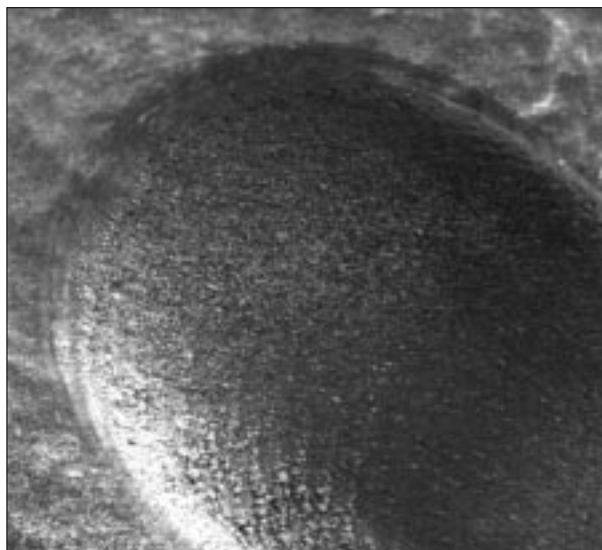


# Fast Scanning Sector Field ICP-MS with Laser Ablation for the Multi-Element Analysis of Elephant Tusk

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## Key Words

- High Resolution ICP-MS
- Laser Ablation
- Finnigan™ ELEMENT2



SEM photo of the ablated track across an elephant tusk sample

## Ivory Trade

### 1989:

- After ~700,000 elephants were slaughtered for their ivory in the previous decade, the 7th Conference of the Parties to CITES (Convention on International Trade in Endangered Species) approved a worldwide ivory ban
  - Ivory price fell from \$300/kg to \$20/kg

### 1997:

- One-off 'experimental' trade (50,000kg) allowed
  - Growing elephant populations
  - Lack of significant poaching
  - Elephant management policies

## Ivory trade - present situation

### 1997-2002:

- Increased poaching activities and trade in ivory and ivory fabricated goods
- Ivory price: \$250/kg

### November 2002: next CITES meeting

- Definition of control & monitoring procedure?
- Relaxation of trade restrictions leading to increased demand...?

## Aim of study

- Are trace element concentrations in elephant ivory representative of ecological regions?
  - Ivory (elephant tusk dentin) contains a Ca deficient hydroxyapatite
  - Other trace elements are incorporated into the dentin
  - Previous work on similar calcified hard biological tissues (fish otoliths etc) have shown this is to be valid
- Assess use of trace metal content as a possible tracer to sources of illegal ivory.

## Why Laser ablation ICP-MS?

- Only small samples required
- Direct sampling
- High sensitivity
- Reduced sample contamination as opposed to sample digestion and subsequent solution based analysis
- Reduced spectroscopic interferences compared to solution based ICP-MS?

## Laser ablation ICP-MS system used

### ICP-MS:

Finnigan™ ELEMENT2  
Single-collector, magnetic sector

### Laser Ablation:

New Wave Research  
UP213AI 213nm Nd:YAG



## Laser ablation of elephant tusk

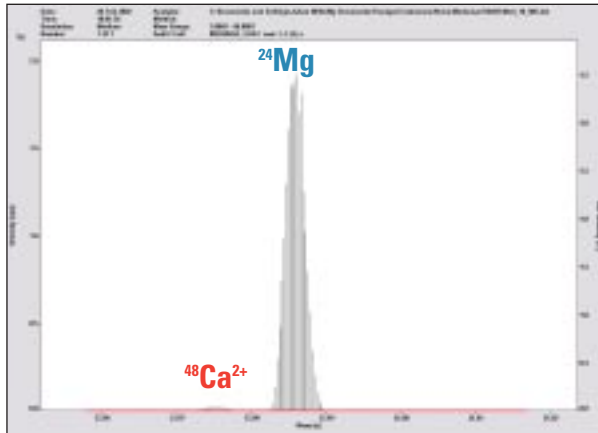
Fitness for purpose:

- Is a high resolution ICP-MS really necessary?
  - Look for interferences

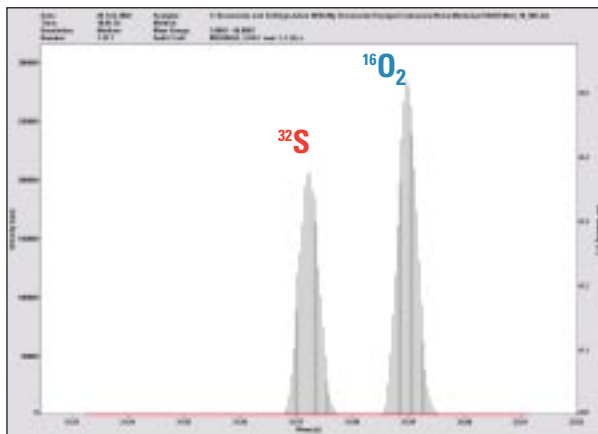
## Sample Matrix

Dentin is the ivory forming mass of the tusk:

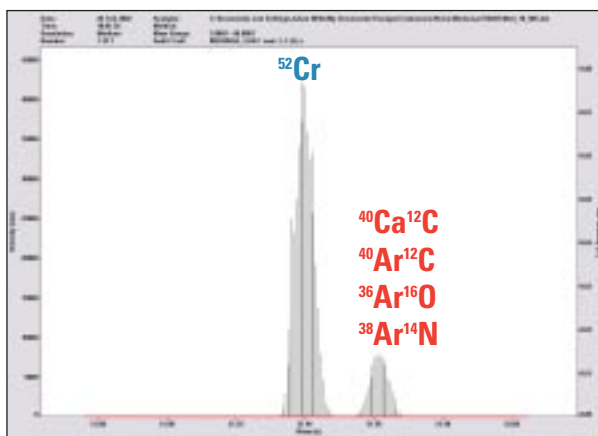
- 20% organic (mostly collagen)
- 80% inorganic
  - Mainly calcium hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ )
  - Some  $\text{CaCO}_3$ ,  $\text{CaF}_2$  and  $\text{Mg}_3(\text{PO}_4)_2$
- ~40% Ca



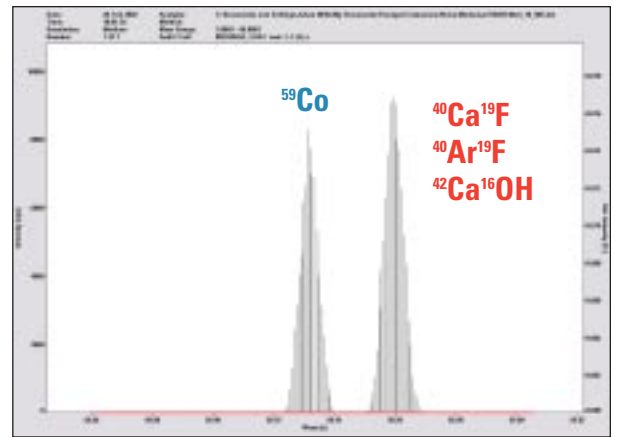
Tusk Interferences  $^{24}\text{Mg}$



Tusk Interferences  $^{32}\text{S}$



Tusk Interferences  $^{52}\text{Cr}$



Tusk Interferences  $^{59}\text{Co}$

## Example:

### laser ablation of elephant tusk

Fitness for purpose:

- High resolution is necessary.
  - Interferences exist in laser ablation ICP-MS
  - Complicated natural matrices lead to complicated ICP-MS spectra
  - Only removal of interferences by a difference in mass can guarantee interference free analysis – independent of matrix type
- Is sector field ICP-MS fast enough?

## Reference

Enhanced sensitivity in inductively coupled plasma sector field mass spectrometry for direct solid analysis using laser ablation (LA-ICP-SFMS)

Christopher Lohrey\* and Rolf Glöckner

Swiss Federal Institute of Technology (ETH) Zurich, Laboratory of Analytical Chemistry, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland  
E-mail: luhre@ionopt.chem.ethz.ch; gloeckner@ionopt.chem.ethz.ch

Received 19th May 2002, Accepted 12th July 2002  
First published as an Advance Article on the web 12th August 2002

### Quote from Conclusion:

The analysis using SF isogen showed that the ion speed of the magnets can no longer be considered the limiting factor in quantitative multielement analysis on tusk. In fact, a gain in both ion optics and field instrument equipped with fast scanning technology in combination with laser systems.

