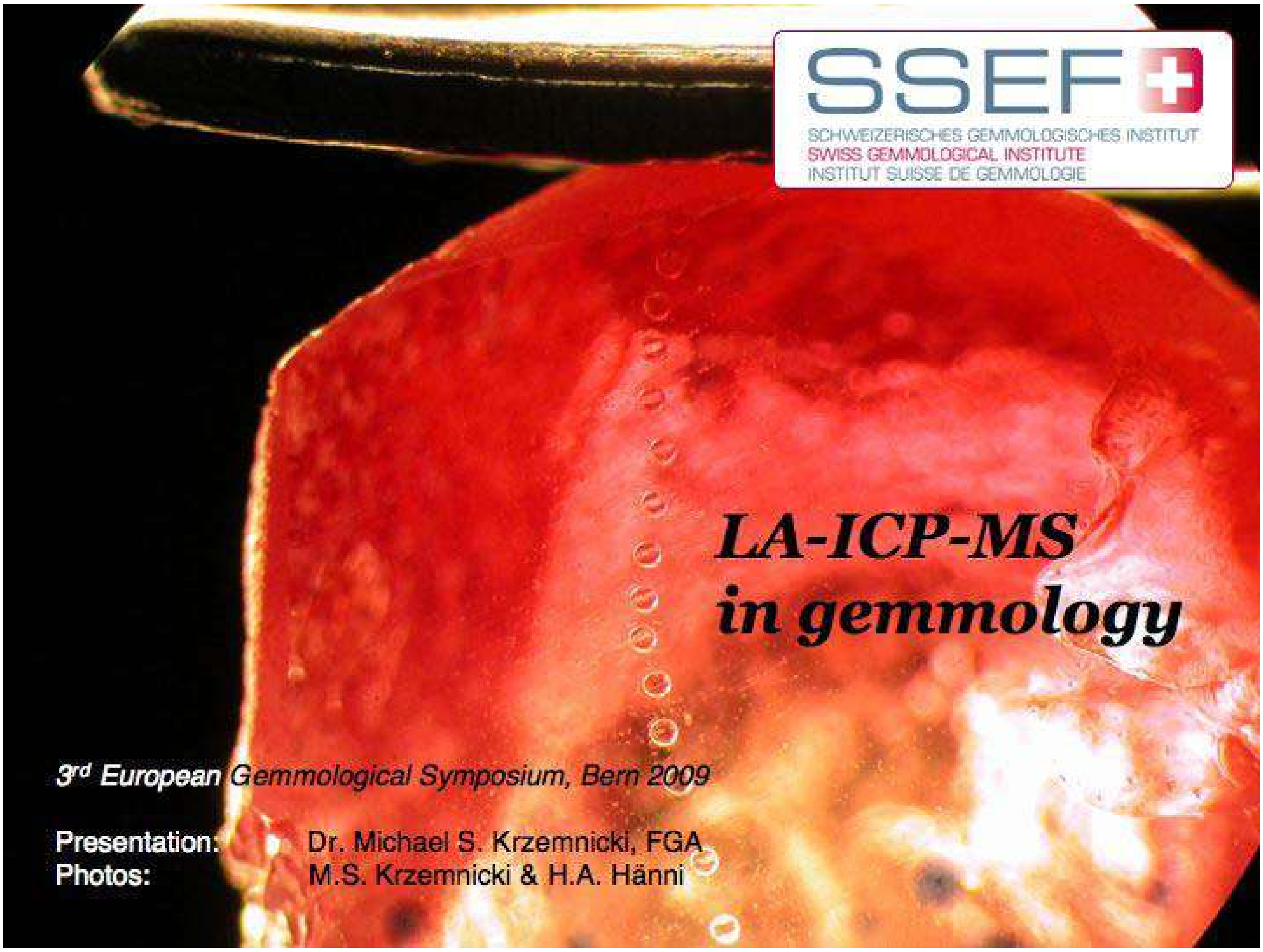

SSEF
SCHWEIZERISCHES GEMMOLOGISCHES INSTITUT
SWISS GEMMOLOGICAL INSTITUTE
INSTITUT SUISSE DE GEMMOLOGIE

LA-ICP-MS in gemmology

3rd European Gemmological Symposium, Bern 2009

Presentation: Dr. Michael S. Krzemnicki, FGA
Photos: M.S. Krzemnicki & H.A. Hänni

The daily work of gemmologists

Dumortierite from Tanzania with distinct pleochroism.

- Identification: what is it ?
- Natural or synthetic ?
- Treated or not ?
- The origin: Where does it come from ?

Apart from microscopic observations and spectroscopic analyses (UV-Vis, NIR, FTIR, Raman) it is important to have chemical data.

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Options for chemical analysis

- X-ray fluorescence (ED-XRF and WD-XRF)

- Energy dispersive spectroscopy coupled with scanning electron microscope (SEM EDS)

- Electron microprobe (EMP)

- Laser induced breakdown spectroscopy (LIBS)

- Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

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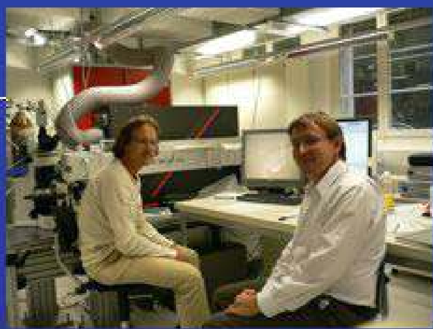
Features of LA ICP MS



Together with Prof. Thomas Pettke at the LA ICP MS in the Geochemical Lab, University of Berne, Switzerland

Chemical analysis of specimens

+ nearly all chemical elements can be analysed
+ up to 50 elements at the same time
+ point analysis (zoning)
+ only minor sample preparation
+ large dynamic range of analysis (from sub-ppm to main element concentrations)
+ quantitative data

- slightly destructive analysis (laser drill holes diameter ca 100 µm)
- how representative are point analyses for the whole stone?
- raw data (qualitative) has to be processed to get quantitative data
- contamination effects
- spike filtering
- highly sophisticated instrument

