


# Assessment of Provenance of Conflict Minerals using the Materialytics Sequencing System (M2S)



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# Prediction of Country of Origin – 98%

10 minerals, 3209 Samples

Material	Chemical Formula	Accuracy in Identifying Country of Origin	Number of Localities
Cassiterite	$\text{SnO}_2$	100%	6
Columbite-Tantalite	$(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$	97%	7
Diamond	C	95%	8
Emerald	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$	98%	10
Gold	Au	100%	3
Ruby	$\text{Al}_2\text{O}_3$	98%	23
Sapphire	$\text{Al}_2\text{O}_3$	98%	17
Tourmaline	$(\text{Na}, \text{Ca}) (\text{Fe}^{2+}, \text{Mg}, \text{Li}, \text{Al})_3 (\text{Al}, \text{Fe}^{3+})_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 \text{OH}_3 (\text{F}, \text{O}, \text{OH})$	98%	7
Wolframite	$(\text{Fe}, \text{Mn})\text{WO}_4$	100%	3

# The Answer is “n”

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- ❑ Many variables;  $n = 40,000$
- ❑ Many samples;  $n = 50,000$  (not all analyzed yet)
- ❑ Before discovering this answer, we started where everyone else does

The idea for this project began in the summer of 2002 with the goal of tracing a gemstone back to its host pegmatite using Laser Induced Breakdown Spectroscopy (LIBS), as a way to inhibit illicit financing.

