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Multi-Element Analysis of Gemstones For Country of Origin Determination

Presentation by

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SSEF

CONTENTS

MULTI-ELEMENT ANALYSIS

- LA-ICP-*TOF*-MS in an Overview

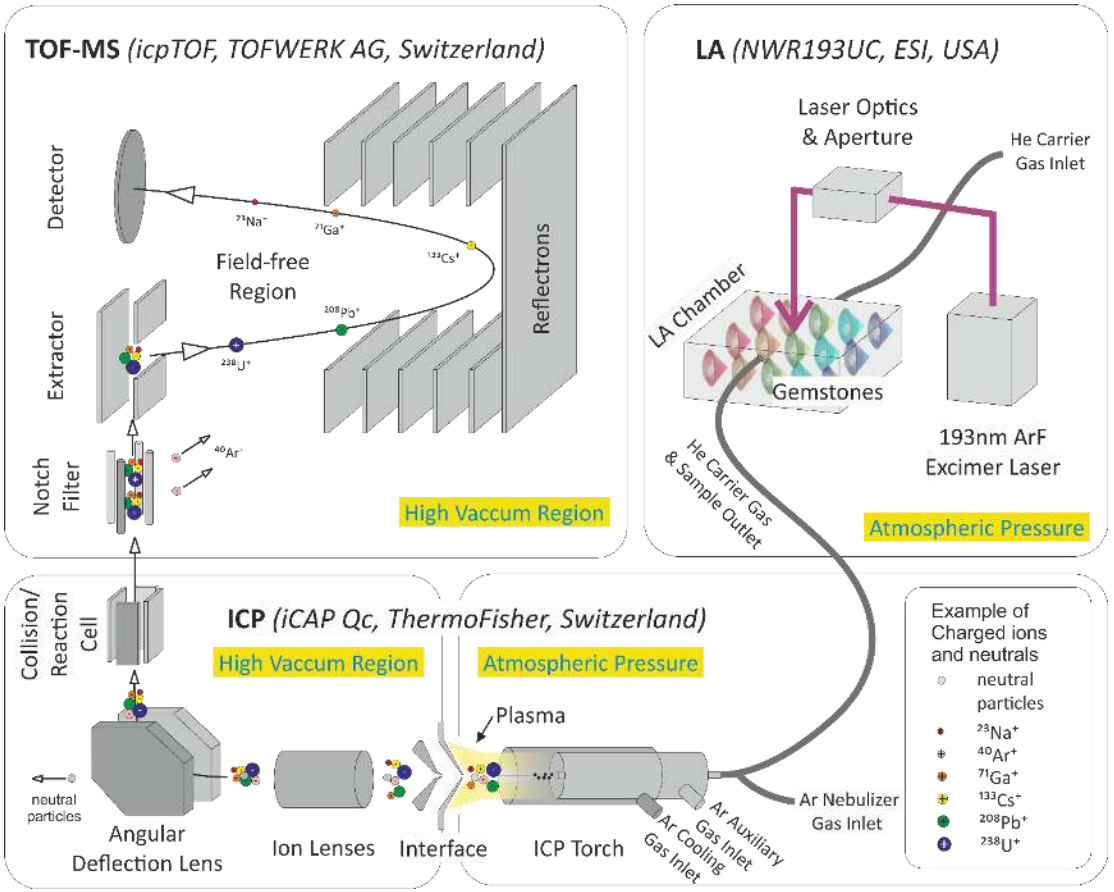
CASE STUDIES

- Blue Sapphire
- Diamond Inclusion
- Emerald
- Cu-Mn-bearing Tourmaline

Burmese ruby of 6.04 ct set in a ring by Edmond Chin (Etcetera Ltd.), sold for a world record price of US$ 551‘000 per carat (Christie‘s Hong Kong, May 2012).

SSEF report 59356 & Appendix.

LA-ICP-TOF-MS IN AN OVERVIEW



- Simultaneous Full Spectrum Acquisition (Li - U)
- Mass Resolving Power (~2500 for ^{238}U)
- Low Limit Of Detection (LOD in ppb level)