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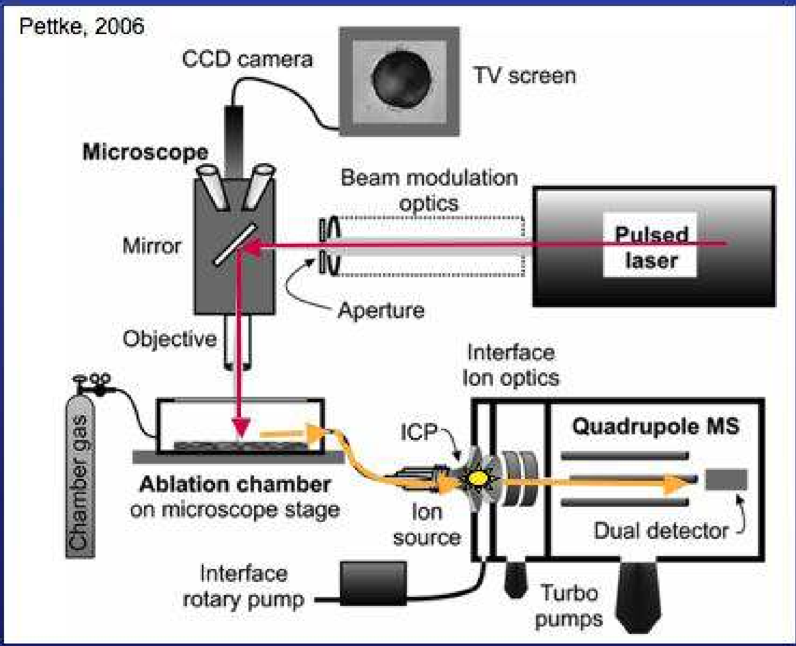
The LA-ICP-MS instrument



Microlas system:
Beam modulation optics to homogenize laser beam energy profile

Lambda Physics, Coherent:
Pulsed nanosecond ArF excimer laser (193 nm)

Perkin Elmer:
DRC-e quadrupole mass spectrometer

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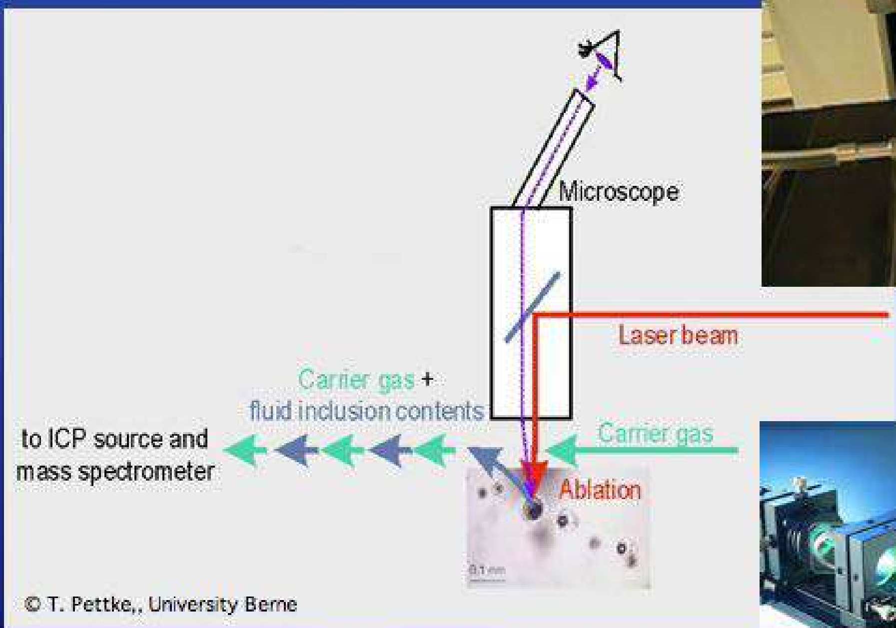
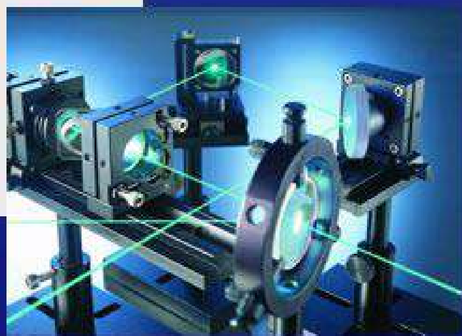
Laser ablation:



Local heating and vaporization



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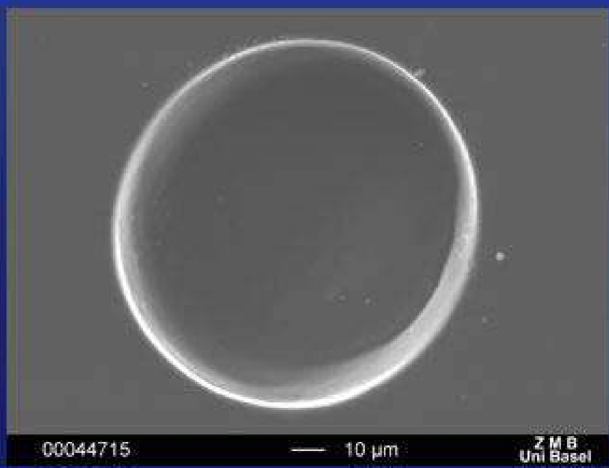
Laser ablation

Important factors for analysis:
- laser wavelength (e.g. 193 nm)
- laser energy (mJ)
- ablation spot geometry
- ablation spot diameter and depth
- ablation pulse length and rate



SEM picture of a laser drill hole

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Inductively Coupled Plasma

Important factors:
- plasma flame stability
- carrier gas
- particle size
- ± complete combustion of particles