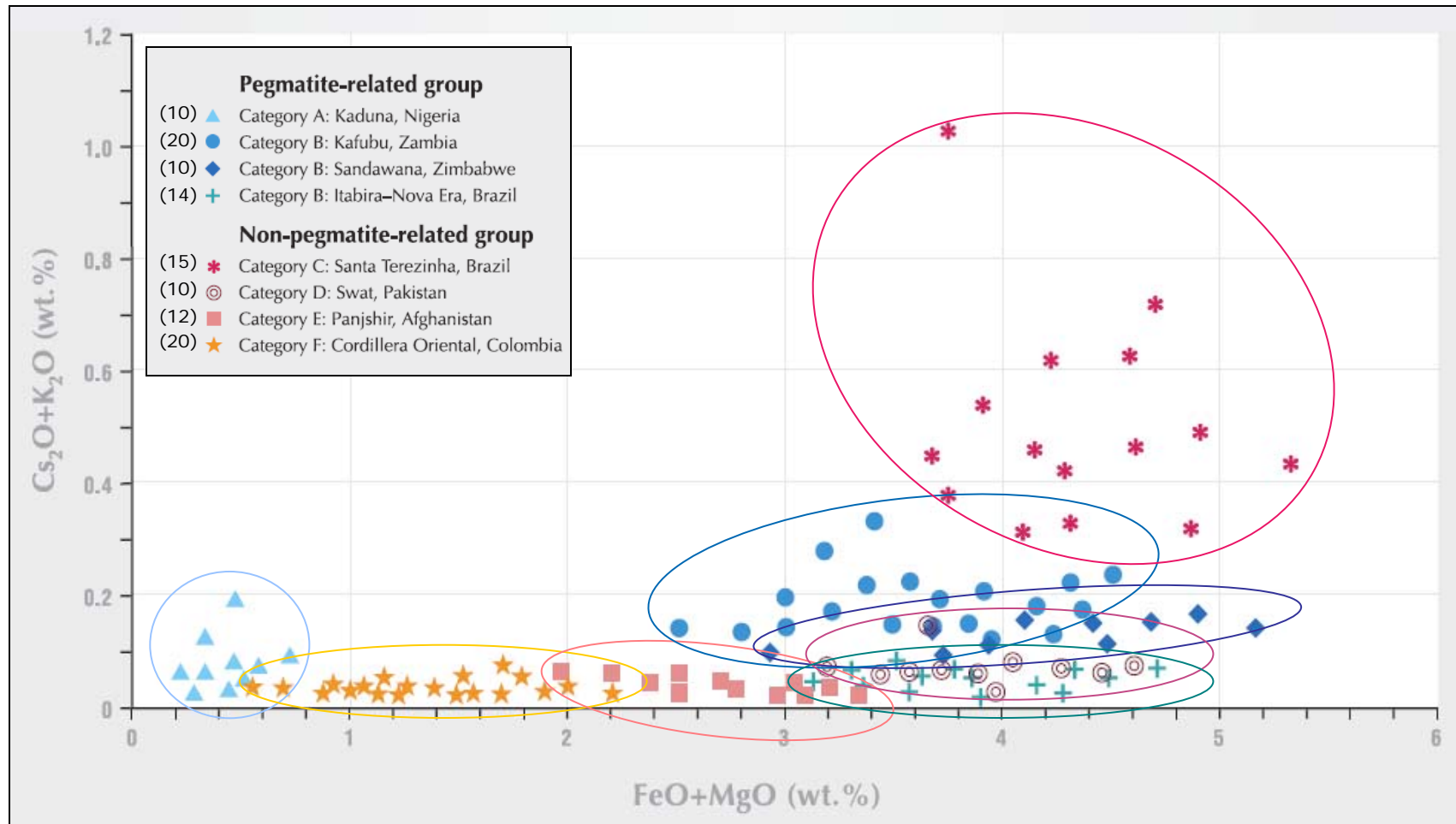


# GSA 2004

- Presented our first round of findings in a poster titled "Trace Element Concentrations of Pegmatite Gems: Tracers of Petrogenesis and Illicit Funding."
- We had 21 samples from 8 countries.
- We approached this question from an Igneous Petrology/Geochemistry