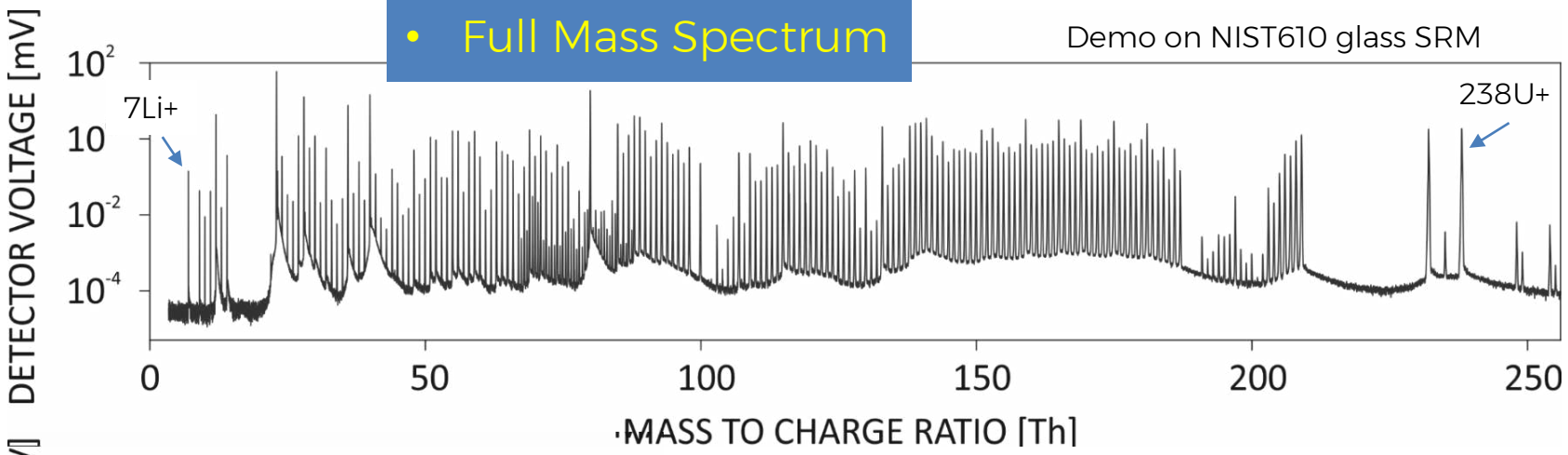
GemTOF @ SSEF
www.gemtof.ch

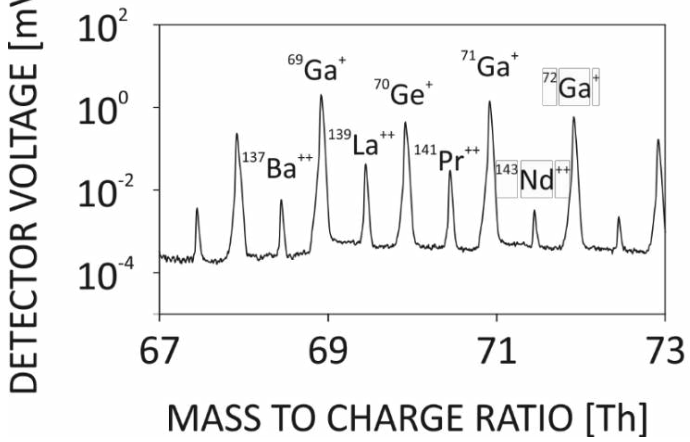
Wang, et al., Simultaneous High Sensitivity Trace- Element and Isotopic Analysis of Gemstones Using LA-ICP-TOF-MS, **Journal Of Gemmology**, *2016*

LA-ICP-TOF-MS IN AN OVERVIEW

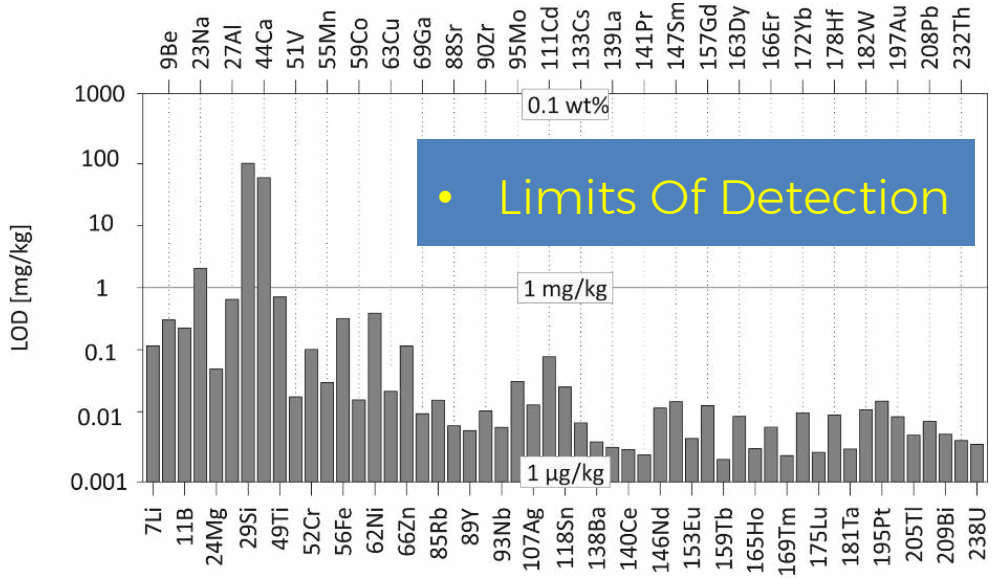
- Full Mass Spectrum

Demo on NIST610 glass SRM





- Mass Resolving Power



- Limits Of Detection

Wang, et al., Simultaneous High Sensitivity Trace- Element and Isotopic Analysis of Gemstones Using LA-ICP-TOF-MS, **Journal Of Gemmology**, *2016*

FIRST Measure, THEN Determine

MULTI-ELEMENT ANALYSIS

- Detection of Rarely Occuring Elements
- Analysis of Diamond (Coloured Gemstone) Inclusion
- Statistical Analysis of the Multi-Element Dataset

BLUE SAPPHIRE PHOTO: SSEF

RARELY OCCURING ELEMENT DETECTION

For Country of Origin Determination In Blue Sapphires

Median concentrations of most frequently occuring elements:

		Mg	Ti	V	Cr	Fe	Ga	Ge	Sn	Ta
Median Conc. [ppm]	Kashmir	28	105	***5***	1.4	***630***	***41***	0.13	***0.25***	***0.01***
	Madagascar	26	113	***11***	1.3	***1119***	***72***	0.17	***0.53***	***0.04***
Occ. Freq. [%]	Kashmir	100	100	100	99	100	100	54	100	62
	Madagascar	100	99	100	96	100	100	63	100	67

V, Fe, Ga, Sn, Ta
Madagascar > Kashmir

Occurance frequency of less frequently occuring elements:

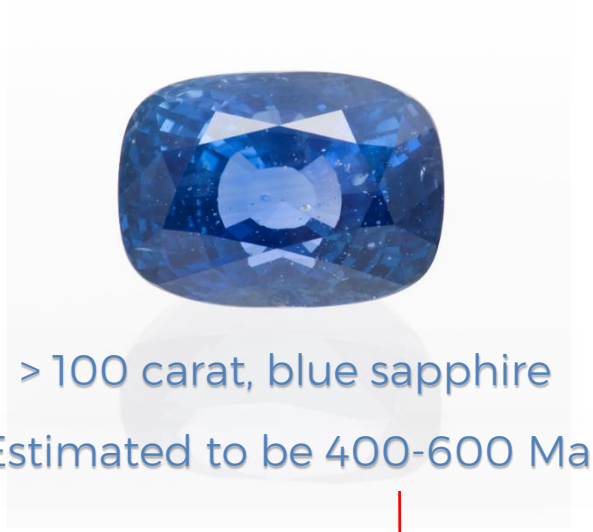
		Be	Zr	Nb	La	Ce	Hf	Th		
Median Conc. [ppm]	Kashmir	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		
	Madagascar	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD		
Occ. Freq. [%]	Kashmir	3.7	***1.7***	***4.3***	4.3	6.6	***2.9***	***6.0***		
	Madagascar	17	***42***	***46***	14	18	***35***	***31***		

Zr, Nb, Hf, Th
more often in Madagascar than Kashmir

Krzemnicki, M.S., **IGC**, *2019*

RARELY OCCURING ELEMENT DETECTION

For Direct Age Dating In Blue Sapphires



> 100 carat, blue sapphire

Estimated to be 400-600 Ma

Kashmir?
30 Ma

Madagascar?
Sri Lanka?
550 Ma

- Age Dating Calculation using NIST610 SRM
- Problem and challenges remain

After Routine Trace Element Analysis:

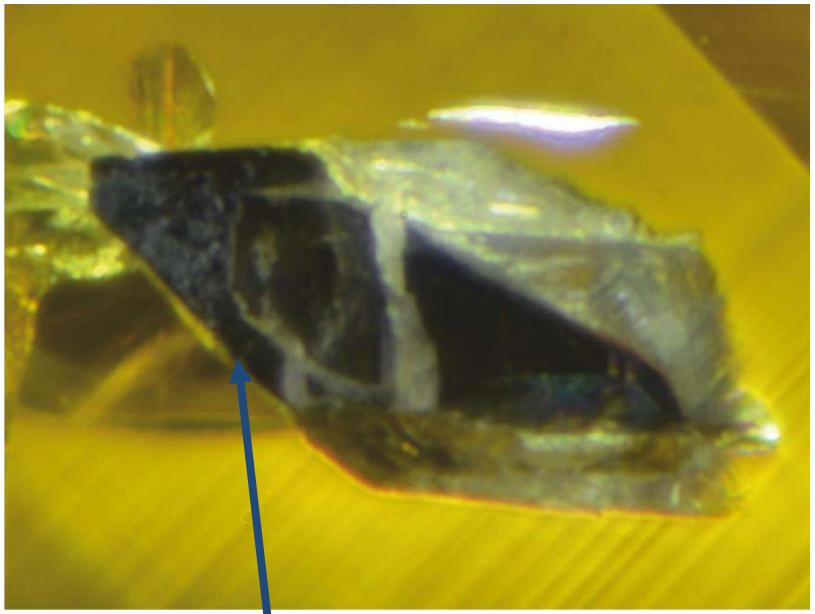
232Th —decay→ 208Pb — Sequential Measurement includes

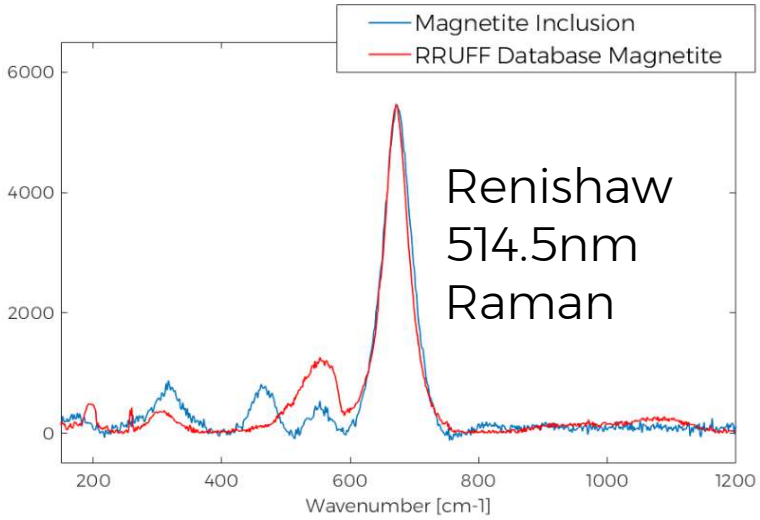
~~204Pb~~ ~~206Pb~~ ~~207Pb~~ ~~202Hg~~ ~~204Hg~~ — Simultaneous Measurement includes