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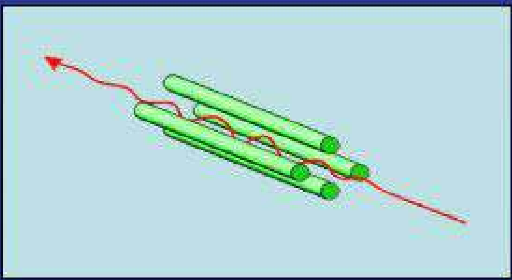
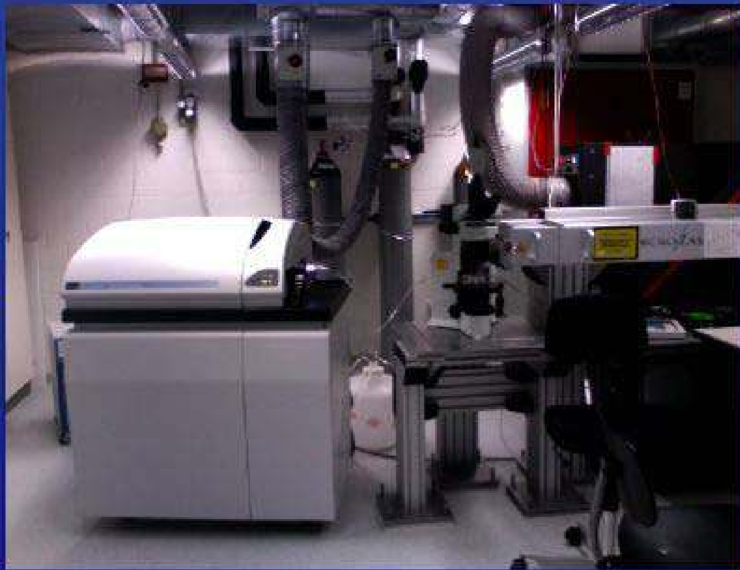
Mass spectrometer

Important factors:
- ions (isotopes) are detected on the basis of their mass/charge ratio
- Beware of superpositions by recombined molecules
  (eg. ArO interferes with ^{55}Mn, and ^{56}Fe)



Quadrupole MS



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Measuring

- the samples are positioned in the sample chamber together with the standards.
- the sample chamber is then connected with the tubes for floating with the carrier gas.

Paraiba-tourmalines from Brazil, prepared for testing with LA ICP MS

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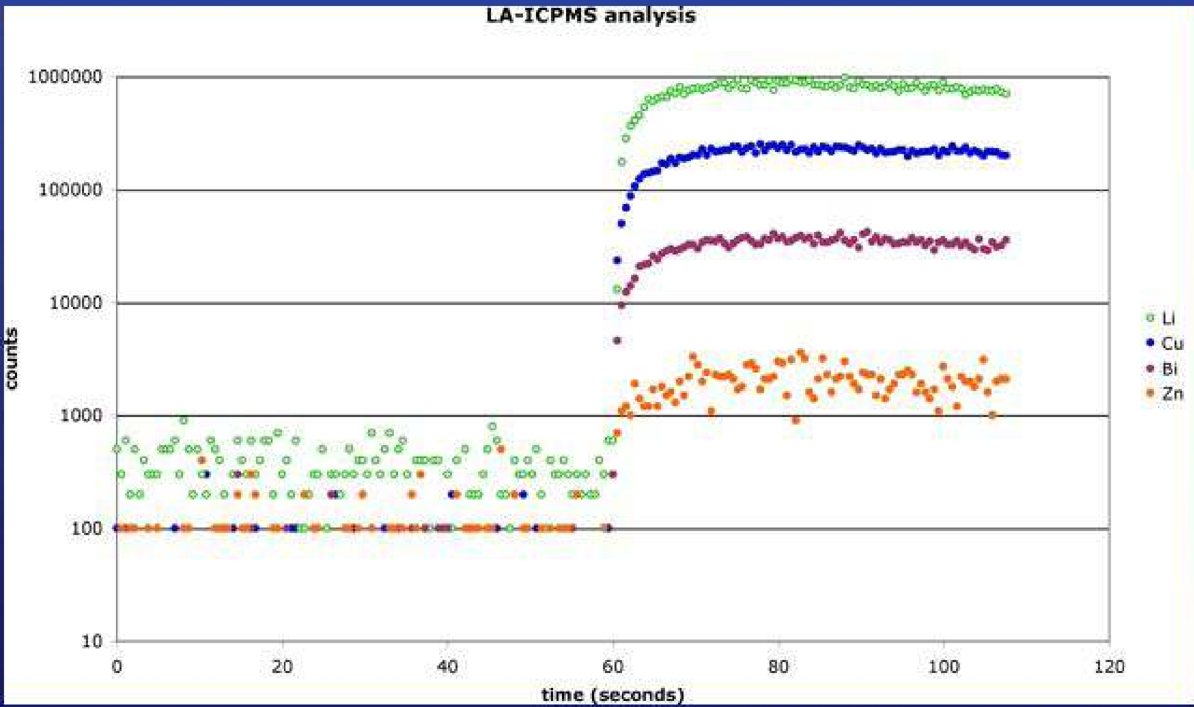
What do we get?

Chemical concentration signal versus time



Raw data has to be processed...

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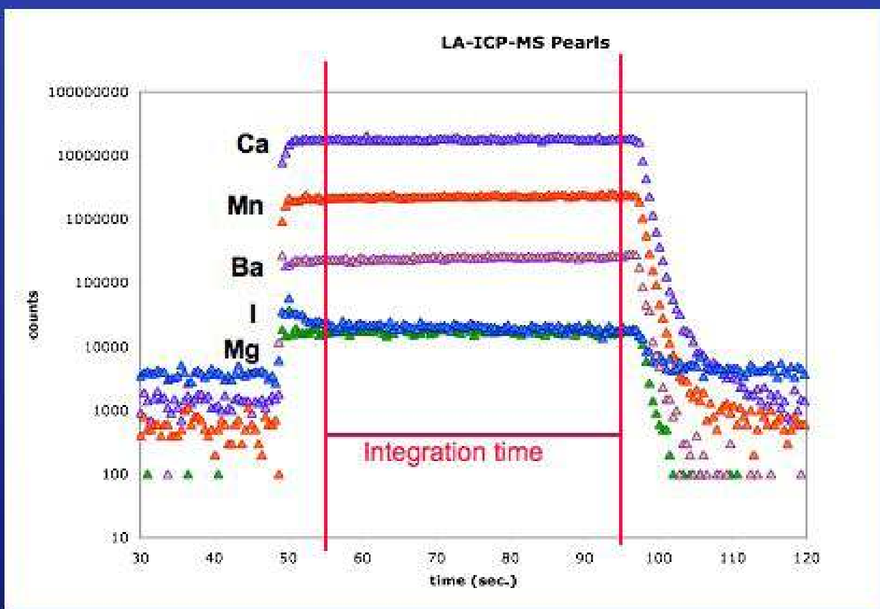
Data processing