J. Anal. At. Spectrosc., 2002, 17, 10

## Scan parameters used:

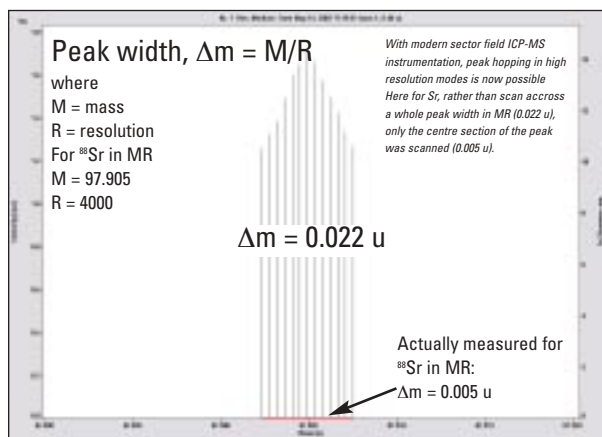
- Medium resolution ( $R=4000$ )
  - Visible, guaranteed freedom from interferences
- 27 isotopes measured
  - $^7\text{Li}$  -  $^{238}\text{U}$
- Time / sweep: 7.3s
  - Analysis time / sweep: 6.6s
  - Delay (magnet and electrical settling time): 0.7s
  - 9 sweeps in 66s
- Duty Cycle: 90%

## Example:

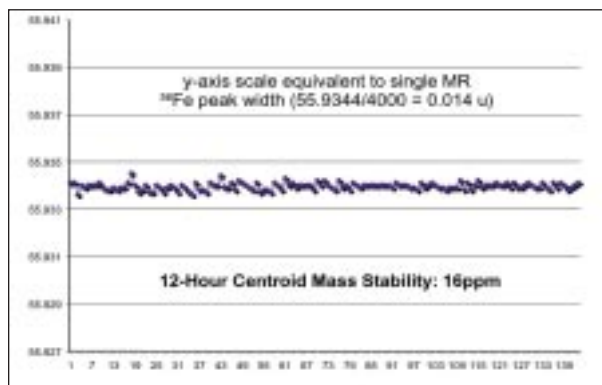
### laser ablation of elephant tusk

Fitness for purpose:

- High resolution is necessary
  - Interferences exist in laser ablation ICP-MS
  - Complicated natural matrices lead to complicated ICP-MS spectra
  - Only removal of interferences by a difference in mass can guarantee interference free analysis – independent of matrix type
- Sector field ICP-MS is fast enough
  - New magnet technology more than doubles scan speed (Thermo Electron Application Note AN30011\_E)
- Is the mass calibration accurate & stable?



Is the mass calibration accurate & stable?



Twelve Hour  $^{56}\text{Fe}$  (MR) Mass Stability

## Example:

### laser ablation of elephant tusk

Fitness for purpose:

- High resolution is necessary
  - Interferences exist in laser ablation ICP-MS
  - Complicated natural matrices lead to complicated ICP-MS spectra
  - Only removal of interferences by a difference in mass can guarantee interference free analysis – independent of matrix type
- Sector field ICP-MS is fast enough for laser analysis
  - New magnet technology more than doubles scan speed (Thermo Electron Application Note AN30011\_E)

- Mass calibrations are accurate & stable
  - Peak jumping now possible in high resolution