DIAMOND INCLUSIONS PHOTO: SSEF

ELEMENTAL ANALYSIS OF INCLUSIONS

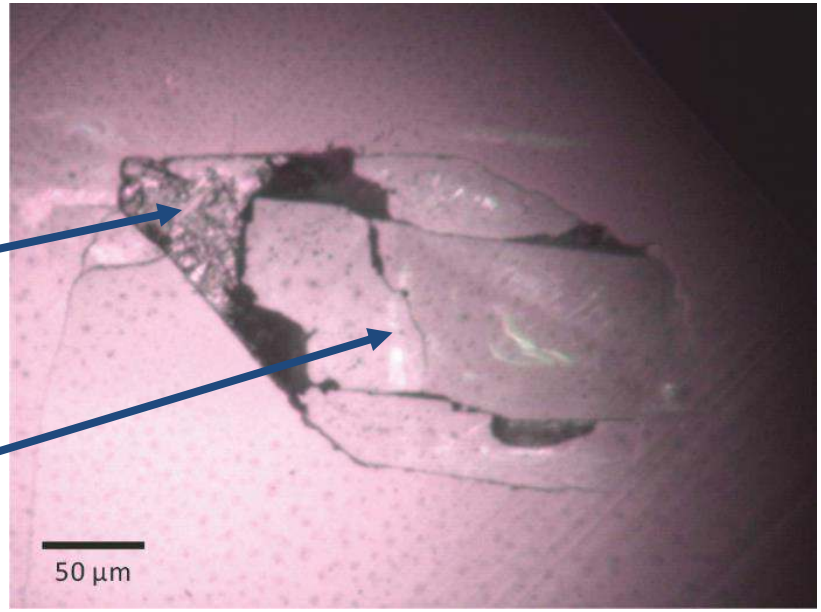
In Magnetite Inclusion in Diamond





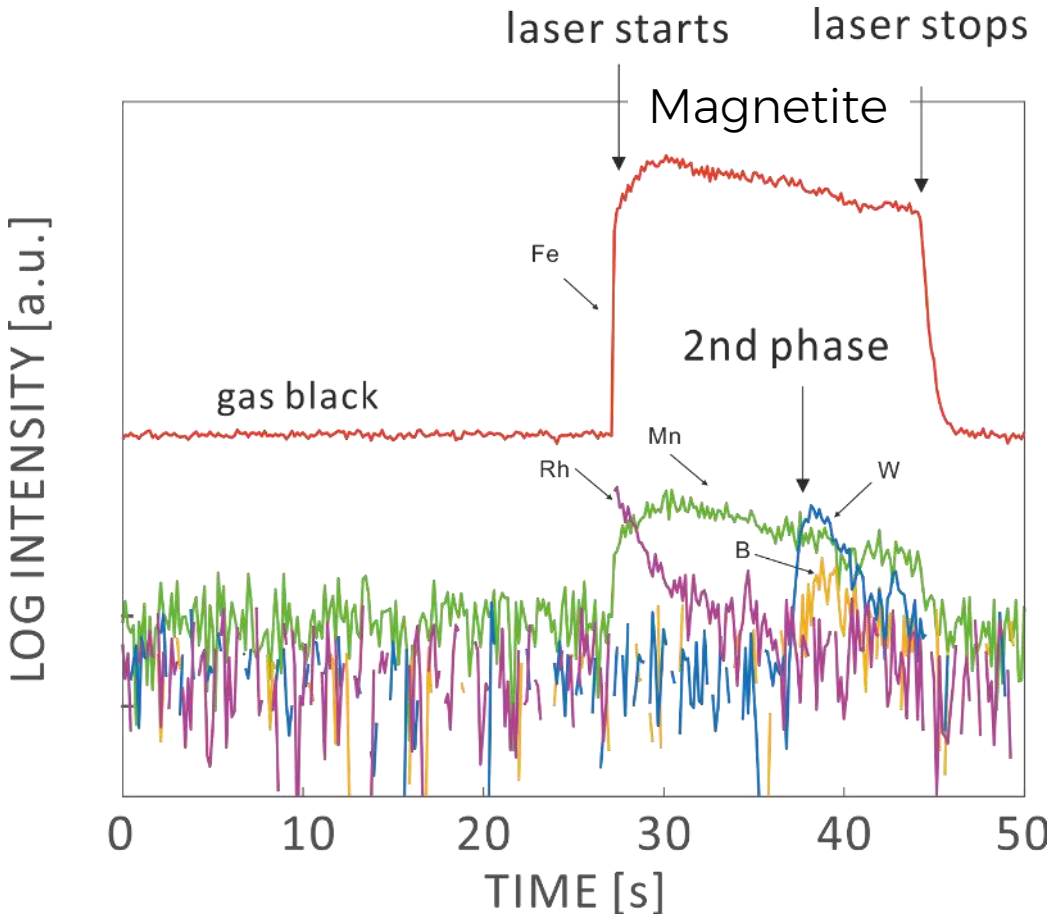
Magnetite
Fe_3O_4

Covered by
diamond



ELEMENTAL ANALYSIS OF INCLUSIONS

LA-ICP-TOF-MS Transient Signal of Magnetite

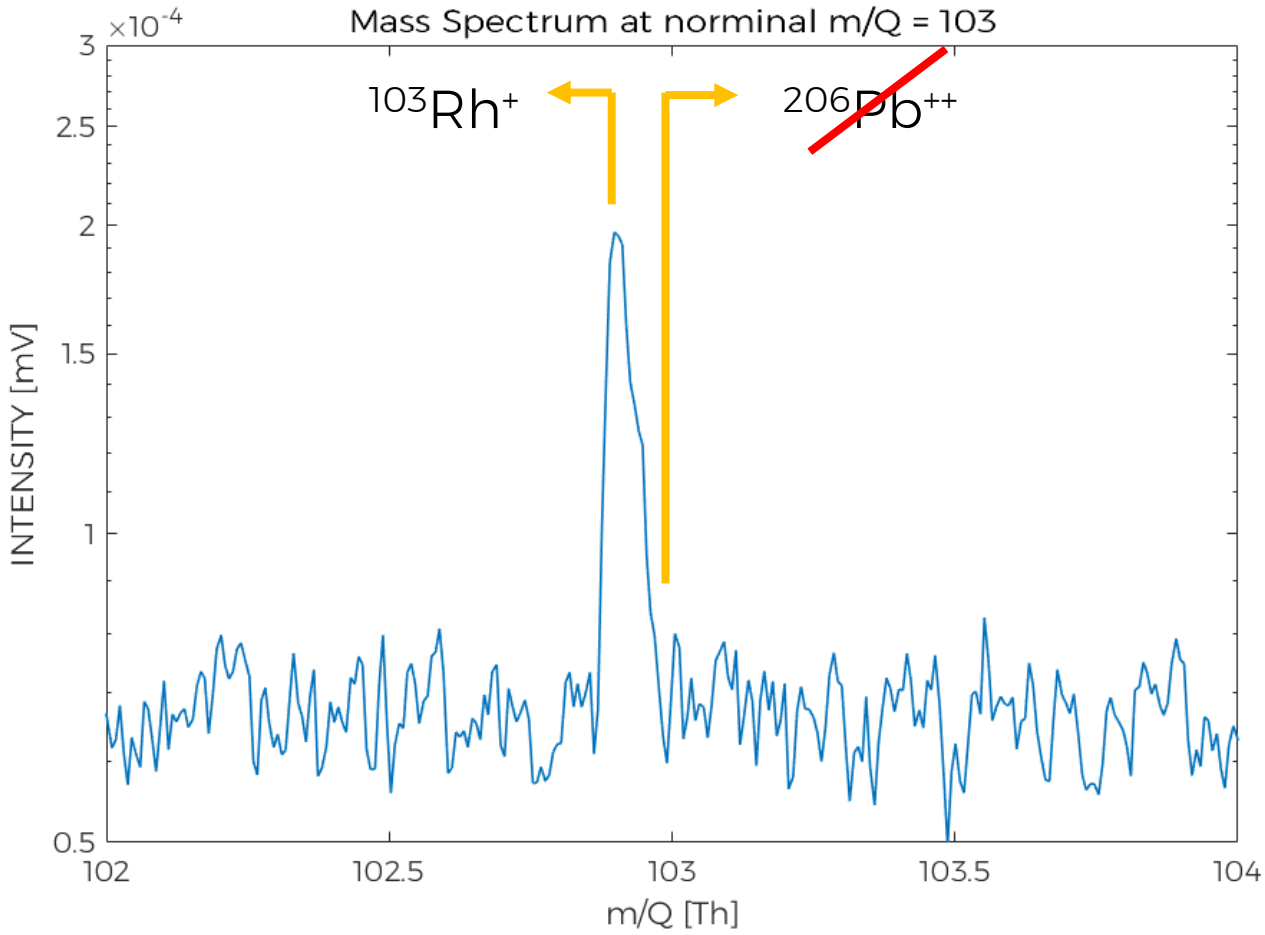


Three parts in Transient Signal:

- Transient signal following **Fe** in red;
  V, Cr, Mn, Co, Ni, Cu, Zn, Ge, Mo, Sn, Pb (?)
- '2nd Phase' in the magnetite;
  B, W, Pb
- Surface contamination, due to polish;
  Rh (103),
  Pb (206, 207, 208)
  Sn

