# Ultra-fast Inclusion Analysis with the ARL iSpark Optical Emission Spectrometer

## A new tool for quality control of precious metals

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# Introduction

**Collaboration with MKS PAMP, Barbara Badiello and Ilaria Cereghetti**

- MKS PAMP needed an efficient analysis of inclusions that are critical for a customer purchasing a high-grade gold product
- SEM/EDX analyses outsourced until then not satisfactory
  - Not fully representative
  - Only performed on product lots to be sent to the customer
  - Analysis results after several days
- MKS PAMP asked us to develop a method for their existing ARL iSpark allowing to
  - Evaluate type and quantity of inclusions
  - Ensure delivery of product with the minimum critical inclusions


ARL iSpark

# Topics

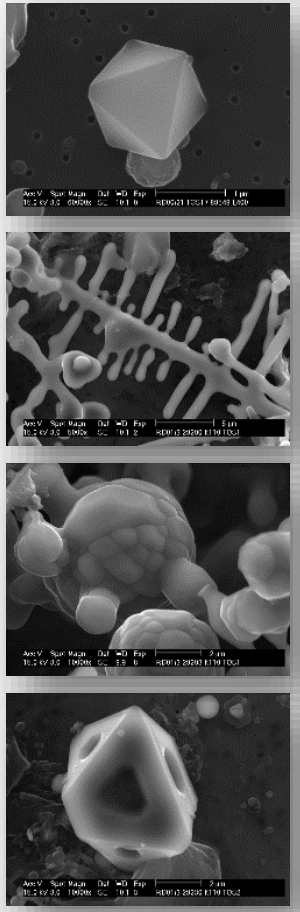
1. Ultra-Fast Inclusion Analysis
2. Application in Fine Gold / Collaboration with MKS PAMP
3. Potential for Applications in Precious Metals
4. Concluding Remarks

# Ultra-fast Inclusion Analysis

# Inclusions

- Small particles embedded in the metal matrix
- Large variety of compositions, structures and morphologies
- In many cases : critical !
  1. Can be detrimental to metal properties, responsible for defects or failures of the final product
  2. Can cause complaints or rejection of products by customers
  3. Can cause process issues

} Costly !



R. Dekkers et al., Metallurgical and Materials Transactions B, Vol. 24BB, 2003, No. 2, 161-171

# Ultra-fast Inclusion Analysis

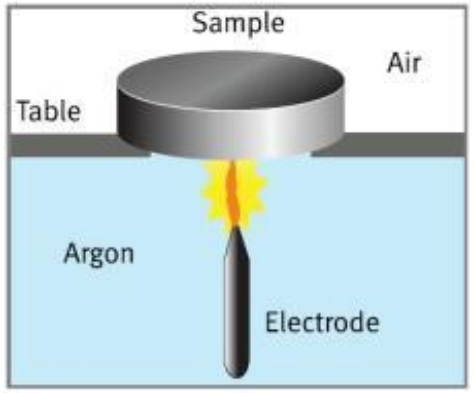
- Spark-DAT inclusion analysis is used by steelmakers since over 20 years

- Allows
  - Fast check of inclusions in the process
    - Dedicated analyzers too slow (e.g., SEM/EDX)
  - Very significant savings


In steel, checking inclusion contents in production saves up to 1 Mio $ per year

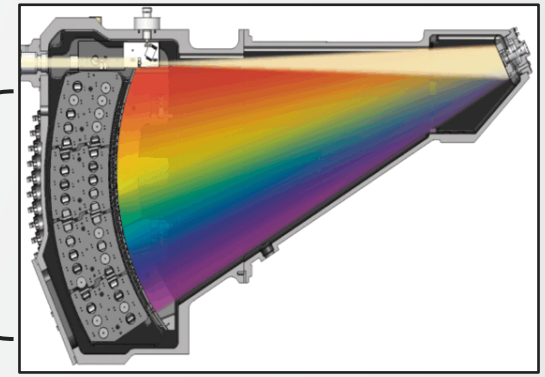
# How does it work ?