Using Lamtrace program by S.E. Jackson

homogeneous signal



Careful setting of integrals for data processing is important

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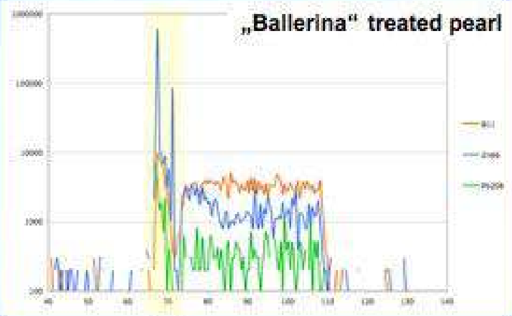
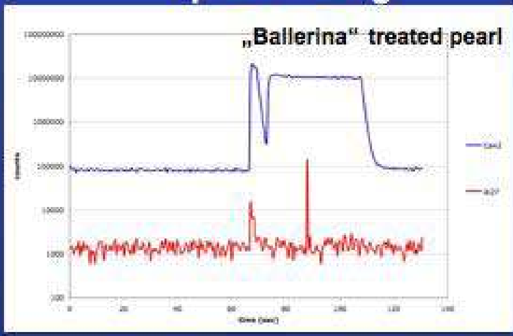
Data processing

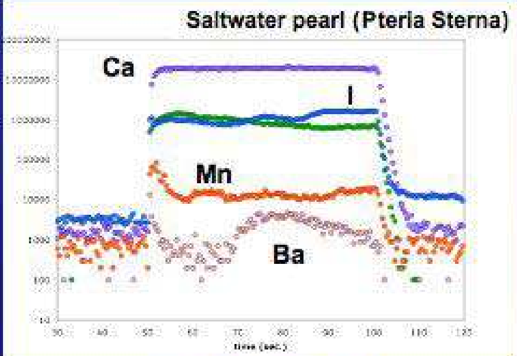
Using Lamtrace program by S.E. Jackson

Surface contamination

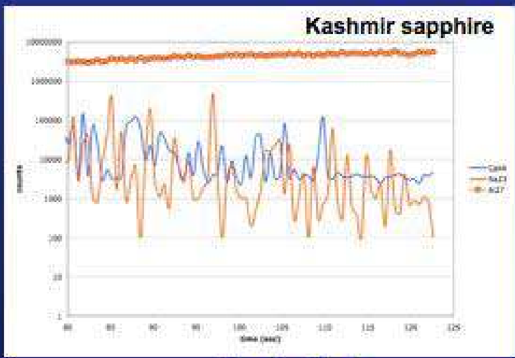


Spike filtering





zoned signal



Included

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What do we get?

Quantitative chemical data

ORIGIN	Li_2O wt%	Be ppm	B_2O_3 wt%	Na_2O wt%	Mg ppm	Al_2O_3 wt%	K ppm	CaO wt%	Sc ppm	Ti ppm	V ppm
Mozambique	1.392	14.793	5.597	2.468	0.494488	42.3	171.8	0.27936	1.598	261.25	1.056
Mozambique	1.393	14.566	5.571	2.638	0.349761	40.3	190.3	0.24024	1.657	561.70	1.795
Mozambique	1.392	14.793	5.597	2.468	0.494488	42.3	171.8	0.27936	1.598	261.25	1.056
Mozambique	1.698	3.550	5.667	2.446	1.380952	41.1	199.0	0.08619	2.755	425.80	1.117
Mozambique	1.326	6.382	5.464	2.098	0.304554	44.6	141.0	0.10261	1.446	19.64	0.362
Mozambique	2.043	6.187	5.252	1.946	0.476398	42.9	122.2	0.14390	0.765	6.35	0.204

ORIGIN	MnO wt%	Fe ppm	Ni ppm	CuO wt%	Zn ppm	Ga ppm	Sr ppm	Nb ppm	Sn ppm	Ta ppm	Pb ppm	Bi ppm
Mozambique	3.847	130.976	2.557	0.363	7.309	379	0.211	2.153	7.555	1.003	40.0	252.038
Mozambique	4.308	152.740	2.504	0.583	14.613	378	0.262	1.614	6.989	0.766	37.1	228.025
Mozambique	3.847	130.976	2.557	0.363	7.309	379	0.211	2.153	7.555	1.003	40.0	252.038
Mozambique	3.960	950.372	1.955	0.225	54.830	418	0.081	0.444	6.940	0.350	8.1	25.444
Mozambique	1.188	10.968	1.466	0.177	0.933	446	0.027	0.849	4.612	0.540	8.3	49.574
Mozambique	0.125	14.520	<0.785	0.036	0.532	533	<0.017	1.107	4.982	0.516	7.1	64.244

ORIGIN	MnO wt%	Fe ppm	Ni ppm	CuO wt%	Zn ppm	Ga ppm	Sr ppm	Nb ppm	Sn ppm	Ta ppm	Pb ppm	Bi ppm
Mozambique	3.847	130.976	2.557	0.363	7.309	379	0.211	2.153	7.555	1.003	40.0	252.038
Mozambique	4.308	152.740	2.504	0.583	14.613	378	0.262	1.614	6.989	0.766	37.1	228.025
Mozambique	3.847	130.976	2.557	0.363	7.309	379	0.211	2.153	7.555	1.003	40.0	252.038
Mozambique	3.960	950.372	1.955	0.225	54.830	418	0.081	0.444	6.940	0.350	8.1	25.444
Mozambique	1.188	10.968	1.466	0.177	0.933	446	0.027	0.849	4.612	0.540	8.3	49.574
Mozambique	0.125	14.520	<0.785	0.036	0.532	533	<0.017	1.107	4.982	0.516	7.1	64.244

