Application Note: 30101

Enhancing Laser Ablation ICP-MS Using Sector Field Technology

Key Words

- ELEMENT 2
- Geochronology
- Isotope Ratios
- Laser Ablation
- Multi-Element Analysis

Introduction

Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) has developed over recent years to become a sophisticated tool for the multi-elemental and isotope ratio analysis of solid samples. Besides a true multi-elemental capability, independent of matrix, the major requirements for most geological laser applications in ICP-MS are the highest sensitivity and scan speed. Such demanding analytical pre-requisites often require the most sophisticated instrumentation, such as the Thermo Scientific ELEMENT 2.

This Application Report describes a variety of LA-ICP-MS applications from different scientists to provide a brief summary of the technique in their particular fields of interest. The contributions included are:

- Pb geochronology in zircons (M. Tiepolo et al.)
- Re and Os concentration measurements in molybdenite (I. Rodushkin et al.)
- High mass resolution for non-matrix dependent laser ablation analysis, the isotopic analysis of Pleistocene human remains and the multi-element analysis of fluid inclusions by LA-ICP-MS, (Ch. Latkoczy et al.).

In Situ Pb Geochronology of Zircons

Massimo Tiepolo
Email: tiepolo@crystal.unipv.it
web: http://www_crystal.unipv.it

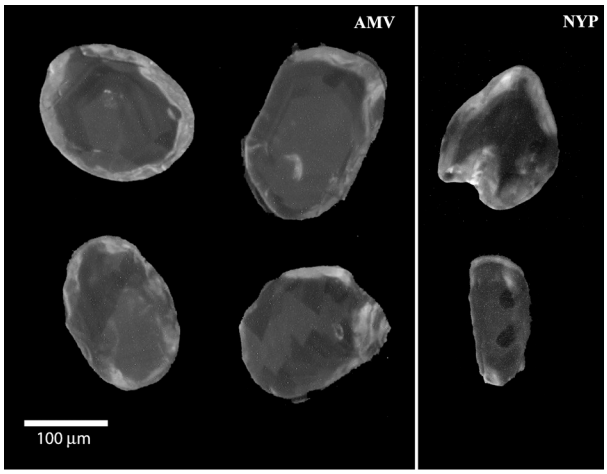

Figure 1: Typical zircons analyzed in this study.

The Pb geochronological capabilities of sector field LA–ICP–MS, based on the coupling of the Thermo Scientific ELEMENT and a 213 nm UV laser, have been tested on a series of zircons (Figure 1) ranging in age between 150 and 577 Ma (Figure 2):

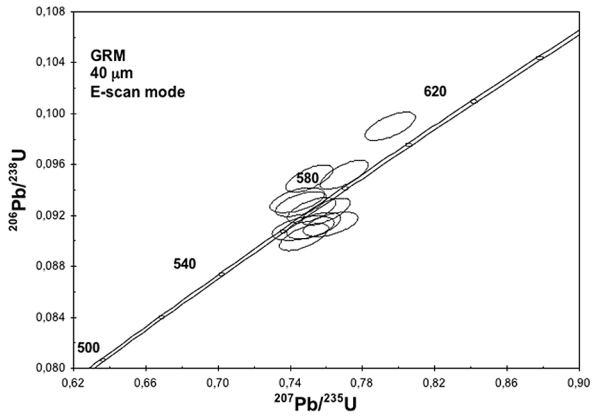

Figure 2: Geochronological determination of zircons.

- Geologically meaningful ages calculated from the ratios $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ and $^{208}Pb/^{232}Th$ can be achieved down to 1 ppm of total Pb in zircon. Reliable $^{207}Pb/^{206}Pb$ ages can be only achieved in zircons with > ~40 ppm of total Pb.
- At a spatial resolution of 40 µm, the electrostatic scan mode (EScan) is more suitable and gives internal precision values on $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ and $^{208}Pb/^{232}Th$ ages to better than 1.1% (for zircons with ~40 ppm of total Pb).
- A spatial resolution of 20 µm can be used on relatively Pb-rich zircons even if the internal precision is about 1.5 times lower than with a spot size of 40 µm.
- Accuracy is not particularly sensitive to scan mode and is more influenced by the total Pb content of zircon, with values ranging between 1 and 5%.

Reference

Tiepolo M., In situ Pb geochronology of zircon with laser ablation–inductively coupled plasma–sector field mass spectrometry. Chemical Geology, 2003, 199, 159-177.