perspective so we reported the following element ratios:

Ratio	Palermo #1 (11 Samples)	Worldwide (10 Samples)
Fe/Zr	(1.42-2.53)	(0.89-1.51)
Fe/Ti	(1.28-4.22)	(0.85-1.40)
Fe/Mg	(1.27-9.99)	(0.70-1.60)

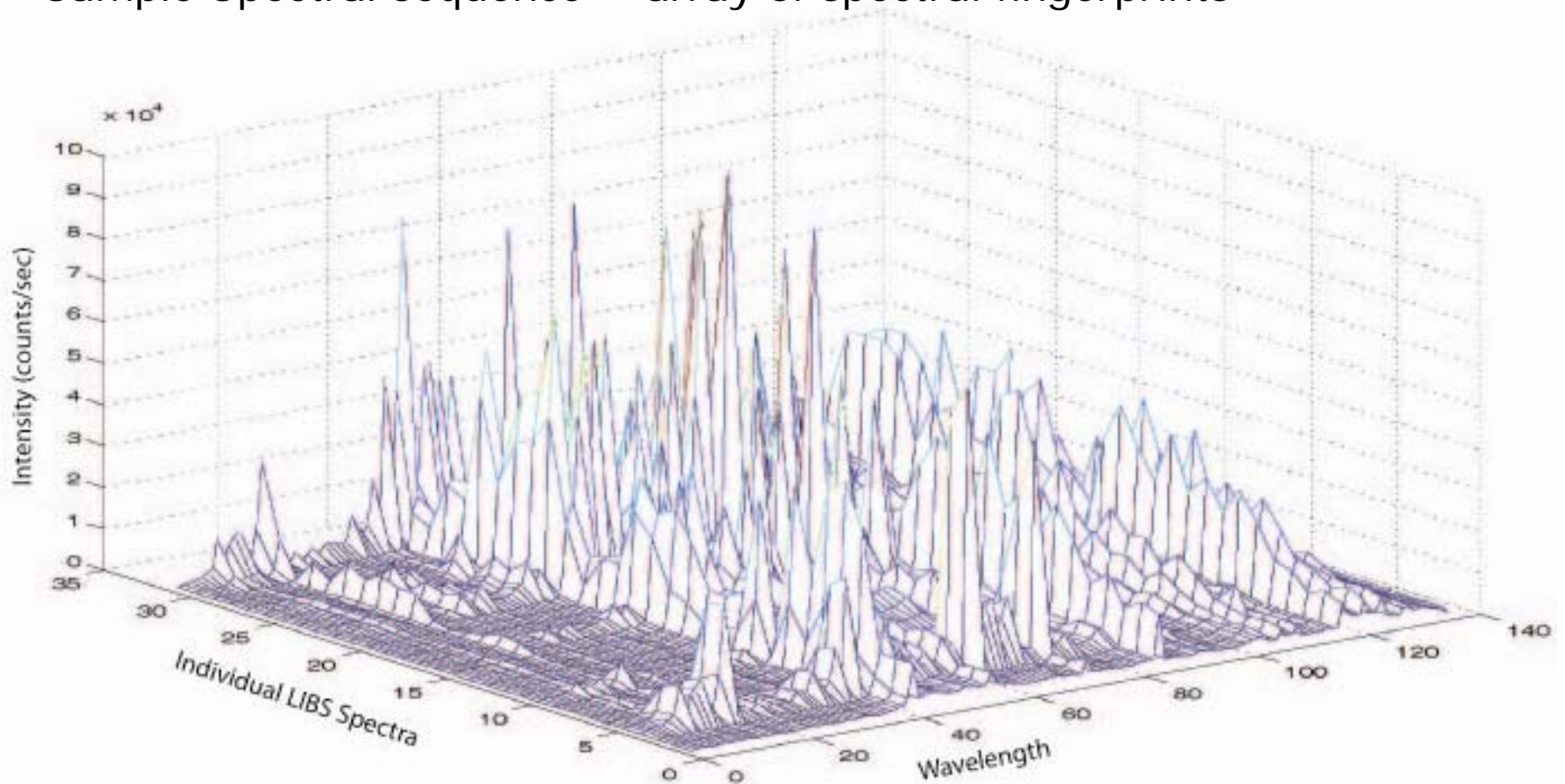
# How traditional geochemistry addresses the question of provenance.