Single sparks



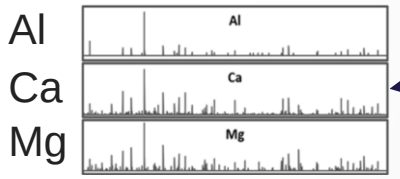

Analytical stand

Light pulses emitted by all elements



Spectrometer optics

Single spark signals




+ Other elements

**Processing**

**Standard OES analysis**

Integrated signals

Calibration curves

**Bulk concentrations**

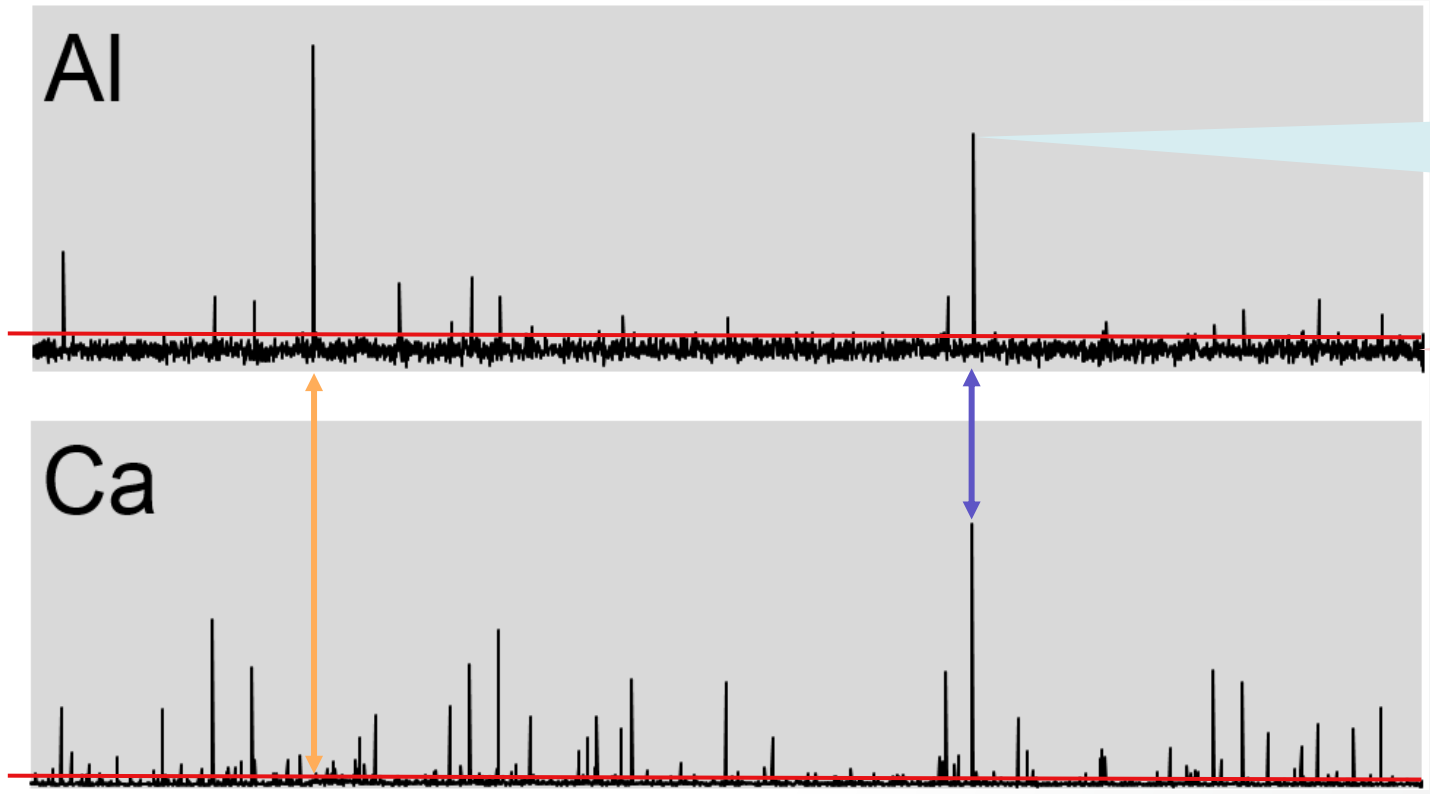
**Inclusion analysis**

Single spark signals

Special algorithms

**Inclusions data**

# How does it work ?




**Peak** ⇒ inclusion

- Inclusion contains Al
- Intensity ∝ volume

**Background signal**

⇒ Matrix content