ELEMENTAL ANALYSIS OF INCLUSIONS

LA-ICP-TOF-MS Transient Signal of Magnetite



High Dimensional
Interference Free

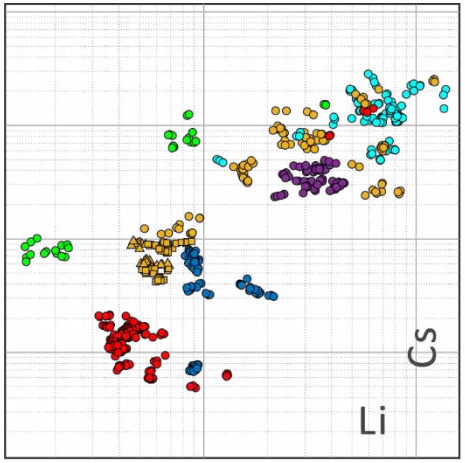
Multi-Element Dataset

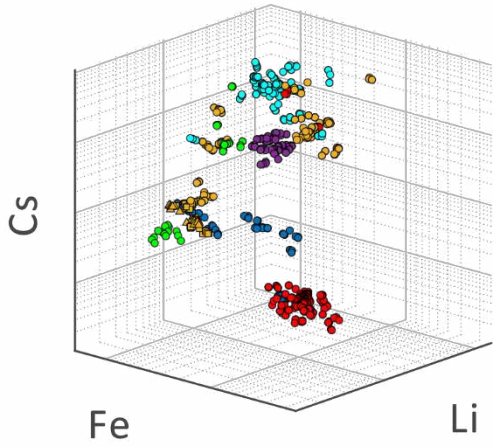
of Gemstones

EMERALD PHOTO: SSEF

COUNTRY OF ORIGIN DETERMINATION

For Emerald Using Multi-Element Dataset



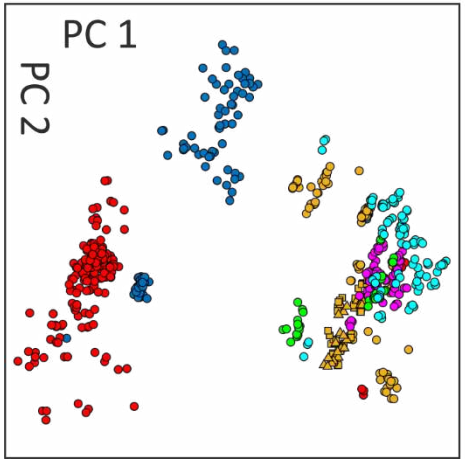


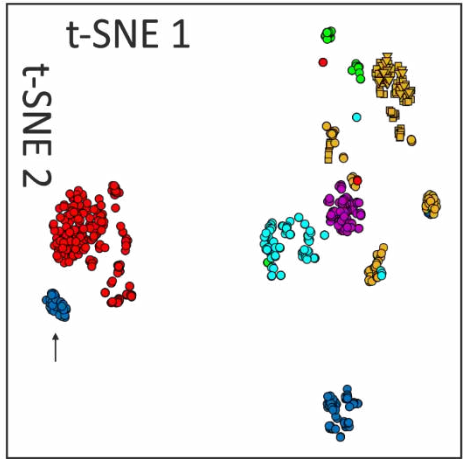
- 700 Analyses on Emerald
- *20* Elements

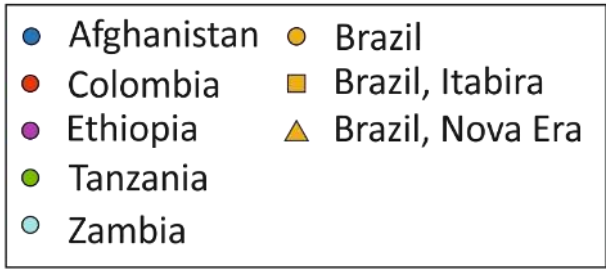
HYPOTHESIS:

Similar Geological Enviornment
Similar Elemental Composition

←→ Same Cluster







Krzemnicki MS, New Emeralds From Afghanistan. **Facette**, *2018*

DIMENSION REDUCTION ALGORITHMS

	t-SNE t-distributed Stochastic Neighbor Embedding	PCA Principle Component Analysis	LDA Linear Discrimination Analysis
Introduced in	2008	1901	1936
Learning Type	unsupervised	unsupervised	supervised
Need Sample Label?	no	no	yes
Results Related to Label?	no	no	yes
Linearity	non-linear	linear	linear
Computer Power	heavy	low	low
Result Interpretation	moderate to difficult	rather easy	moderate

L. van der Maaten, **J. Machine Learning Research,** 2008

PARAIBA TOURMALINE PHOTO: SSEF

COUNTRY OF ORIGIN DETERMINATION

For Cu-Mn-bearing Tourmaline Using Multi-Element Dataset

- 1000 Analyses on Cu-bearing Tourmaline
- All Colour Materials
- 37 Elements
- Element Results Only

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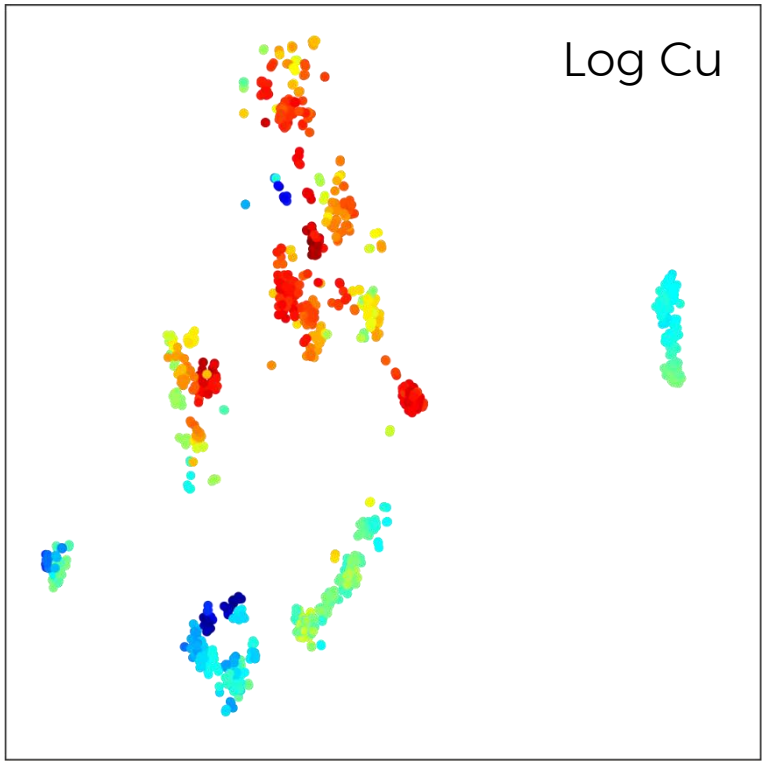

