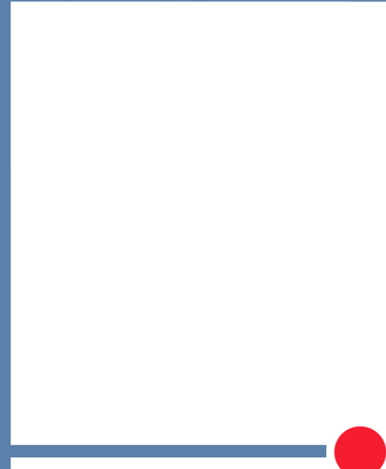




# **Základy přípravy vzorků automatizovaným tavením**

**Tomáš Černohorský**

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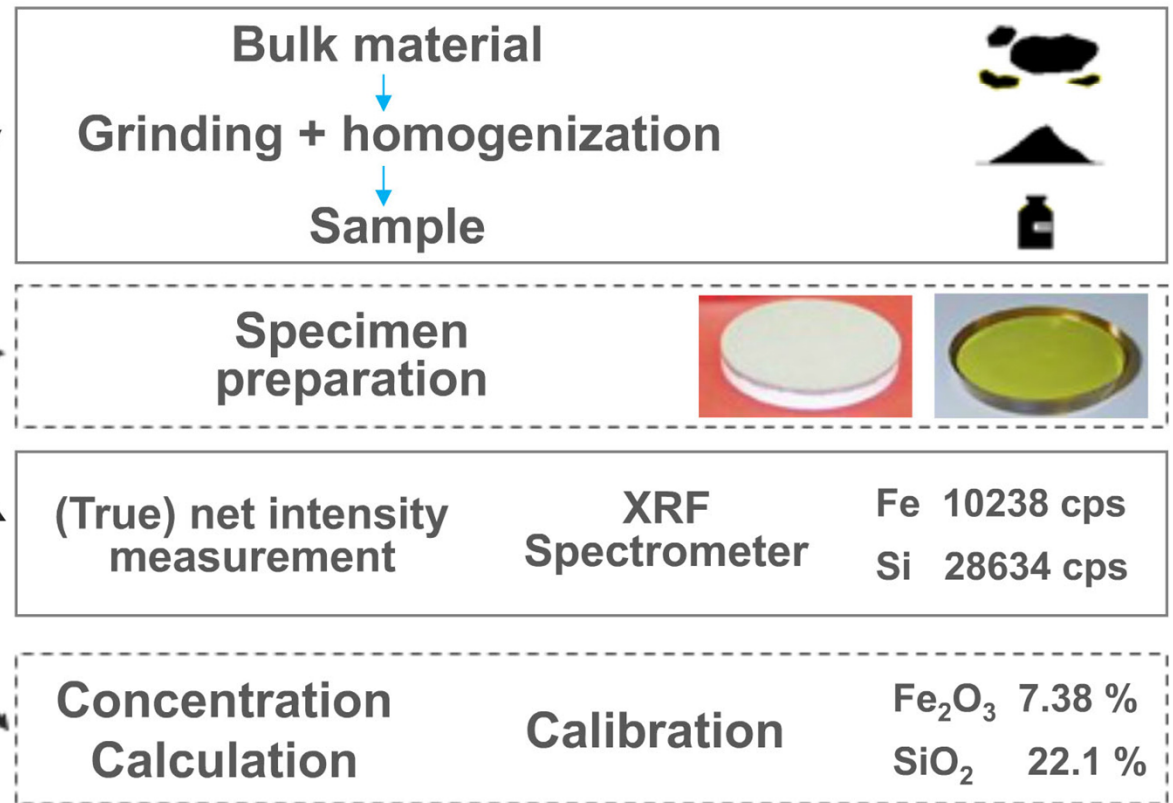
# Overview

## Subjects:

- A. Introduction to sample preparation by fusion
- B. Benefits of Fusion for XRF
- C. Benefits of Fusion for ICP
- D. Basics of Sample Preparation by Fusion