**No peak coincidence**

Inclusion contains Al, but no Ca

**Peak coincidence**

The inclusion contains Al and Ca

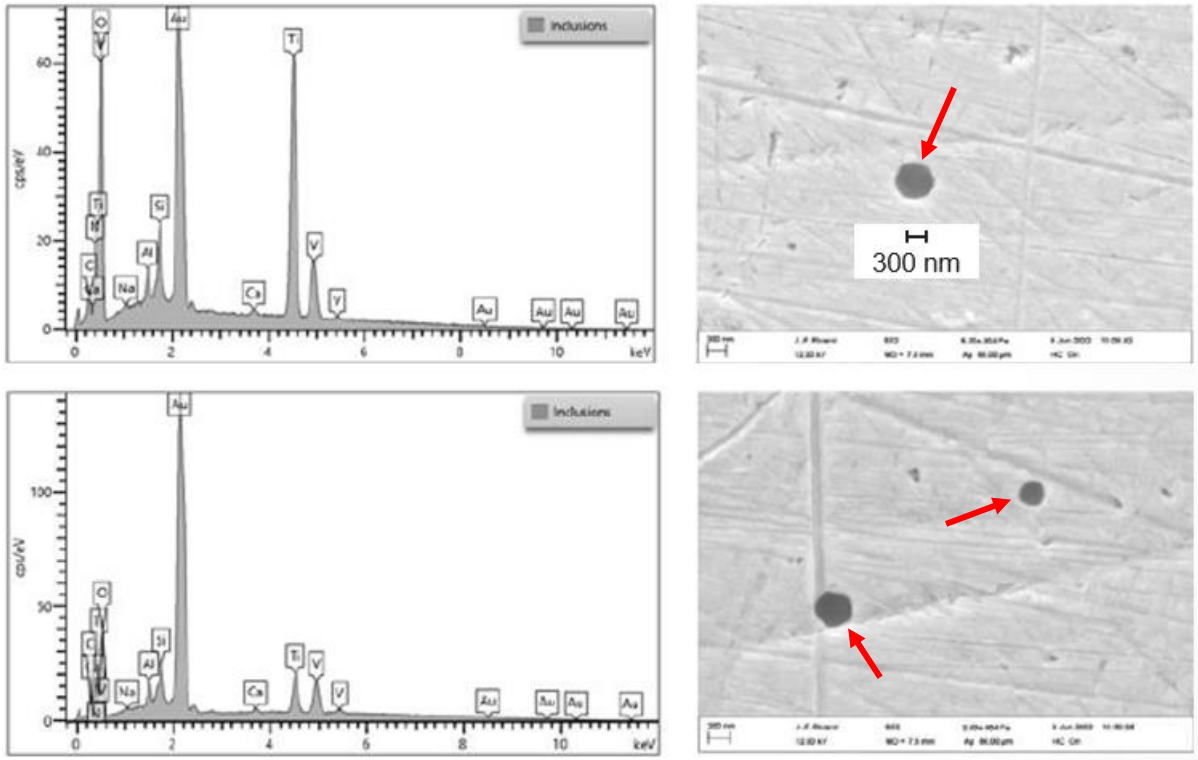
Special data treatments deliver inclusions data

- Type / composition
- Number
- Size / size distribution
- Concentration
- ….

# Application in Fine Gold / Collaboration with MKS PAMP

# Origin of MKS PAMP's Need

- A customer of MKS PAMP complained that some high-grade gold grains supplied by MKS PAMP contained inclusions creating visual defects in gold alloy products made from these grains