Thermo SCIENTIFIC

Determination of Re and Os Concentrations in Molybdenite

Ilia Rodushkin
Email: ilia.rodushkin@analytica.se
web: http://www.analytica.se

Figure 3: Thermo Scientific ELEMENT 2 with New Wave UP213 laser system.

The ^{187}Re–^{187}Os geochronometer applied to molybdenite has been demonstrated to be remarkably robust, surviving intense rock deformation and high-grade thermal metamorphism. In molybdenite virtually all Os is produced by the radioactive decay of ^{187}Re to ^{187}Os. Successful dating by isotope dilution techniques is dependent on careful preparation of the mineral separate and on the appropriate choice of spikes. Both the Re and Os contents of molybdenites are highly variable, requiring pre-information for the preparation of the correct spike amounts. LA-ICP-MS (Figure 3) is therefore used as a rapid tool for Re and Os determination in molybdenite, since sample preparation for LA-ICP-MS consists of only the separation of the molybdenite, followed by grinding and pressing to form pellets.

External calibration with internal standardization using a matrix-matched standard has been found to be the best quantification approach for Re, providing results that are indistinguishable from data obtained by solution based ID-ICP-MS (within the limits of measurement precision). The accuracy of ^{187}Os quantification by LA-ICP-MS is poorer than compared to Re, as its determination requires the correction of a severe isobaric interference from ^{187}Re. Consequently, the determination only gives results that are more accurate for the older and higher in Os molybdenite samples.

References

Malinovsky D., Rodushkin I., Axelsson M.D., and D.C. Baxter, Determination of rhenium and osmium concentrations in molybdenite using laser ablation double focusing sector field ICP-MS. Journal of Geochemical Exploration, 2004, 81, 71-79.

Malinovsky D., Rodushkin I., Baxter D. and B. Öhlander, Simplified method for the Re-Os dating of molybdenite using acid digestion and isotope dilution ICP-MS. Analytica Chimica Acta, 2002, 463, 111-124.

Multi-Element Trace Analysis of Synthetic Mineral Materials

Christopher Latkoczy, Magne Ødegard and Detlef Günther
Email: Latkoczy@inorg.chem.ethz.ch
web: http://www.analytica.ethz.ch

The quantification of trace elements in synthetically prepared mineral standards used for microanalysis (rutile TiO_2, apatite $Ca_3(PO_4)_2$ and fluorite CaF_2) by LA-ICP-MS coupled to a 193 nm ArF - Excimer laser system was investigated. A commercially available standard silicate reference material (NIST SRM 612) was used as a one point calibration standard. Using such a non-matrix matched calibration procedure, a highly linear correlation between the measured and nominal concentrations for elements doped to the material was established (Figure 4).

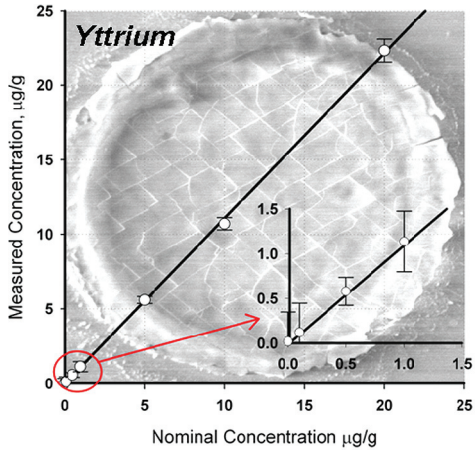

Figure 4: Typical 193 nm ArF - Excimer laser crater in CaF_2. Calibration curve using NIST SRM 612 as external standard.

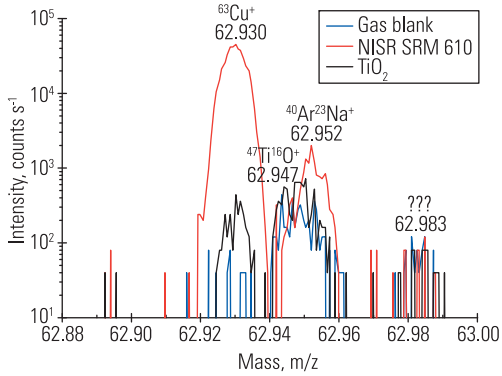

Figure 5a: Medium resolution (R = 4000) spectrum at m/z 63 separating ^{63}Cu from the main interferences.