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Research at SSEF using LA-ICP-MS

- Beryllium-diffusion treated orange sapphires
- Beryllium diffusion treated blue sapphires
- Beryllium in untreated sapphires
- Chrysoberyl grown on sapphire
- Alexandrite from different origins
- Emeralds from different origins
- Pezzottaite from Madagascar and Afghanistan
- Shells, Pearls and treated pearls
- Musgravite and Taaffeite
- Vanadium tourmaline from Madagascar
- Cu-Mn bearing tourmaline from Brazil, Nigeria and Mozambique
- Colour zoning in corundum
- Spinels from different origins

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1. Example: beryllium diffusion treated orange sapphire

Sapphire: LA-ICPMS Resultate

Comments	Be	Na	Mg	Al2O3	Si	P	Ti	V	Cr	Mn	Fe	Zn	Ga	Zr
measured mass	9.00	23.00	25	27.0	29	31	49	51.0	53.0	55.00	57	66.0	71	90.000
	ppm	ppm	ppm	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Saph K, profile, rim	6.55	0.37	65	99.8	222	12	76	12.5	423.2	0.15	1516	0.8	54	<0.013
Saph K, profile	6.97	0.37	63	99.8	159	10	75	12.5	413.5	<0.30	1516	0.6	54	<0.008
Saph K, profile	5.02	<0.37	71	99.8	173	11	78	13.4	453.9	<0.31	1702	0.7	57	<0.015
Saph K, profile	4.74	1.41	74	99.8	192	12	80	14.2	482.1	<0.49	1803	0.9	62	<0.015
Saph K, profile	3.31	0.82	71	99.8	251	13	79	14.2	468.0	<0.39	1889	0.8	61	<0.016
Saph K, profile	4.22	0.89	72	99.8	212	15	82	14.6	475.8	<0.31	1819	0.7	62	<0.026
Saph K, profile	3.10	<0.82	69	99.8	157	14	83	14.9	485.6	<0.68	1866	1.0	63	<0.027
Saph K, profile, core	1.98	<0.74	67	99.8	243	15	74	14.5	474.9	<0.41	1858	0.9	62	0.017
Saph K, profile, core	2.86	0.74	68	99.8	200	13	77	14.1	468.9	<0.54	1842	1.1	60	<0.022
Saph K, profile	2.60	0.74	72	99.8	237	13	81	14.4	500.1	<0.31	1912	1.2	64	<0.024
Saph K, profile	4.18	1.41	65	99.8	218	13	79	14.1	478.8	<0.49	1990	0.7	61	0.026
Saph K, profile	4.28	0.89	66	99.8	176	10	77	13.3	441.5	<0.39	1757	0.7	57	<0.013
Saph K, profile	5.11	1.19	64	99.8	151	11	77	15.3	464.5	<0.31	1702	1.0	55	<0.013

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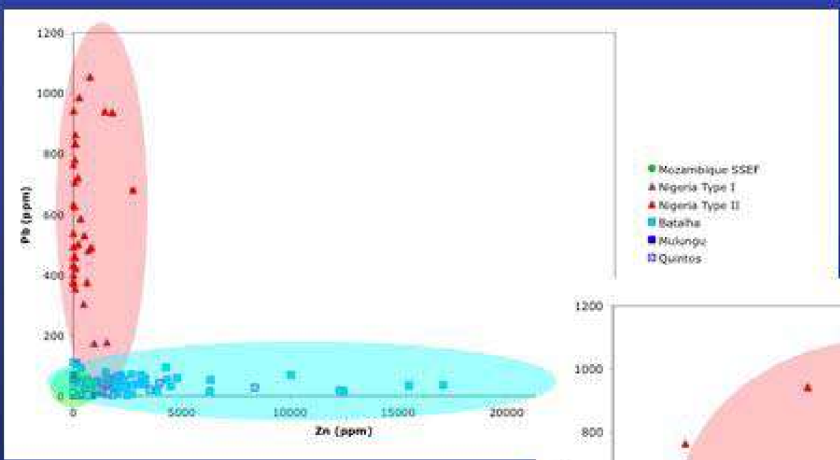
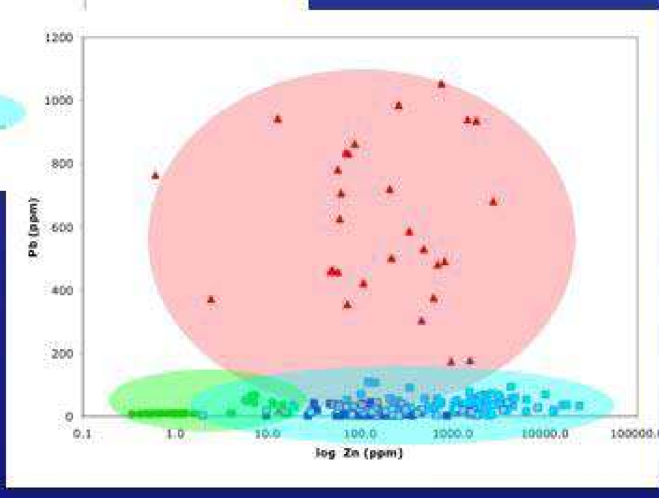
Copper-bearing Tourmaline („Paraiba“)

LA ICP MS analysis of „Paraiba“ tourmaline:

Pb versus Zn (ppm)