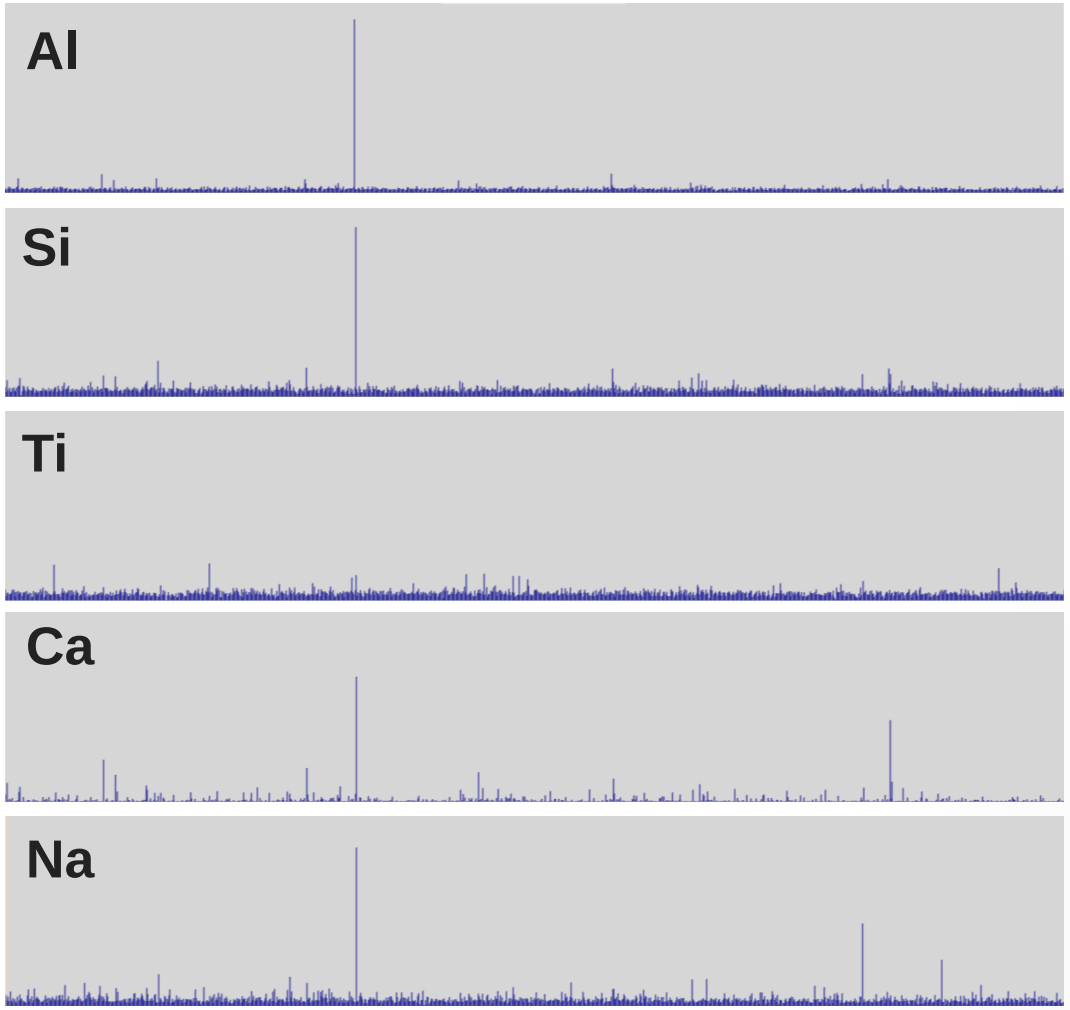



SEM/EDX analyses performed by the customer on grains

## Oxide inclusions

- Main elements: Si, Al and Ti
- Minor elements: Ca and Na
- Morphology: spherical
- Size: 0.2 to 1 µm
- Density: 3 particles / $mm^2$

# Can Spark-DAT Measure These Critical Inclusions ?




Spark-DAT run-charts of some fine gold grain material

- Peaks observed on run charts of main and minor inclusion elements !

# Samples

**9 samples from melts of 4 production batches**

- Spark OES analysis (8 runs)

| | | | Concentration [ppm] | | | |
|---|---|---|---|---|---|---|
| Batch | Melt | Sample | Al | Si | Ti | Au% |
| 1 | 1 | **1-01 M** | 0.3 | 0.7 | 0.2 | 99.996 |
| | 2 | **1-02 M** | 0.5 | 0.5 | 0.5 | 99.996 |
| 2 | 1 | **2-01 M** | 0.6 | 0.7 | 0.6 | 99.997 |
| | 2 | **2-02 M** | 0.4 | 0.4 | 0.6 | 99.993 |
| | 5 | **2-05 M** | 0.3 | 0.3 | 0.2 | 99.992 |
| | 6 | **2-06 M** | 0.4 | 0.4 | 0.5 | 99.998 |
| 3 | 11 | **3-11 M** | 0.2 | 0.3 | 0.0 | 99.992 |
| | 12 | **3-12 M** | 0.3 | 0.4 | 0.8 | 99.997 |
| 4 | 1 | **4-01 M** | 0.3 | 0.6 | 0.2 | 99.996 |

- Ideal case for inclusion analysis !
  - Al, Si and Ti < 1ppm in all the samples

High likelihood of obtaining quantitative results on critical inclusions for the customer

# Practical Details

- Sampling
  - Gold sampled in melt
    - Before pouring grains
  - Casted in graphite mold
- Surface preparation: milling machine
- Combined inclusion and elemental analysis
  - 4 runs (measurements)
  - Total analysis time : 2-3 minutes
- Inclusions evaluated in 0.14mm$^3$
  - Equivalent to 2.6mg gold
  - Sparked surface: 0.28 cm$^2$

Sampling in melt | Casting in a mold | Chilling

Milling machine

Milled sample

Sample after analysis

# Validation of the Method

**Spark OES data vs. SEM/EDX data**

- Inclusions measured under very different principles
  - Comparison of results not always straightforward !

Thermo Scientific
Phenom ParticleX

- Surface technique
  - $\varnothing_{measured} < \varnothing_{true}$

Sample surface

Thermo Scientific
ARL iSpark

- Volume technique
  - $\varnothing_{measured} = \varnothing_{true}$ ?