(Abduriyim, A. & Kitawaki, H. (2006) Applications of laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) to gemology. *Gems & Gemology*, Vol. 42, No. 2, pp 98–118 )

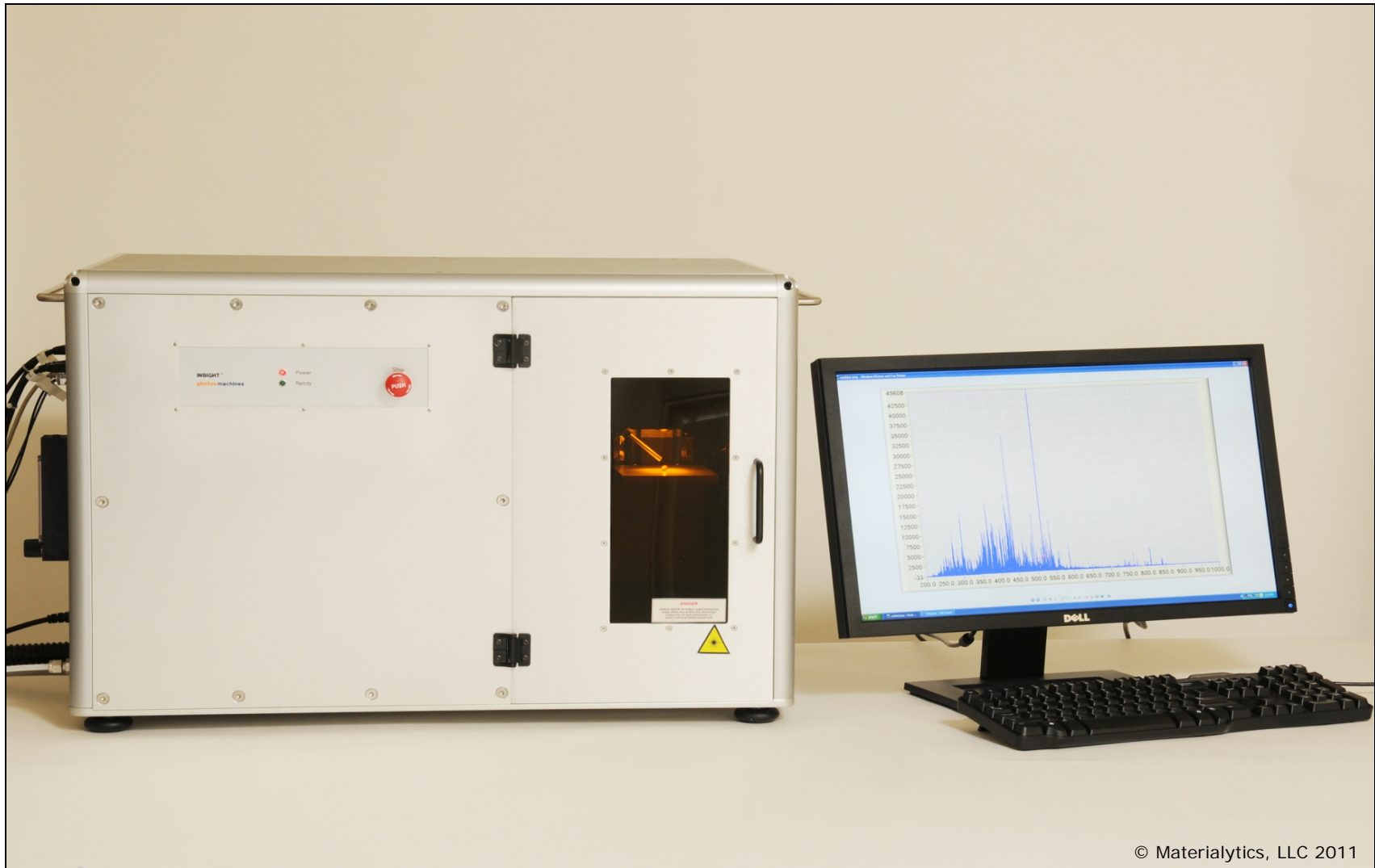
# How M2S address the question of provenance.