The effect of a logarithmic scale

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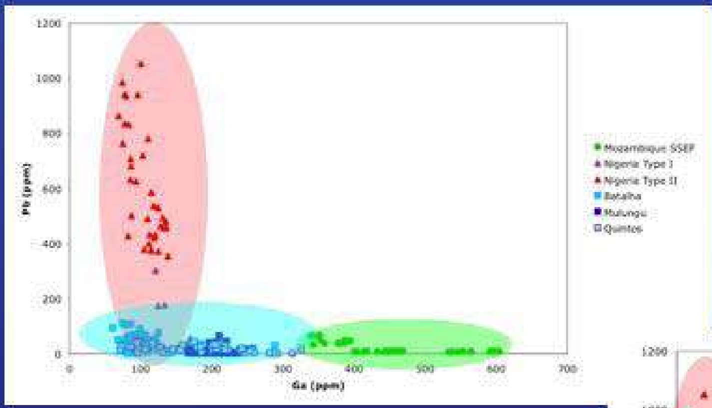
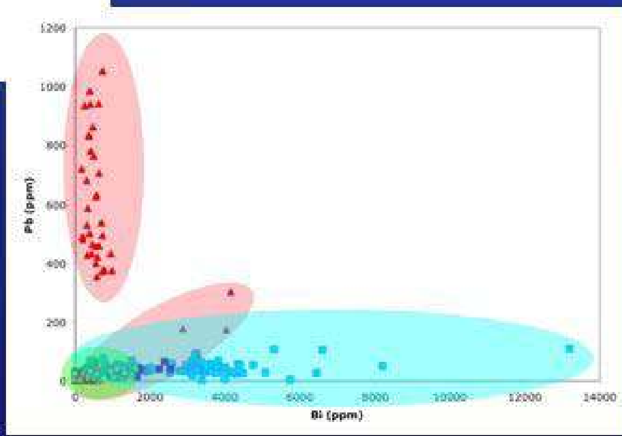
LA ICP MS analysis of „Paraiba“ tourmaline:

Pb versus Ga (ppm)



Pb versus Bi (ppm)



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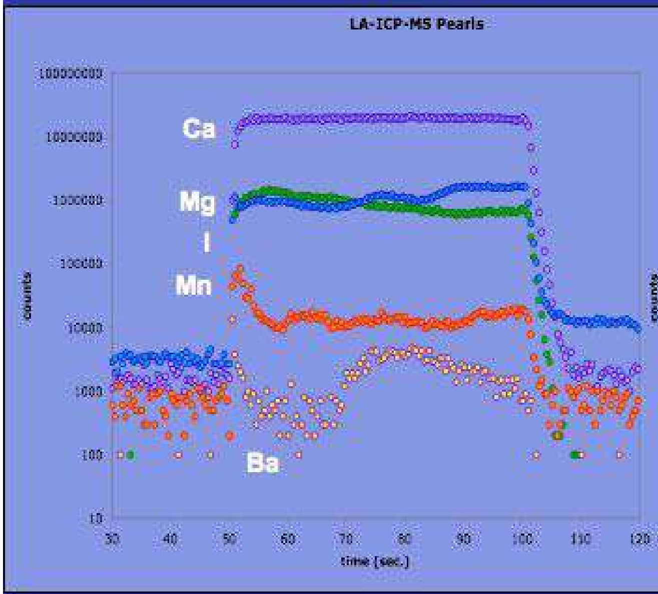
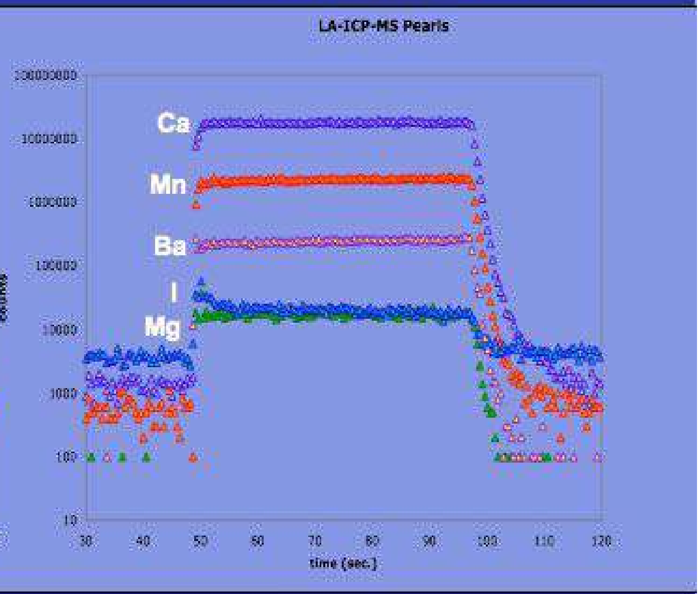
LA ICP MS analysis of Pearls

Saltwater pearl (Pteria Sterna) | freshwater pearl (China, Hyriopsis)





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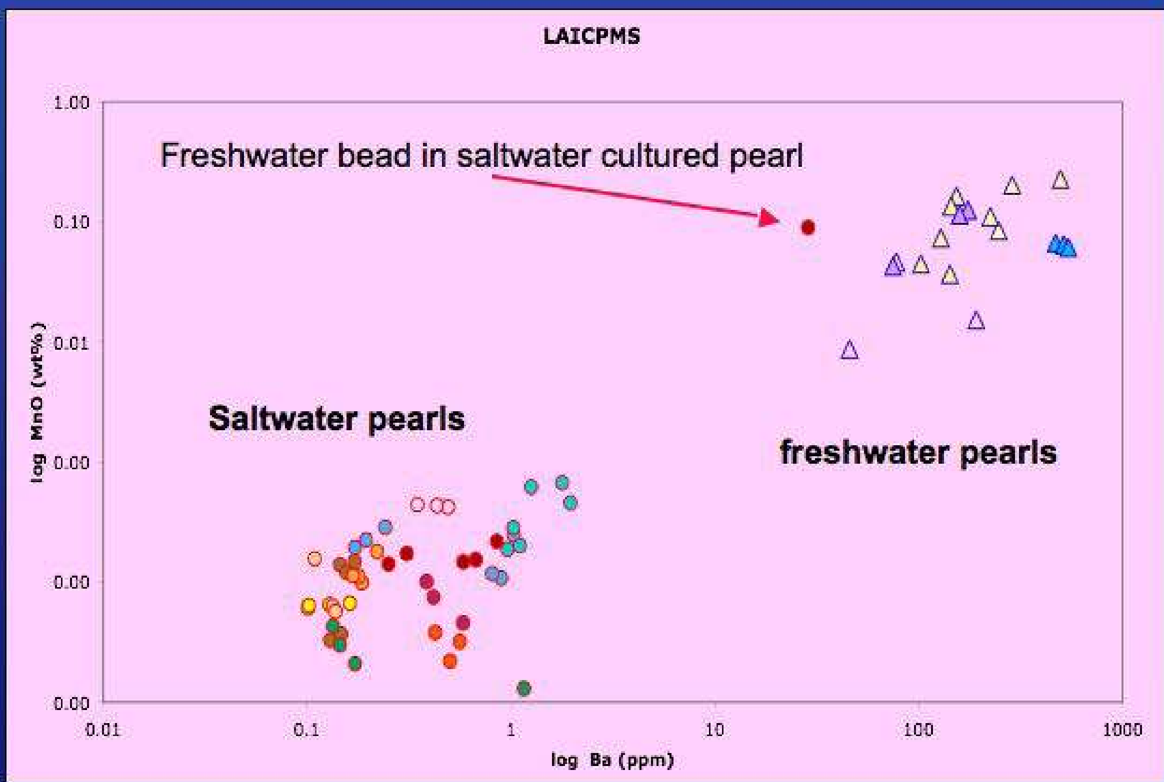
LA ICP MS analysis of Pearls