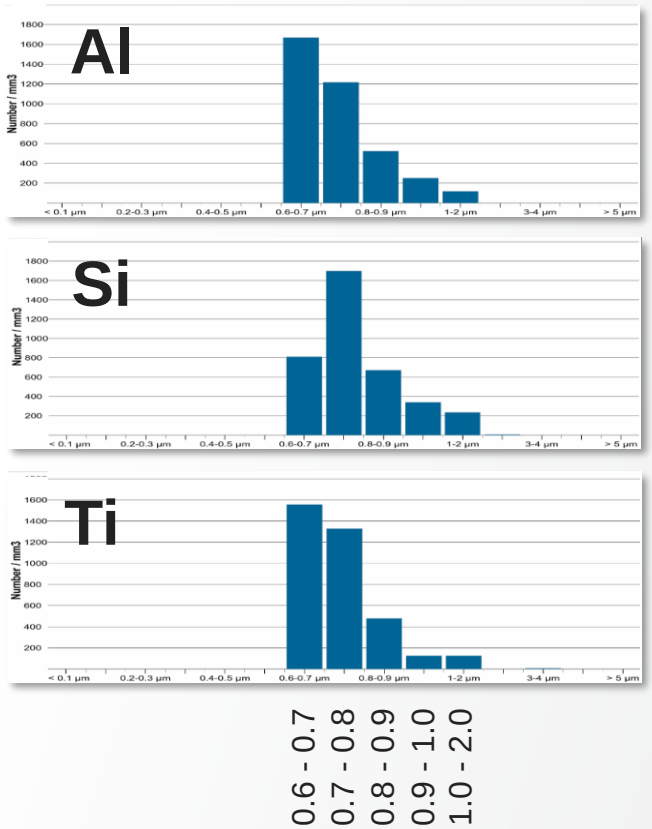
# Validation of the Method

## Size distribution

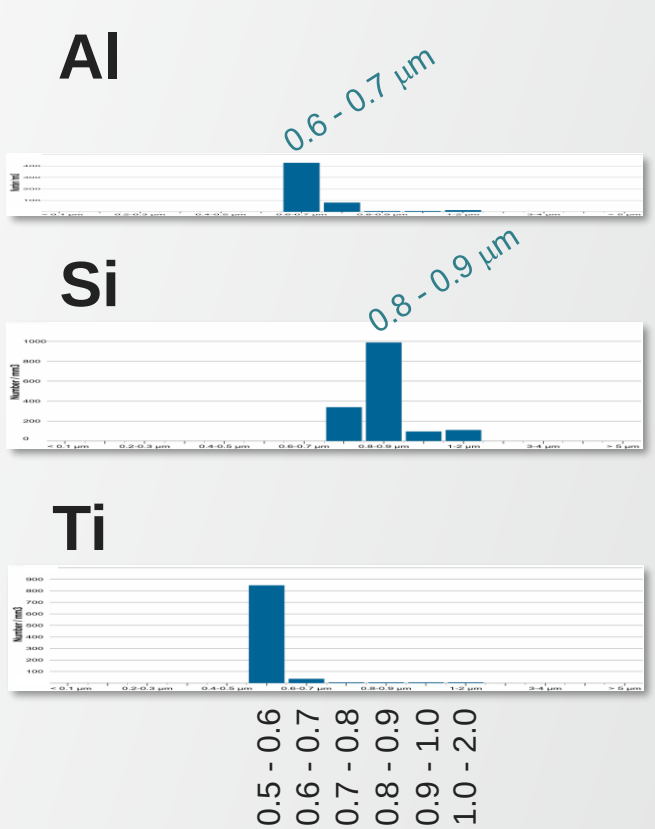
- ESD in µm
  - Equivalent Spherical Diameter
  - Diameter of the sphere having the mass measured with Spark-DAT

- Distribution shows clear differences of inclusion populations in the samples
  - Sample 4-01 M has fewer and smaller inclusions than sample 1-02 M