## System Configuration

### New Wave UP213 AI (Aperture Imaged):

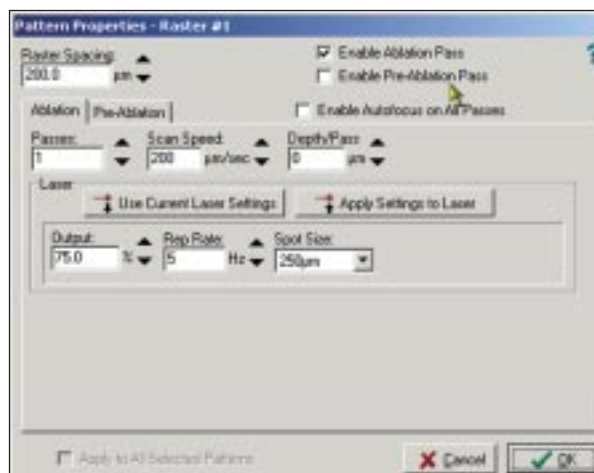
- He as laser cell gas (0.7L/min)
- Mixed with Ar (0.7L/min) before plasma torch
- No spray chamber to aid mixing

### Finnigan ELEMENT2:

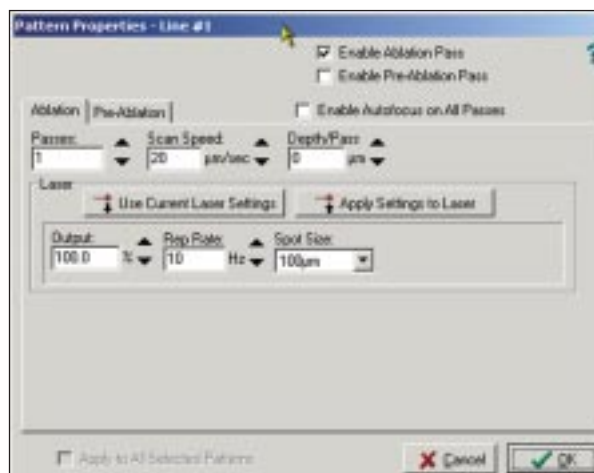
- AI sampler & skimmer cones
- Fast magnet (magnetic scan speed  $m/z$  7 – 240 – 7 < 150ms)
- 200,000cps/ppm Th in NIST glass (100 $\mu\text{m}$  spot)
- ThO/Th ratio: 0.1%

## Measurement Strategy

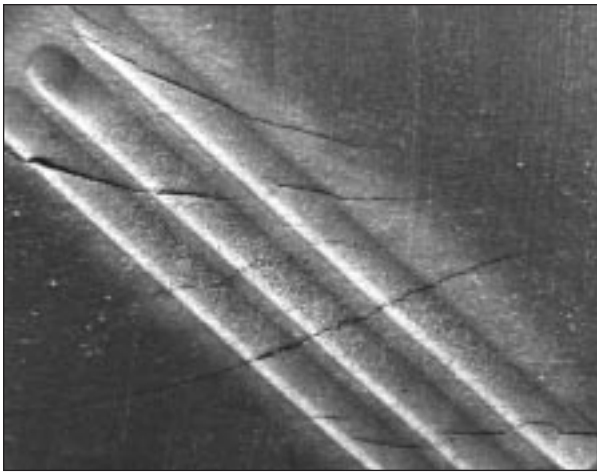
- All analyses made in Medium Resolution ( $R=4000$ )
  - Freedom from Ar based interferences (ArO etc)
  - Freedom from matrix induced interferences (CaO etc)
- Quantification
  - NIST glass standards (610, 612 & 614) for external calibration
  - Blank subtraction using gas blank
  - $^{44}\text{Ca}$  as internal standard



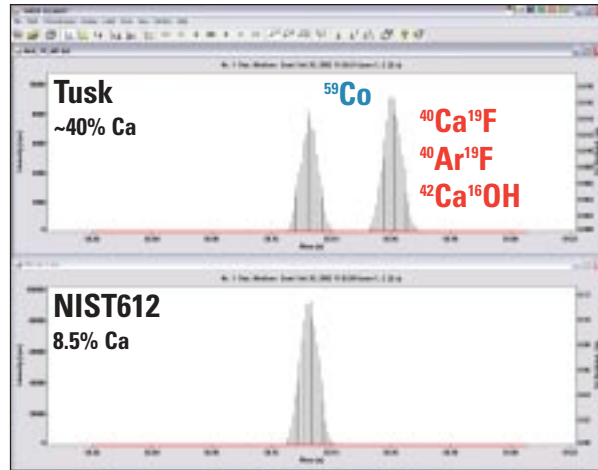
UP213 Pre-ablation parameters: Sample surface initially cleaned (pre-ablation) using these laser parameters (raster pattern).