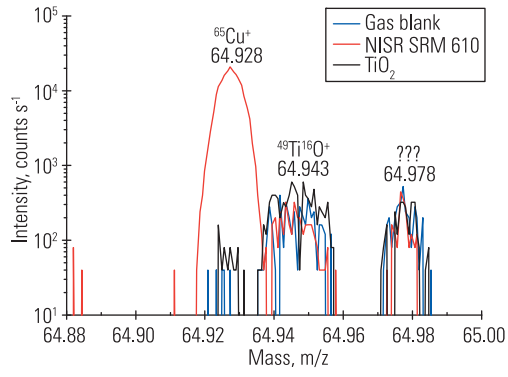

Figure 5b: Medium resolution (R = 4000) spectrum at m/z 65 separating ^{65}Cu from the main interferences.

Furthermore, the enhanced mass resolution capabilities of the instrument was used to identify possible interferences resulting from major sample elements (Figure 5a and 5b). The materials were analyzed using different laser spot sizes, ranging from 10 - 120 µm in order to study the elemental distribution of the elements in the mineral standards. At a spot size of 60 µm, relative standard deviations (RSDs) for 10 consecutive measurements were below 5% for the apatite, below 11% for the fluorite, and below 18% for the rutile (Figure 6). The accuracy for each element in the three synthetic mineral standards was within 15% for most elements in the apatite and fluorite materials, and up to 23% in the rutile. Such LA-ICP-MS studies proved to be very useful in order to characterize the homogeneity of synthetically prepared materials in the micrometer-scale.

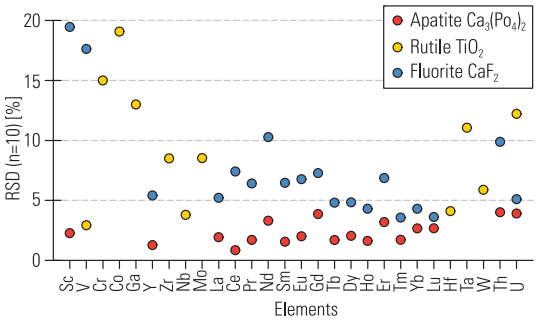

Figure 6: Heterogeneity (expressed as % RSD for ten consecutive measurements) of various elements in the three sample materials.

References

Ødegard,M.; Skar,O.; Schiellerup,H.; Pearson,N.J., Preparation of a synthetic titanite glass calibration material for in situ microanalysis by direct fusion in graphite electrodes: A preliminary characterisation by EPMA and LA-ICP-MS, Geostandards and Geoanalytical Research, 2005, 29(2), 197-209.

Trace Element and Sr Isotopic Ratio Analysis of Pleistocene Human Teeth from the Altai Massif, Russia

Christopher Latkoczy, Bence Viola, Maria Teschler-Nicola, Horst Seidler, Thomas Prohaska, Beat Aeschlimann and Detlef Günther
Email: Latkoczy@inorg.chem.ethz.ch
web: http://www.analytica.ethz.ch

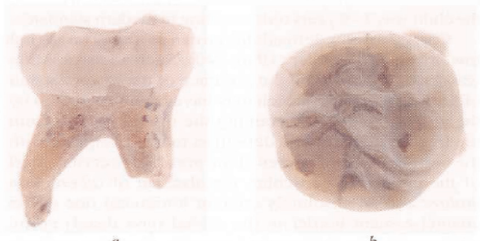

Figure 7a: Second lower right milk molar from Okladnikov cave. Left side: vestibular norm, right side: vertical norm.

In the 1980s, human remains (seven teeth and postcranial fragments) were discovered in two caves in north-western Altai, Siberia. Morphologically and metrically, the Denisova and Okladnikov cave teeth have been compared to both Neanderthals and modern humans (Figures 7a and 7b).

Figure 7b: First lower left premolar from Okladnikov cave. Left side: distal norm. Right side: vertical norm.

In this study, we applied LA-ICP-MS to perform a multielement analysis to assess the probability of individual association for these human remains (Figure 8).

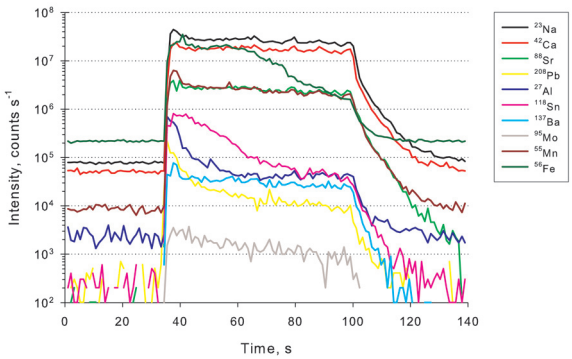

Figure 8: Multielemental laser analysis trace.