**Sample 1-02 M**




**Sample 4-01 M**

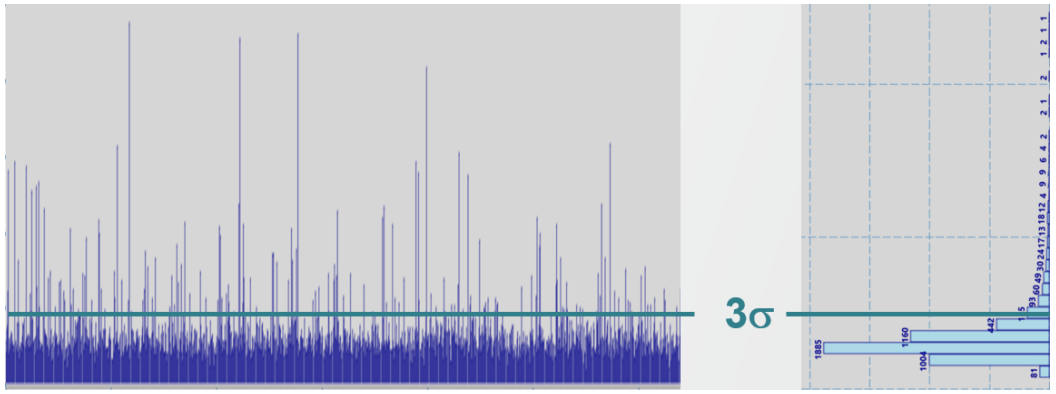



Data agree well with SEM/EDX data ➔ Good validation of the method !

# Data for Routine Inclusion Assessments

## Total number of inclusions

- All signals above noise are counted
  - Threshold at 3σ




Al intensity run-chart and distribution in sample 1-02 M

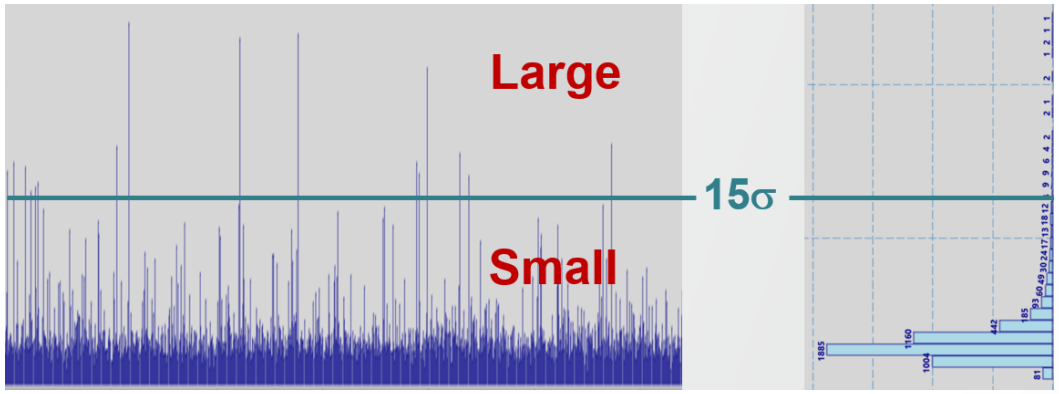
| Total number of peaks per mm$^3$ | | | |
|---|---|---|---|
| **Sample** | **Al** | **Si** | **Ti** |
| **1-01 M** | 650 | 2504 | 1676 |
| **1-02 M** | 2858 | 3161 | 2999 |
| **2-01 M** | 1603 | 2356 | 1426 |
| **2-02 M** | 569 | 1145 | 1145 |
| **2-05 M** | 1034 | 2039 | 2105 |
| **2-06 M** | 842 | 2297 | 1913 |
| **3-11 M** | 547 | 1049 | 1057 |
| **3-12 M** | 598 | 1463 | 1994 |
| **4-01 M** | 525 | 1271 | 1049 |

Up to 3x fewer peaks than in other samples !

# Data for Routine Inclusion Assessments

## Number of large inclusions

- Large inclusions have generally higher impact on metal properties
- Larger signals are counted
  - Threshold higher than 3σ




Al intensity run-chart and distribution in sample 1-02 M

| Number of large peaks per mm$^3$ | | | |
|---|---|---|---|
| **Sample** | **Al** | **Si** | **Ti** |
| **1-01 M** | 52 | 532 | 67 |
| **1-02 M** | 244 | 429 | 177 |
| **2-01 M** | 178 | 155 | 15 |
| **2-02 M** | 23 | 52 | 37 |
| **2-05 M** | 59 | 185 | 141 |
| **2-06 M** | 89 | 303 | 148 |
| **3-11 M** | 52 | 96 | 67 |
| **3-12 M** | 52 | 81 | 155 |
| **4-01 M** | 23 | 67 | 30 |

Up to 7x fewer large peaks than in other samples!