Sample Spectral sequence = array of spectral fingerprints

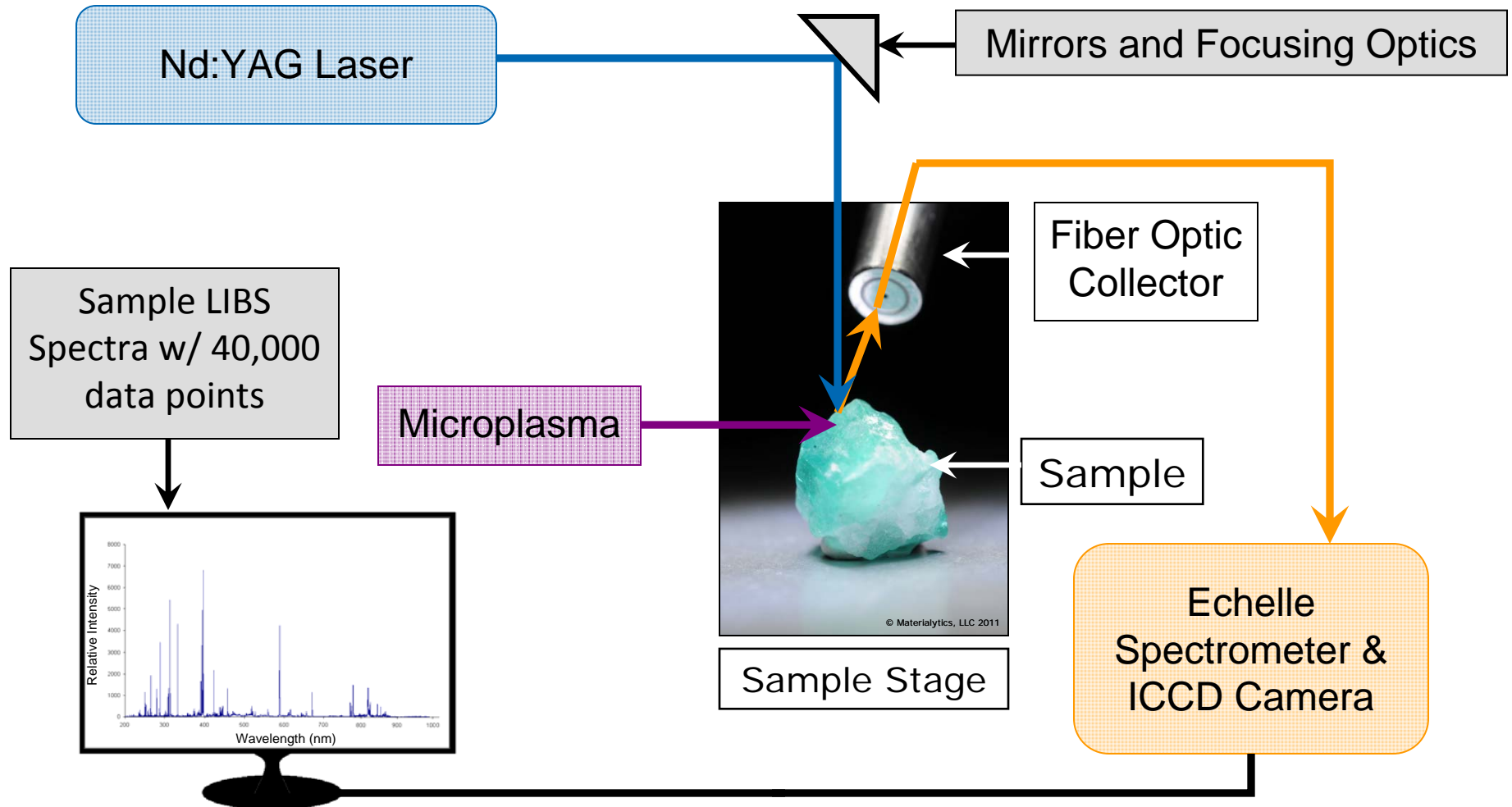




# Laser Induced Breakdown Spectroscopy



# How a LIBS system works.





# Adaptive Pattern Recognition

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- ❑ For every shot collected we collect tens of thousands of data points.
- ❑ For comparison, LA-ICP-MS collects approximately 30 data points\*.
- ❑ We collect tens of shots per sample, for a total of more than 2 million data points per sample.
- ❑ We use over 70 million data points to begin to characterize a locality.
- ❑ No model building

\*Abduriyim, A. & Kitawaki, H. (2006) Applications of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to gemology. *Gems & Gemology*, Vol. 42, No. 2, pp 98–118

# Adaptive Pattern Recognition

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- Evaluation of the data indicates that the signals are both linear and non-linear.
- In many cases, there are multiple signals embedded within each spectrum.
  1. First phase: analyzes the data to determine the quality of the signal generated by the LIBS analysis, ensuring high signal to noise ratio
  2. Second phase: development of the Sequence Reference Database (SRD) using spectral sequences from known samples from known locations
  3. Third phase: matches unknown sequences to the known sequences in the SRD using Leave-One-Out-Cross-Validation and adaptive signal matching model

# More Samples



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DT# 1001 GSA Meeting 2011

- Over the past four years, we have collected:
  - Over 50,000 samples
  - Over 60 countries
  - 330 different locations
- Samples must be well collected.
- Numerous cross checks need to be in place
- If they aren't the pattern recognition software will know and will not allow the samples into the SRD