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Unheated sapphire from Kashmir of 42.29 ct

Colour zoning in corundum

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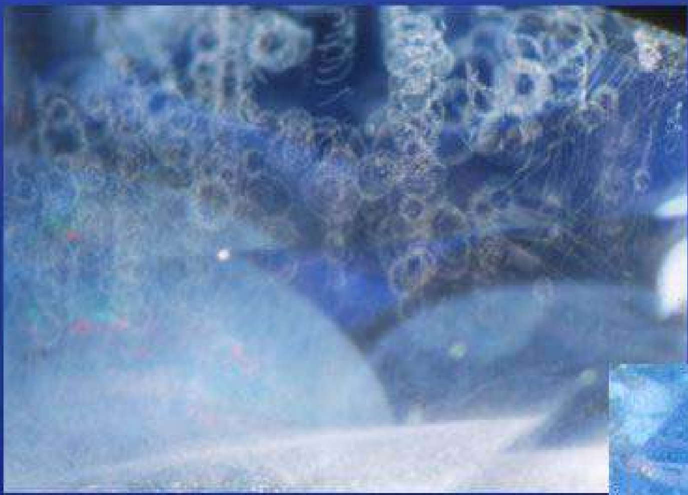
Beryllium in sapphire

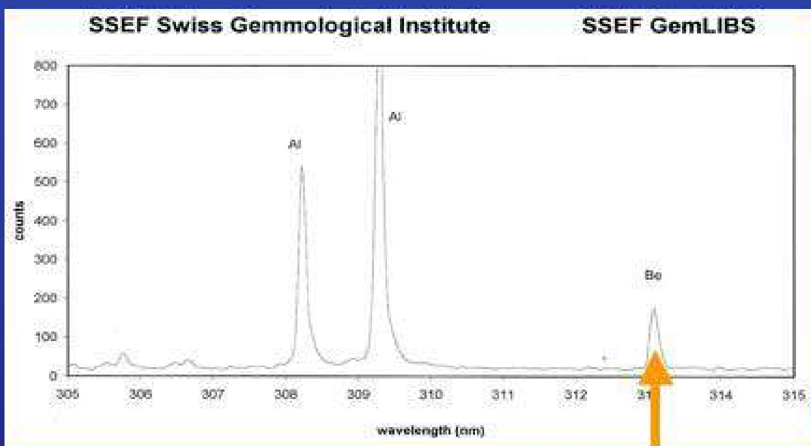


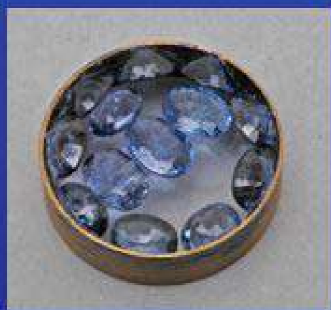
3-dimensional jellyfish-like internal structures in Be-diffusion treated sapphires.
© GAAJ

Planar curved structures in basaltic sapphire

© SSEF Swiss Gemmological Institute

Beryllium in diffusion treated sapphire





LLD FACTOR = 1

LAM-ICP-MS RESULTS - DETECTION LIMIT FILTERED
user = Be diffusion treated sapphires (Gübelin-SSEF project); f
spike, inclusions and surface contamination filtered data !!

	samples	wt%	colour	origin	inclusions cloudy diffusion features & curved dust tracks	LAICPMS Be concentration	Filter = <1 X LLD Isotopic mass Comments	Li 7 ppm	Be 9 ppm	B 11 ppm	Na2O 23 wt%	MgO 25 wt%	Al2O3 27 wt%
22nog12	SNBL Be_01	0.796	blue		distinct	moderate		0.156	7.507	2.859	0.000007	0.00870	99.8
22nog13								<0.339	8.114	4.675	0.000187	0.01016	99.8
22nog14								<0.135	5.511	3.049	0.000022	0.00927	99.8
22nog06	SNBL Be_02	0.811	blue		moderate	moderate		<0.264	9.078	4.587	<0.000007	0.00858	99.8
22nog07								<0.256	7.676	5.574	0.000041	0.00948	99.8
22nog08							Na contamination	<0.214	8.708	4.864	0.000126	0.01054	99.8

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Beryllium in untreated sapphire

Some sapphires may contain locally low amounts of beryllium.

