either on data of the uppermost surface or on data of the surface interior
- By element profiling in lateral direction and depth, the sample of interest can be isolated
- The isotope analysis with LIMS is feasible and can be improved by applying depth profile analysis, data filtering and linear intensity correlation methods.
- Quantitative isotope analysis of microstructures can be conducted providing that there are no isobaric clusters
- Combining LMS with microscope camera system for planetary surfaces would be necessary while studying microstructures (CAMAM)

[M. Tulej et al., 2014, GGR 38]

Thank you for your attention!

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Supplementary:
Elements in Bach sample: quantitative

Element	Location_32 (M1) Fraction [%] ± Abs. Error	Location_48 (M1) Fraction [%] ± Abs. Error	Total (M1) Fraction [%] ± Abs. Error	Location_36 (M2) Fraction [%] ± Abs. Error	Location_44 (M2) Fraction [%] ± Abs. Error	Total (M2) Fraction [%] ± Abs. Error
Li	0.06 (0.01)	0.15 (0.003)	0.31 (0.01)	0.35 (0.01)	0.20 (0.01)	0.15 (0.003)
B	1.77 (0.05)	3.17 (0.02)	2.21 (0.02)	5.00 (0.08)	4.24 (0.05)	2.31(0.02)
N	1.39 (0.03)	1.06 (0.01)	0.25 (0.01)	0.57 (0.02)	0.39 (0.01)	0.38(0.002)
F	0.32 (0.02)	0.48 (0.01)	0.53 (0.01)	0.83 (0.02)	0.78 (0.03)	0.38 (0.01)
Si	7.31 (0.08)	6.93 (0.04)	3.43 (0.04)	5.74 (0.05)	5.52 (0.08)	3.43(0.01)
P	0.25 (0.02)	0.23 (0.01)	0.51 (0.01)	0.60 (0.03)	0.32 (0.02)	0.26(0.01)
S	3.97 (0.09)	4.26 (0.04)	3.22 (0.04)	14.30 (0.13)	11.37 (0.10)	6.64(0.02)
Cl	2.60 (0.10)	4.63 (0.04)	3.36 (0.04)	2.07 (0.03)	2.44 (0.05)	2.22(0.01)
Ti	1.35 (0.07)	0.90 (0.02)	1.32 (0.02)	1.81 (0.03)	1.27 (0.03)	1.73 (0.03)
Mn	49.95 (0.43)	49.79 (0.16)	43.79 (0.16)	36.55 (0.19)	46.90 (0.17)	53.80(0.03)
Fe	14.60 (0.23)	18.47 (0.10)	27.47 (0.10)	21.83 (0.12)	17.07 (0.09)	21.07 (0.09)
Ni	4.31 (0.08)	2.37 (0.03)	2.11 (0.03)	2.34 (0.04)	1.96 (0.04)	1.19(0.004)
Co	13.63 (0.13)	12.13 (0.25)	6.97 (0.03)	7.53(0.05)	8.00 (0.06)	6.27(0.01)
	Li: 4.60(0.60) ppm; V: 60(50) ppm; Cr: 10 ppm N, Al, Cu, Zn: atomic fraction values are less certain due to isobaric interferences with clusters			Li: 3.00(50) ppm; V: 2.60(5) ppm; Cr: 30 (2) ppm N, Al, Cu, Zn: atomic fraction values are less certain due to isobaric interferences with clusters		

Host elements content (C,O,Na,Mg,K,Ca): 70-80%

Filaments:
-Similar composition

-Bio-relevant elements

-B, F, Cl may refer to salty water origin

- No evidence for mineralogical context

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