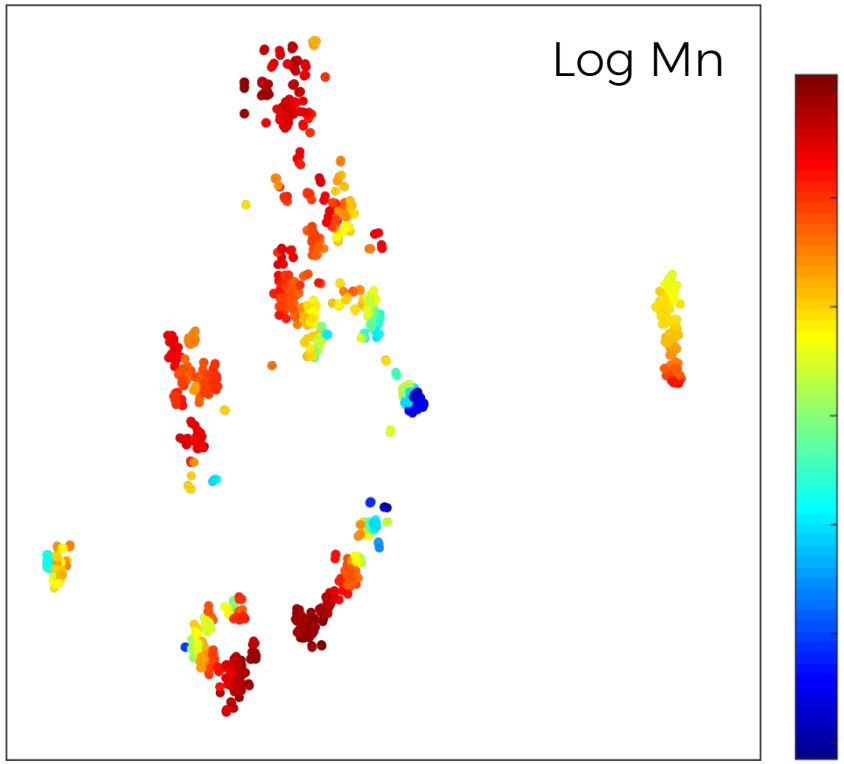

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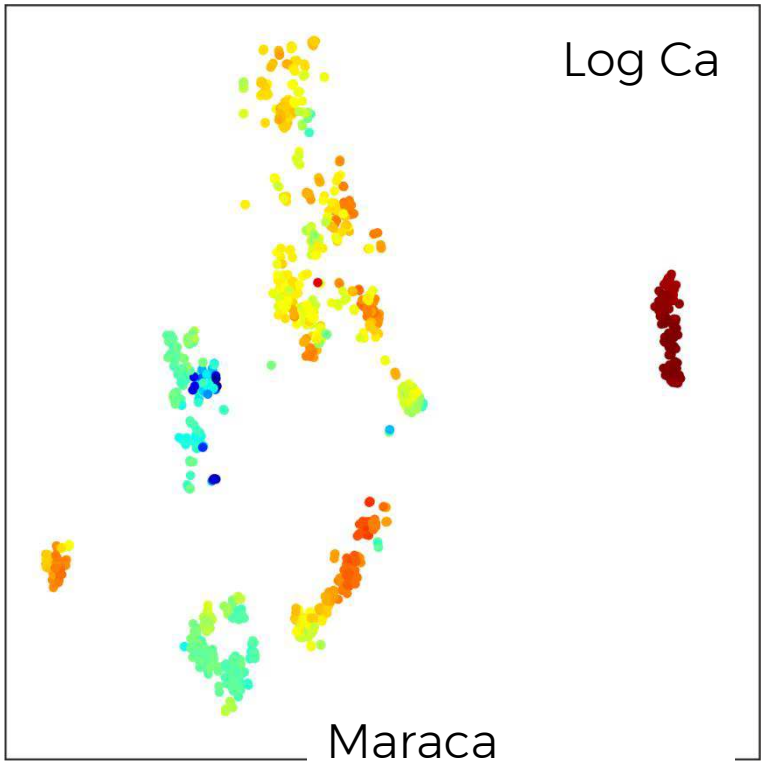
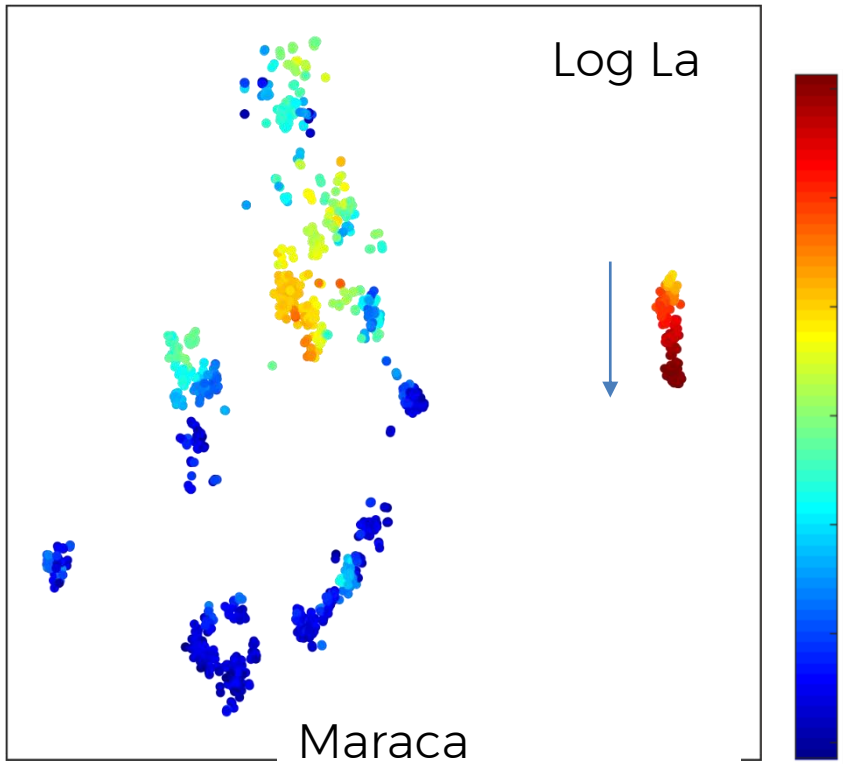