# Reduce Traces of Analysis

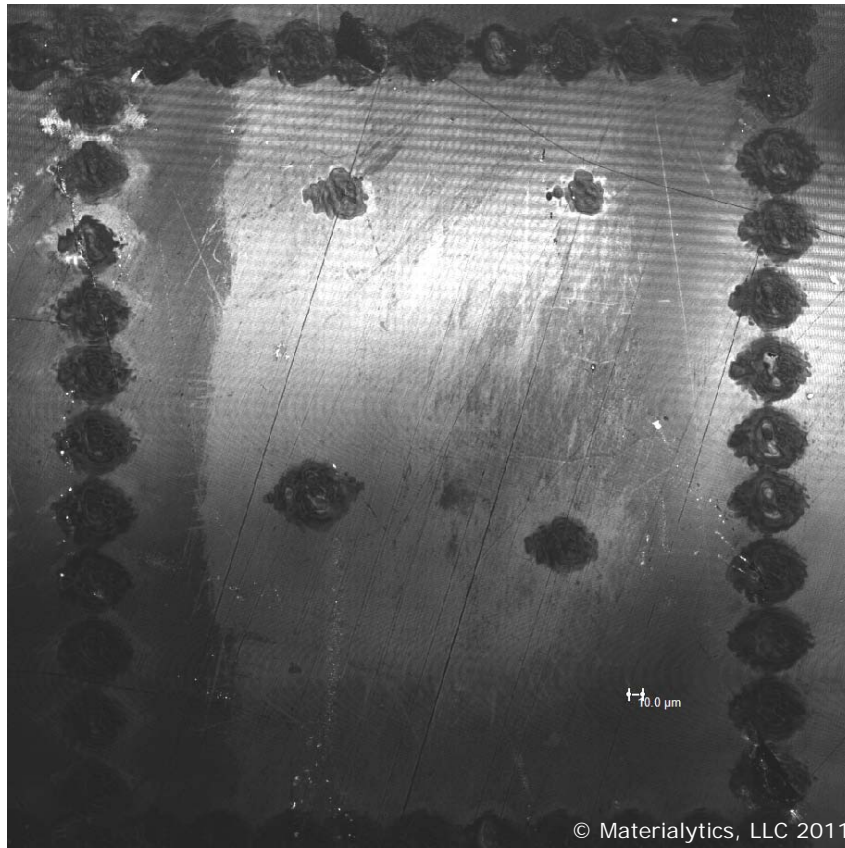


The traces of analysis range in size from sub 10 – 150 microns depending on numerous analytical conditions.

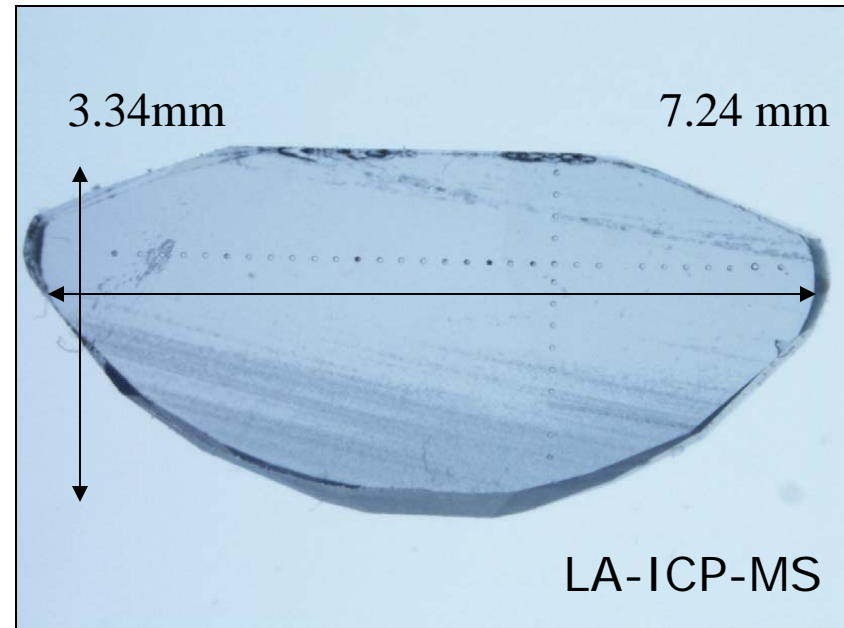
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# LIBS versus LA-ICP-MS

## Traces of Analysis Comparison



Confocal Microscope Image of M2S Analyzed Sample



DuToit, G., Thanachakaphad, J., Scarratt, K. (2009) Beryllium Treated Blue Sapphires: Continuing market observations and update including the emergence of larger size stones. June 25th 2009. *On-going Research*, <http://www.giathai.net/lab.php>