# Data for Routine Inclusion Assessments

## Inclusion concentration

- Proportional to number and size
  - A mix of the two most critical parameters in term of impact on metal quality

| Inclusion concentration [ppm] | | | |
|---|---|---|---|
| **Sample** | **Al** | **Si** | **Ti** |
| **1-01 M** | 0.01 | 0.16 | 0.02 |
| **1-02 M** | 0.10 | 0.12 | 0.14 |
| **2-01 M** | 0.07 | 0.10 | 0.05 |
| **2-02 M** | 0.01 | 0.03 | 0.04 |
| **2-05 M** | 0.02 | 0.04 | 0.03 |
| **2-06 M** | 0.02 | 0.06 | 0.06 |
| **3-11 M** | 0.01 | 0.02 | <0.01 |
| **3-12 M** | 0.01 | 0.04 | 0.10 |
| **4-01 M** | 0.01 | 0.04 | 0.01 |

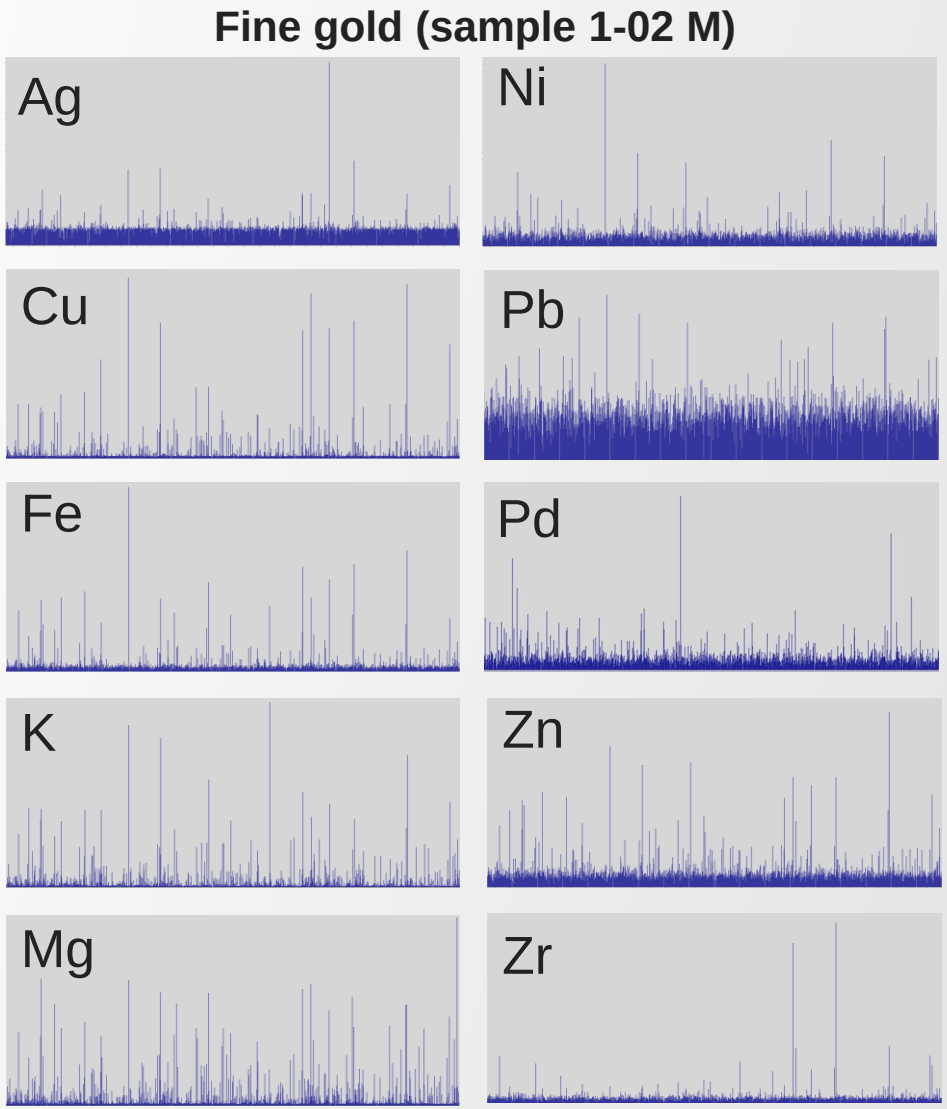
Up to 8x smaller concentration than in other samples!

Quick evaluation of the different types of critical inclusions and their quantity !