Maraca
Mozambique →
High Ca content



Maraca
Mozambique →
High REE content

Milisenda, et al, IGC, 2017

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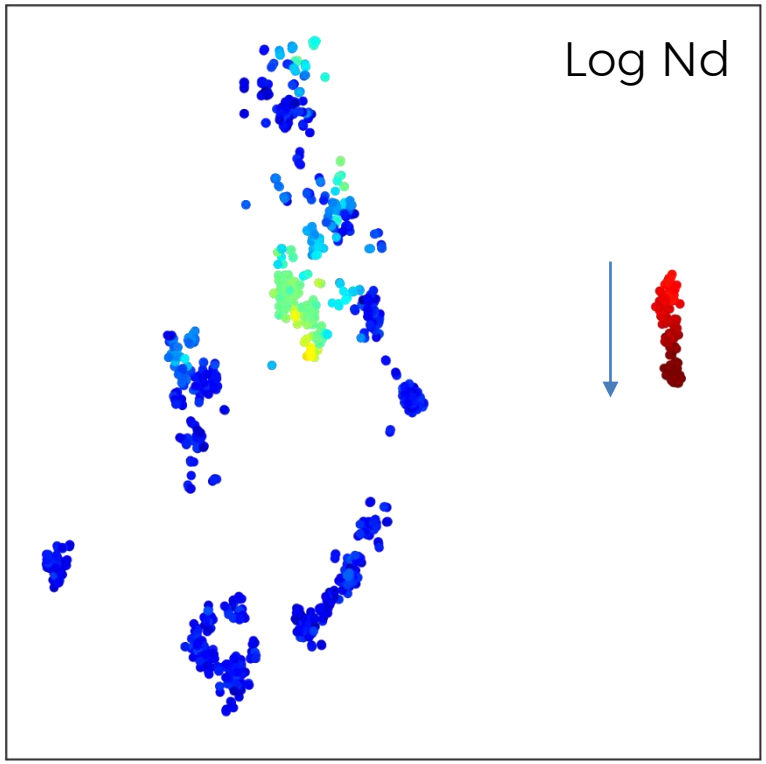

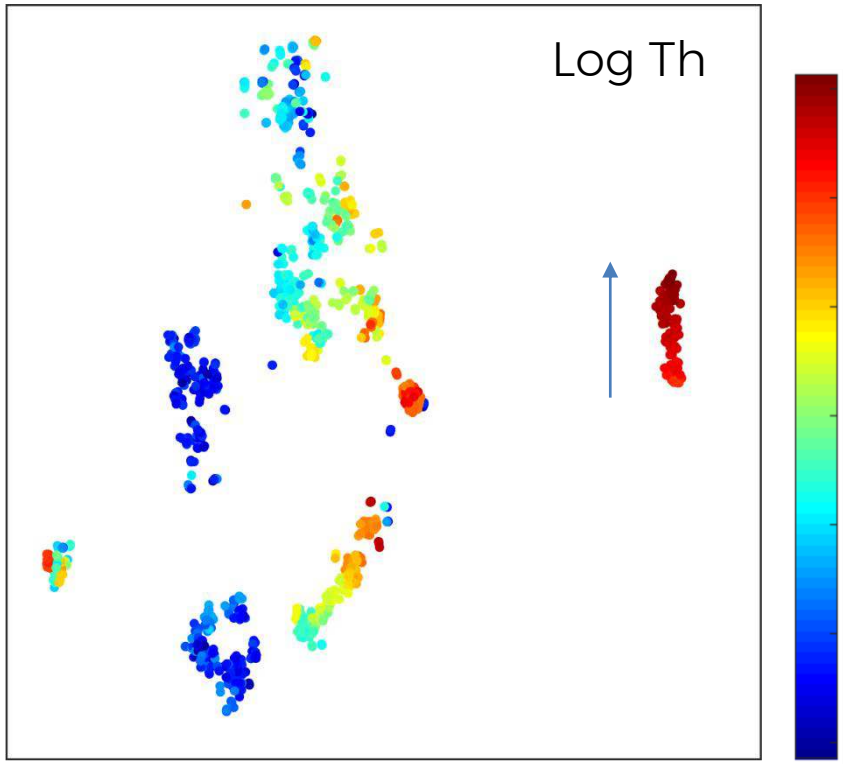

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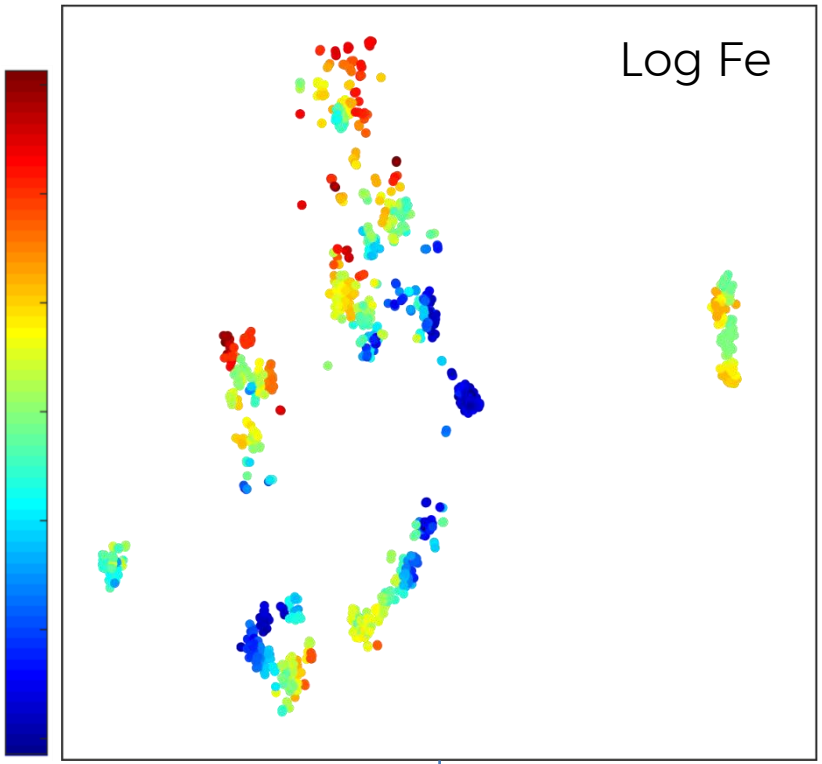

What about Green Coloured Cu-bearing Tourmaline?