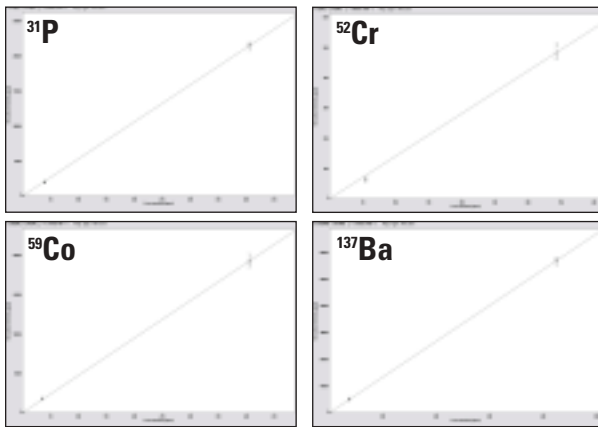
UP213 Analysis parameters: Three measurements made at different sites using these laser parameters (line pattern).



Three line patterns on the cleaned tusk surface



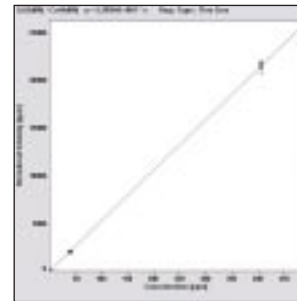
<sup>59</sup>Co: Comparison of interferences



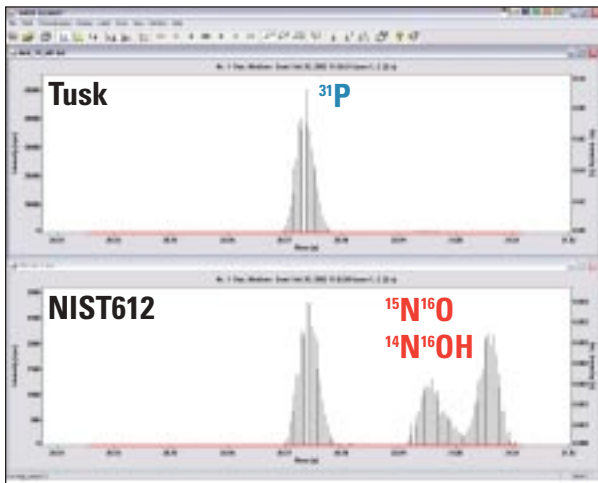
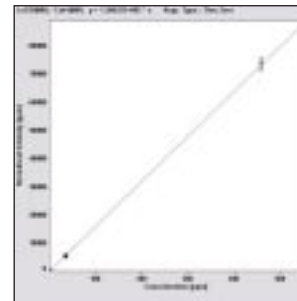
NIST Glass Calibration Lines

## Results

	<sup>52</sup> Cr(MR)
LoD (ppm)	0.02
Site 1 (ppm)	0.37
Site 2 (ppm)	0.37
Site 3 (ppm)	0.39
Average (ppm)	0.38
%RSD	3.5



	<sup>139</sup> La(MR)
LoD (ppm)	0.002
Site 1 (ppm)	0.038
Site 2 (ppm)	0.039
Site 3 (ppm)	0.042
Average (ppm)	0.040
%RSD	5.2



<sup>31</sup>P: Comparison of interferences

## Conclusions

High resolution sector-field ICP-MS is an ideal elemental detector for laser ablation analyses in complex environmental samples:

- Only high mass resolution can guarantee interference free multi-elemental analysis - independent of the sample matrix - with a single set of analysis parameters.
- Historical concerns of:
  - Scan speed
  - Mass accuracy
  - Mass stability
 are no longer an issue with current instrumentation.
- Sector field ICP-MS provides improved detection limits due to a better signal to noise ratio and interference-free analysis.
- Due to the higher sensitivity, lower laser energies can be used and smaller samples analysed.

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