# Potential for Applications in Precious Metals

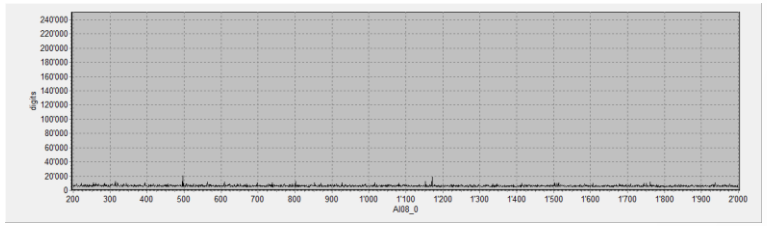
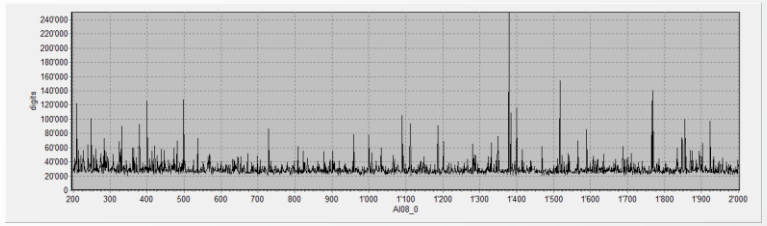
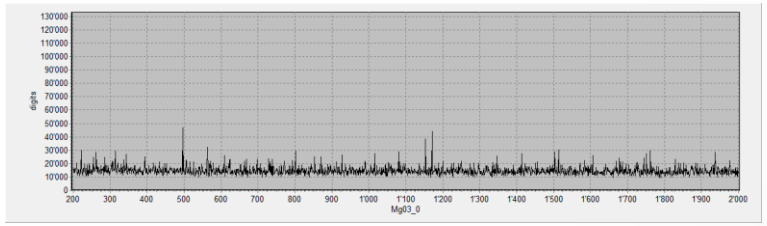
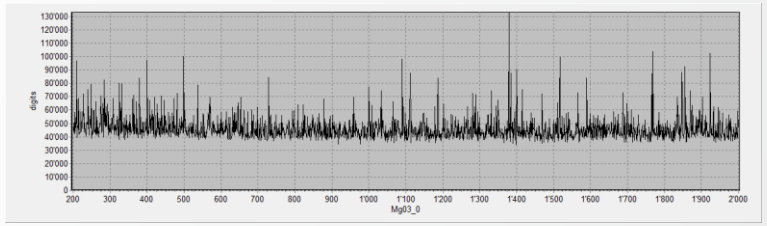
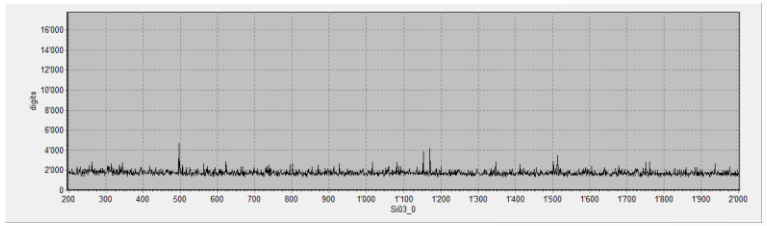
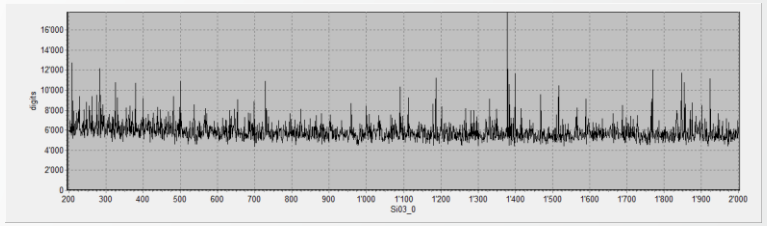
# Applications in Precious Metals

- Potentially, many different inclusions are measurable in all fine precious metals
  - Most of the inclusion elements are detectable, even uncalibrated ones
    - But not the base element
- Inclusion analysis also possible in precious metal alloys
  - Most of the inclusion elements are detectable, even if no calibration at all
    - But neither the base, nor the alloying elements
- Application can be beneficial every time inclusions impact an important property of the metal, e.g.,
  - Visual aspect in jewellery
  - Resistance of small parts in dentistry
  - Conductivity in electronics



# Applications in Precious Metals

## Fine Silver

| | LBMA Ag RM1 | LBMA Ag RM2 |
|---|---|---|
| Al |  |  |
| Mg |  |  |
| Si |  |  |

# Concluding Remarks

# Conclusion

- Ultra-fast inclusion analysis in fine precious metals is possible with the ARL iSpark

- The method developed with MKS PAMP
  - Provides the information needed by MKS PAMP to evaluate inclusions in type, size and quantity
  - Offers MKS PAMP different solutions to guarantee a minimum of critical inclusions in the product delivered to their customers, i.e.,
    - Sorting of the suitable grain lots
    - Optimization of the production process to minimize the inclusion content
    - Implementation of a routine control of inclusions in the process

- Similar applications, capable of controlling inclusions that have a critical impact on product properties, are possible in all types of precious metals!

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# Thank you

To know more on ARL iSpark and ultra-fast inclusion analysis, visit www.thermofisher.com/oes

Or contact jean-marc.bohlen@thermofisher.com