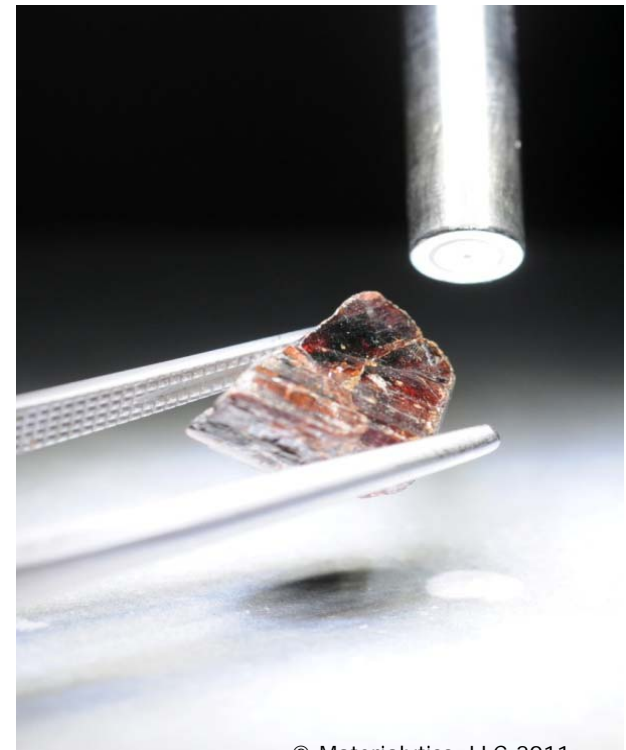
# Putting the pieces together

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- ❑ Adaptive Pattern Recognition Software
- ❑ The beginning of a statistically viable sample set
- ❑ Using an analytical technique with a lot of information
- ❑ An analysis process that leaves minimal traces of testing
- ❑ Minimum of 30 samples per location, multiple shots per sample
- ❑ LIBS analysis parameters vary based on material to ensure the maximum signal is collected

# Geomaterials Analyzed

- ❑ 2010 Dodd-Frank Act and Tom Lantos Block Burmese JADE Act of 2008
- ❑ Conflict minerals are minerals mined in conditions of armed conflict and human rights abuses:
  - **Cassiterite**
  - **Columbite**
  - Diamonds
  - Emerald
  - **Gold**
  - **Ruby**
  - Sapphire
  - **Tantalite**
  - Tourmaline
  - **Wolframite**



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# Gemstones – Small Pilot Studies

Material	Chemical Formula	Accuracy in Identifying Country of Origin	Number of Localities	Number of Samples
Diamond	C	95%	8	245
Emerald	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$	98%	10	301
Ruby	$\text{Al}_2\text{O}_3$	98%	23	912
Sapphire	$\text{Al}_2\text{O}_3$	98%	17	860
Tourmaline	$(\text{Na}, \text{Ca}) (\text{Fe}^{2+}, \text{Mg}, \text{Li}, \text{Al})_3 (\text{Al}, \text{Fe}^{3+})_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 \text{OH}_3 (\text{F}, \text{O}, \text{OH})$	98%	7	207

# Metals – Small Pilot Studies

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Material	Chemical Formula	Accuracy in Identifying Country of Origin	Number of Localities	Number of Samples
Cassiterite	$\text{SnO}_2$	100%	6	180
Columbite-Tantalite (COLTAN)	$(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$	97%	7	324
Gold	$\text{Au}$	100%	3	90
Wolframite	$(\text{Fe}, \text{Mn})\text{WO}_4$	100%	3	90

# Summary of Results - 3209 Samples

Material	Chemical Formula	Accuracy in Identifying Country of Origin
Cassiterite	$\text{SnO}_2$	100%
Columbite-Tantalite	$(\text{Fe}, \text{Mn})(\text{Nb}, \text{Ta})_2\text{O}_6$	97%
Diamond	C	95%
Emerald	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$	98%
Gold	Au	100%
Ruby	$\text{Al}_2\text{O}_3$	98%
Sapphire	$\text{Al}_2\text{O}_3$	98%
Tourmaline	$(\text{Na}, \text{Ca}) (\text{Fe}^{2+}, \text{Mg}, \text{Li}, \text{Al})_3 (\text{Al}, \text{Fe}^{3+})_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 \text{OH}_3 (\text{F}, \text{O}, \text{OH})$	98%
Wolframite	$(\text{Fe}, \text{Mn})\text{WO}_4$	100%



# The Road Ahead

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- Diversifying our Database
  - We need more samples from more locations to complete the study – Antarctica please!
- Improving our LIBS system
  - We have used and abused our LIBS system in ways the designers never could have thought of until you have put as many hours on the laser and miles (yes, miles) on the sample stage as we have.
- So far, M2S has been able to successfully analyze every material we've attempted; we're excited for what will come across our sample stage next.

# Thanks to our team of consultants!

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This was an interdisciplinary effort so thanks to our:

- Catalogers
- Combustion Engineers
- Geochemists
- Logisticians
- Mathematicians
- Optics Engineers
- Plasma Physicists
- Photographers
- Programmers
- System Operators
- Technology Team



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The road ahead is not always clear.



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