Furthermore, we used an optimized fast-scan method to measure the isotope ratio of $^{87}Sr/^{86}Sr$ in dentine and enamel to study possible migration patterns (Figure 9 and Table 1).

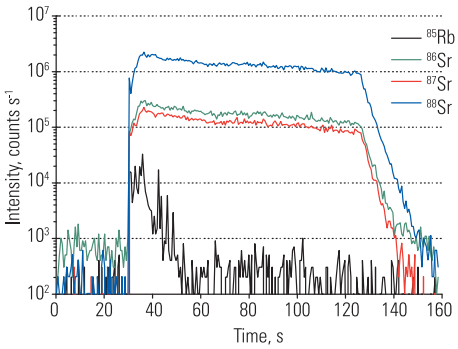

Figure 9: Strontium isotopic laser analysis trace.

$^{87}Sr / ^{86}Sr$			
Enamel	0.711	0.711	avg
	0.710	0.001	std
	0.710	0.15%	rsd
	0.712		
	0.712		
Dentine	0.710	0.711	avg
	0.711	0.001	std
	0.712	0.09%	rsd
	0.711		
	0.710		

Table 1: Results from the Sr isotopic analysis.

Our preliminary results showed that further work is necessary to assess the amount and pattern of intra-individual variations in multi-element and isotopic composition, as well any possible effect from the post-depositional environment. We could not reach fully conclusive results on individual associations, but our results do not support previous claims that the Okladnikov cave teeth originate from only two individuals. Strontium isotope ratios in the Okladnikov sample indicate within the measurement uncertainty that the individual did not migrate, at least not to regions with strongly different geological substrate. Further information on regional geology and isotopic composition will help to clarify this question.

References

Shpakova, E.G., Derevianko, A.P., The interpretation of odontological features of Pleistocene Human Remains from the Altai, Archaeology, Ethnology and Anthropology of Eurasia, 2000, 1, 125-138.

Analysis of Fluid Inclusions Using Sector Field LA-ICP-MS

Christopher Latkoczy and Detlef Günther
Email: Latkoczy@inorg.chem.ethz.ch
web: http://www.analytica.ethz.ch

Microscopic fluid inclusions in minerals are the main source of information about the chemical composition of fluids associated with large-scale material transport in the Earth's interior. Hydrothermal transport processes are responsible for the natural enrichment of metal resources in many ore deposits. For the multi-element analysis of the microscopic fluid inclusions (typically 5 - 50 µm in diameter), LA-ICP-MS has become one of the most promising techniques owing to the recent progress in laser optics design and the development of high-sensitivity, fast-scanning ICP mass spectrometers.

Isotope	Accurate Mass	Method Mass Offset	Mass Window	Mass Range	Magnet Mass	Settling Time	Sample Time	Samples Per Peak	Segment Duration	Search Window	Integration Window	Scan Type	Detection Mode	Integration Type
Li7	7.0155	-0.0021	20	7.013 - 7.018	7.011	0.100	0.0020	50	0.020	100	100	ESan	Both	Average
B11	11.0009	-0.0008	20	11.005 - 11.012	11.009	0.015	0.0020	50	0.020	100	100	ESan	Both	Average
Na23	22.9892	0.0023	20	22.982 - 22.997	22.989	0.030	0.0020	50	0.020	100	100	ESan	Both	Average
Mg25	24.9853	0.0034	20	24.977 - 24.994	22.969	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
K39	38.9632	0.0180	20	38.950 - 38.976	38.963	0.026	0.0020	50	0.020	100	100	ESan	Both	Average
Ti49	48.9473	0.0247	20	48.931 - 48.964	38.963	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Mn55	54.9375	0.0046	20	54.919 - 54.956	54.938	0.019	0.0020	50	0.020	100	100	ESan	Both	Average
Fe57	56.9349	0.0219	20	56.916 - 56.954	54.938	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Cu65	64.9273	0.0049	20	64.906 - 64.949	54.938	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Zn66	65.9255	0.0049	20	65.904 - 65.947	54.938	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
As75	74.9211	0.0076	20	74.896 - 74.946	74.921	0.019	0.0020	50	0.020	100	100	ESan	Both	Average
Rb85	84.9113	0.0072	20	84.883 - 84.940	74.921	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Sr88	87.9051	0.0061	20	87.876 - 87.934	74.921	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Zr93	89.9042	0.0061	20	89.874 - 89.934	74.921	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Mo97	96.9055	0.0074	20	96.873 - 96.938	74.921	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Ag107	106.9046	0.0115	20	106.869 - 106.940	106.905	0.025	0.0020	50	0.020	100	100	ESan	Both	Average
Sn118	117.9011	0.0114	20	117.862 - 117.940	106.905	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Sb123	122.9037	0.0111	20	122.863 - 122.945	106.905	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Ce133	132.9049	0.0088	20	132.861 - 132.949	106.905	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Ba137	136.9053	0.0086	20	136.860 - 136.951	106.905	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
La139	138.9058	0.0212	20	138.860 - 138.952	138.906	0.021	0.0020	50	0.020	100	100	ESan	Both	Average
Ce140	139.9049	0.0186	20	139.858 - 139.952	138.906	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
W182	181.9477	0.0164	20	181.887 - 182.008	181.548	0.024	0.0020	50	0.020	100	100	ESan	Both	Average
Tl205	204.9739	0.0155	20	204.906 - 205.042	181.548	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Pb208	207.9761	0.0149	20	207.907 - 208.045	181.548	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Bi209	208.9798	0.0134	20	208.910 - 209.050	181.548	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
Th232	232.0375	0.0116	20	231.960 - 232.115	181.548	0.001	0.0020	50	0.020	100	100	ESan	Both	Average
U238	238.0502	0.0479	20	237.971 - 238.130	238.050	0.027	0.0020	50	0.020	100	100	ESan	Both	Average