LAM-ICP-MS RESULTS - DETECTION LIMIT FILTERED
user = GAAJ and Vincent sapphires, Madagascar, no heat, file = 21fea0

	Comments	Filter = <1	Li	Be	B	Na2O	MgO	Al2O3
LLD FACTOR =	1	Isotopic m	7	9	11	23	25	27
			ppm	ppm	ppm	wt%	wt%	wt%
21fea15	MIMK 005, 120 um		<0.073	0.312	0.556	<0.000005	0.002004	99
21fea16			<0.157	<0.280	0.747	<0.000005	0.002797	99
21fea17			<0.194	<0.474	<0.426	<0.000005	0.003125	99
21fea18			<0.169	<0.328	0.580	<0.000004	0.003442	99
21feb03	MIMK002, 120 um		<0.220	<0.439	<0.797	<0.000007	0.00365	99
21feb04			<0.273	<0.572	<0.607	<0.000006	0.00437	99
21feb05			<0.112	<0.416	<1.112	<0.000006	0.00431	99
21feb12	MIMK004, 120 um		<0.251	<0.613	0.677	0.000009	0.02340	99
21feb13			<0.357	<0.694	<0.870	<0.000007	0.01699	99
21feb14			<0.404	2.004	<1.144	<0.000009	0.03307	99
21feb15			<0.170	<0.551	<0.892	<0.000010	0.01832	99
21feb16			0.296	1.446	<1.028	0.000008	0.03156	99

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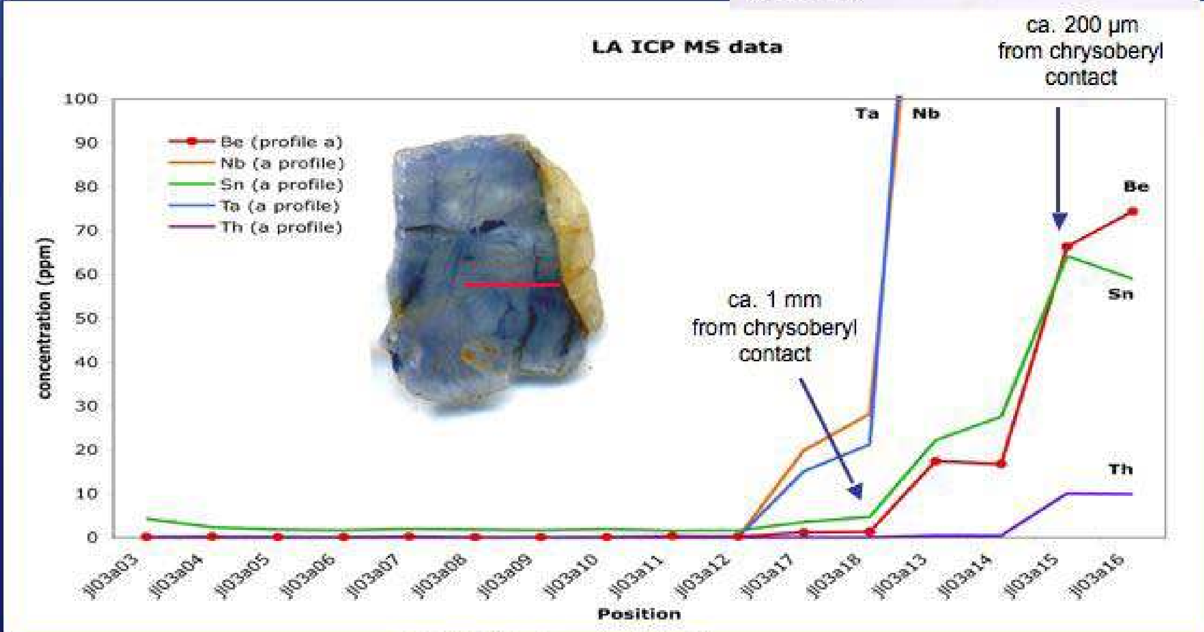
Chrysoberyl on Sapphire



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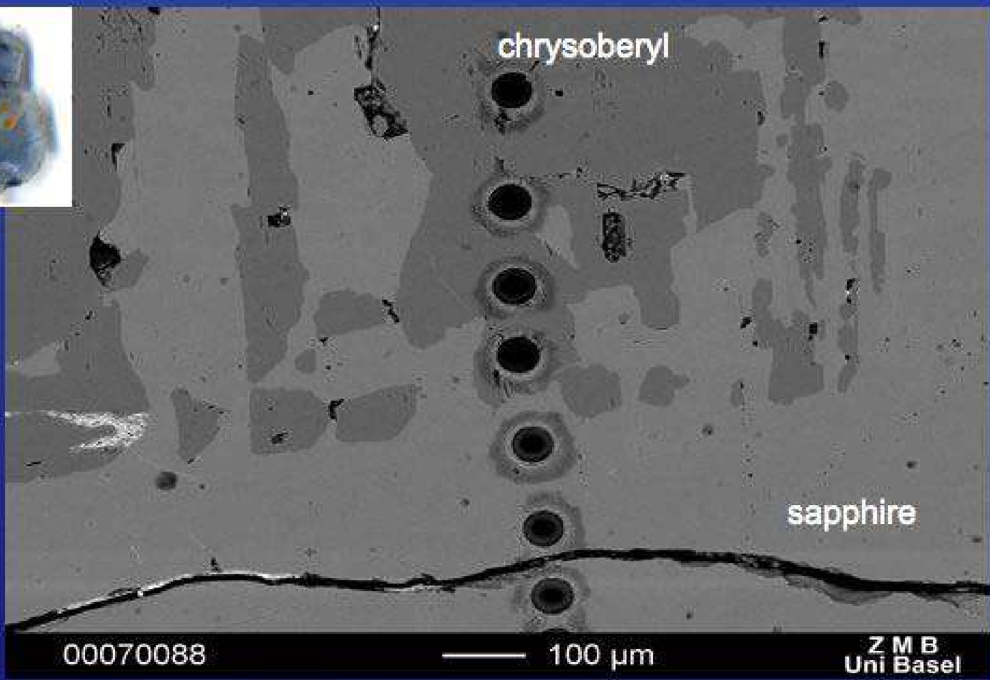
Chrysoberyl on Sapphire



SEM micrographs (backscattered electrons), showing a dense syngenetic intergrowth of chrysoberyl with sapphire

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Last week in Sri Lanka...

Thank you for your attention

Prof. Thomas Pettke, dipl. min. Pierre Lefèvre, and Dr. Michael S. Krzemnicki at the LA-ICP-MS in the Institute of Geological Sciences, University of Bern (Switzerland).

before... ...and after a LA-ICP-MS session

SSEF offers LA-ICP-MS course for gemmologists in August 2009 !