W. Wight,. IGC, 2019

Bacik, et al. **Acta Geologica Slovaca**, *2015*

COUNTRY OF ORIGIN DETERMINATION

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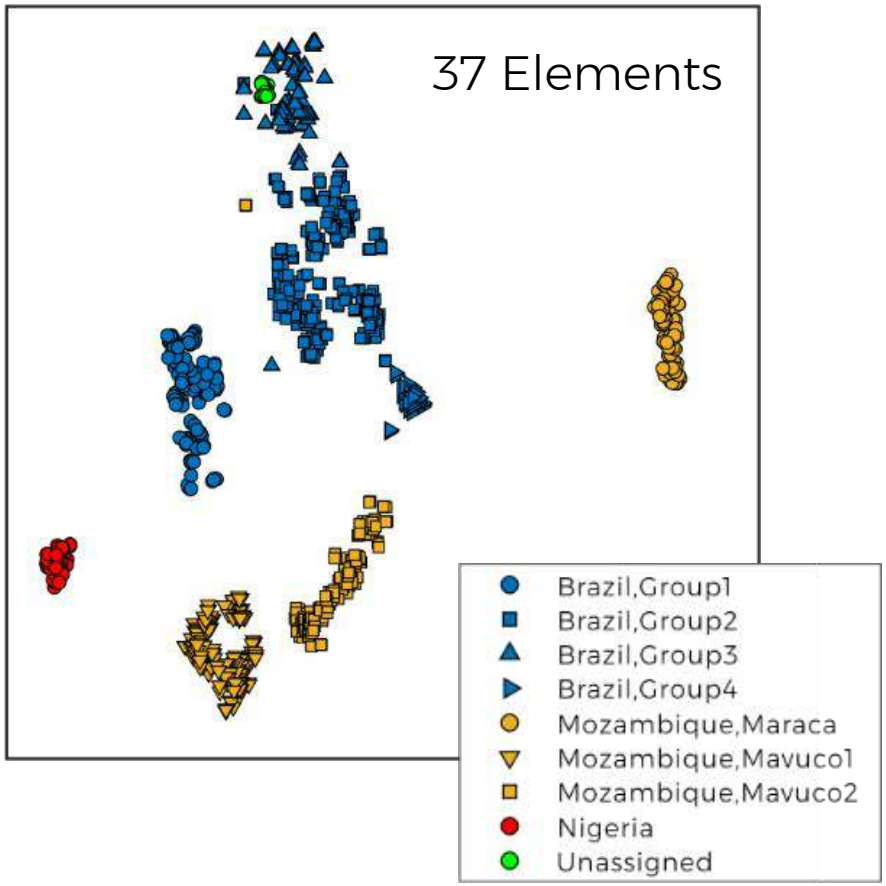

- 1000 Cu-bearing Tourmaline analyses
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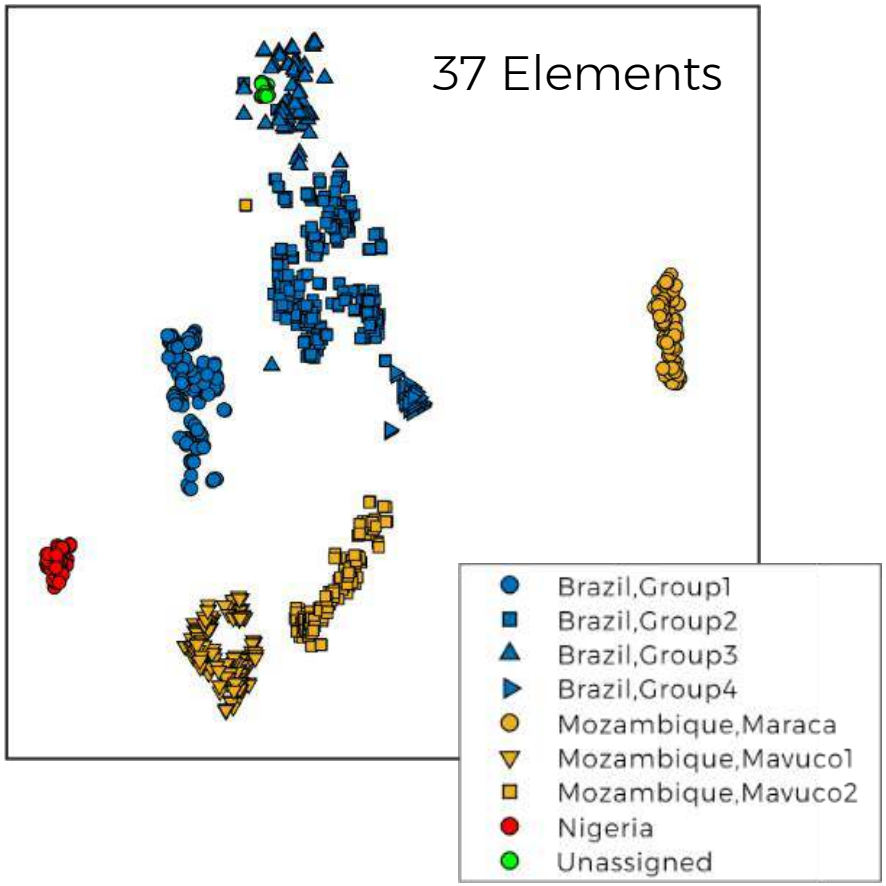

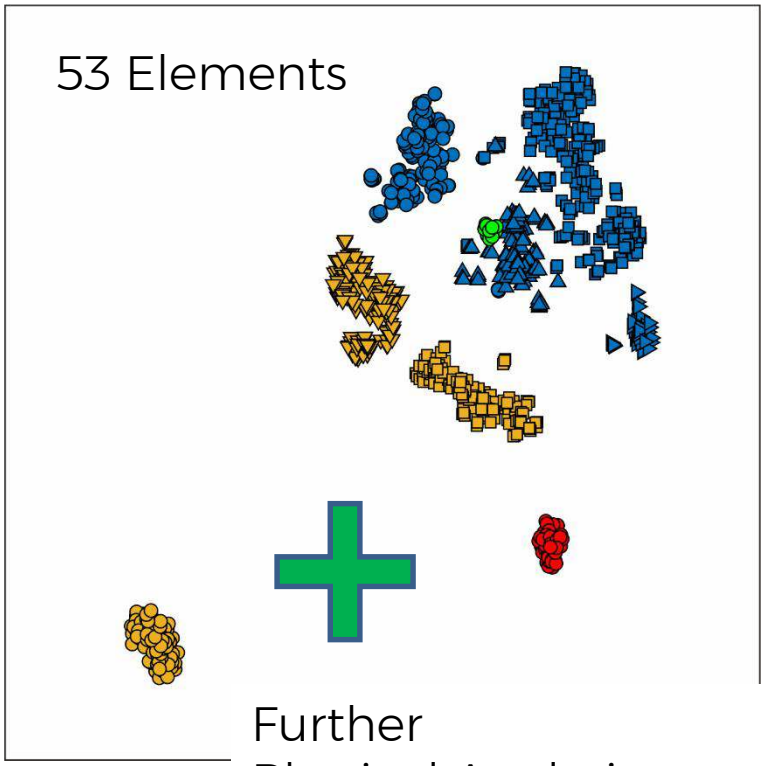

Further
Physical Analysis
Chemical Analysis
Microscopic Features

SUMMARY

Multi-Element Analysis using LA-ICP-*TOF*-MS

- Detect Rarely Occuring Elments
- *In-situ* Analyze Unidentified Inclusions and Pseudo - Depth Profile
- Non-Linear Dimension Reduction Method t-SNE helps to Cluster Analyses of Similar Elemental Compositions

Complementary Information to Gemmologists

- Country of Origin Determination of Various Coloured Gemstones

THANK YOU

Town Silhouette in Sunshine near Paraíba Tourmaline mining area, Parahlas, Brazil.