Figure 9: ELEMENT Method file used for the analysis of fluid inclusions.

The latest improvement in the Thermo Scientific ELEMENT 2 scan speed allows magnetic jumps from the lowest mass analyzed, ^{7}Li, to the highest mass, ^{238}U, in only 90 ms. The jump back to the lowest mass is performed in < 50 ms.

The method developed for the analyses of 28 major, minor and trace elements, covering a concentration range of five orders of magnitude, results in a scan duration of 0.88 s and a duty cycle of 63% (Figure 9).

These analyses were carried out on single natural fluid inclusions (Figure 10) together with a number of experiments to optimize a controlled ablation technique and to test a calibration procedure.

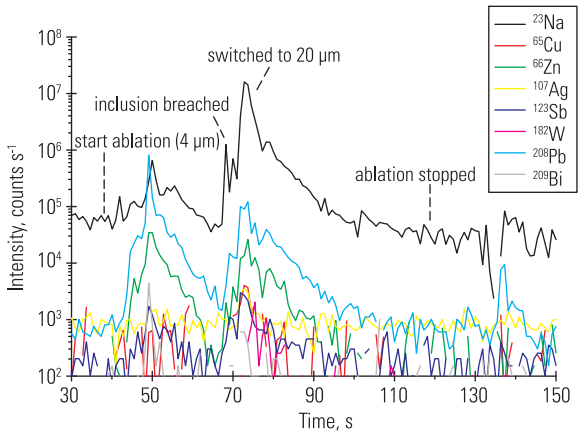

Figure 10: Time resolved laser ablation analysis of a natural fluid inclusion.

The optimized setup for sector field LA-ICP-MS was used together with a laser ablation system based on a 193 nm ArF - Excimer laser. In a procedure to stepwise open complex multiphase inclusions, a small hole (4 µm diameter) was first drilled for the partial release of liquid and vapor, followed by complete drilling out, using a laser spot size covering the entire inclusion.

References

Latkoczy, Ch., and Günther, D., Enhanced sensitivity in inductively coupled plasma sector field mass spectrometry for direct solid analysis using laser ablation (LA-ICP-SF-MS), Journal of Analytical Atomic Spectrometry, 2002, 17, 1264-1270.

Acknowledgements

Thermo Fisher Scientific wants to thank all authors for their contribution.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Australia
+61 2 8844 9500
Austria
+43 1 333 50340
Belgium
+32 2 482 30 30
Canada
+1 800 532 4752
China
+86 10 5850 3588
Denmark
+45 70 23 62 60
France
+33 1 60 92 48 00
Germany
+49 6103 408 1014
India
+91 22 6742 9434
Italy
+39 02 950 591
Japan
+81 45 453 9100
Latin America
+1 608 276 5659
Netherlands
+31 76 587 98 88
South Africa
+27 11 570 1840
Spain
+34 91 657 4930
Sweden/Norway/ Finland
+46 8 556 468 00
Switzerland
+41 61 48784 00
UK
+44 1442 233555
USA
+1 800 532 4752

www.thermo.com

AN30101_E 08/16C