# XRF Analytical Process

## Analytical Process Steps



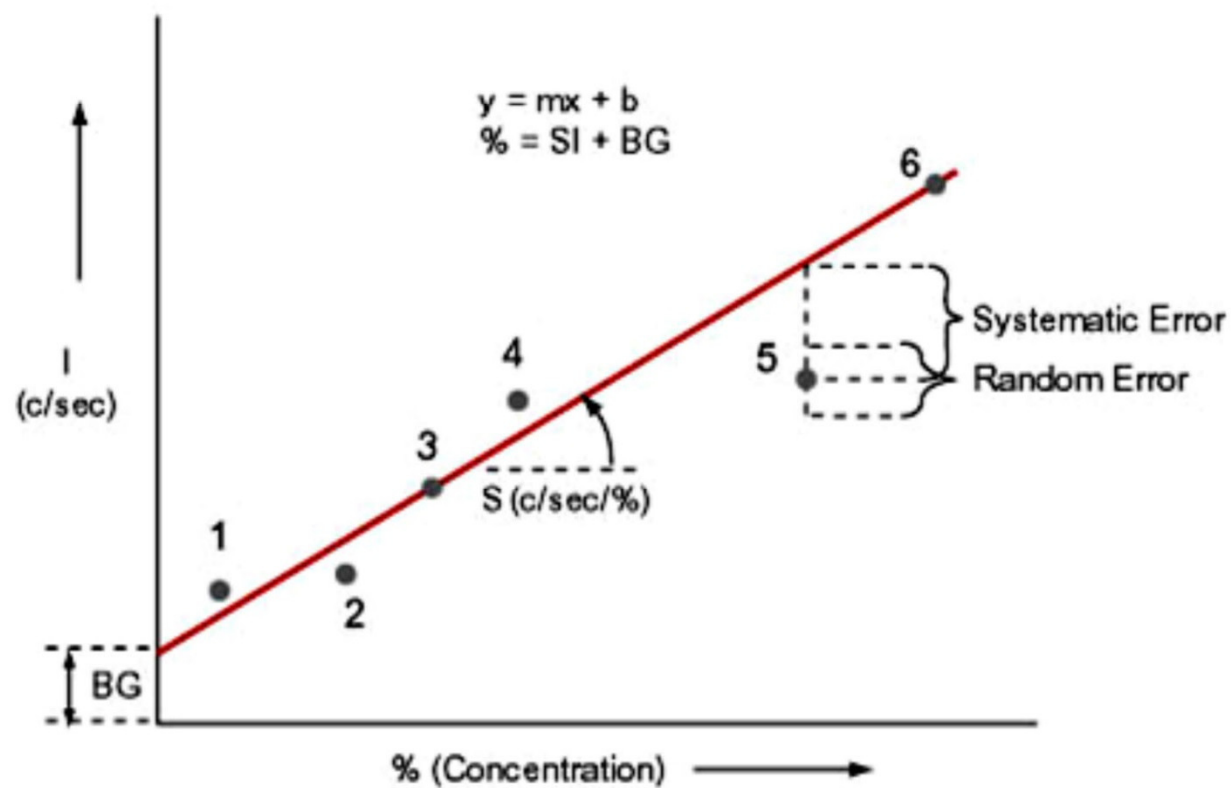
## Contributions to Total Error

$$\varepsilon_{\text{total}} = \sqrt{[(\varepsilon^2)_{\text{counting}} + (\varepsilon^2)_{\text{generator}} + (\varepsilon^2)_{\text{equipment}} + \dots \\ (\varepsilon^2)_{\text{sampling}} + (\varepsilon^2)_{\text{standards}} + (\varepsilon^2)_{\text{corrections}} + (\varepsilon^2) \dots]}$$

---



# Systematic and Random Errors



## 1955 – Prof. Fernand Claisse at Université Laval Fusion

- 1955 - Publishes first work on Fusion Preparation method
- Borate fusions for all oxides
- Removes grain size and mineralogical effects for which there is no other solution



# Meeker Burner and Ring Stand



# Muffle Furnace



## 1970's - Fusion Automation

- Claisse Model 6  
(6 Position)  
Gas Fluxer





# 1980 – Philips Perl'X Automatic Electric Fluxer



# Sample Preparation for XRF Analysis: Natural – Industrial Solids





# Sample Preparation for ICP Analysis





# Sample Preparation by Fusion:

## Equipment for XRF Analysis

4



+



+



+



**ELECTRIC**



**GAS**



# Sample Preparation by Fusion: Equipment for ICP Analysis



## ELECTRIC (Borate and Peroxide)



## (Borate)



## GAS

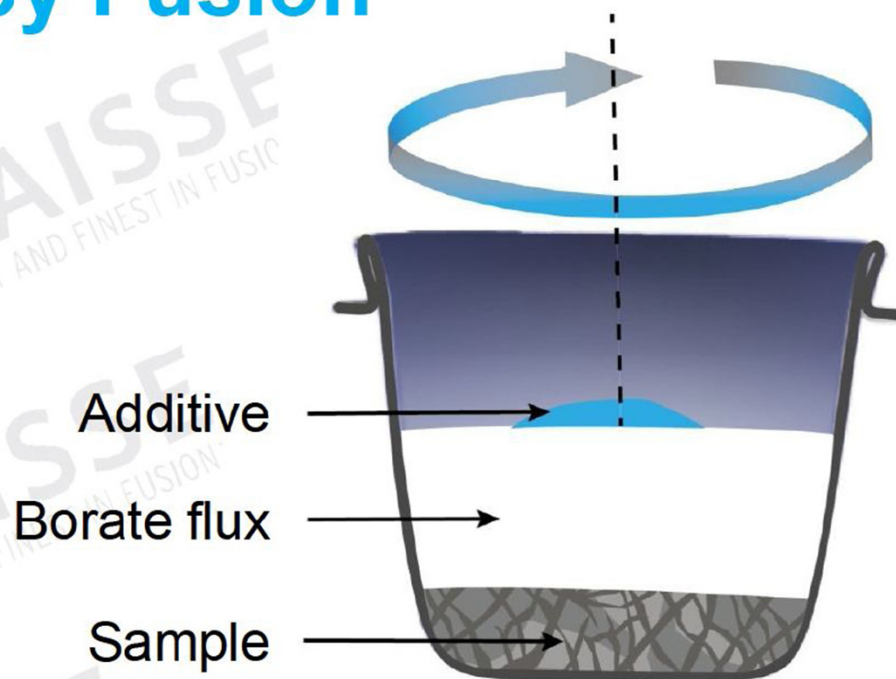
## (Peroxide)



## Sample Preparation by Fusion

1. Add sample
2. Weigh borate flux in the crucible
3. Add additive

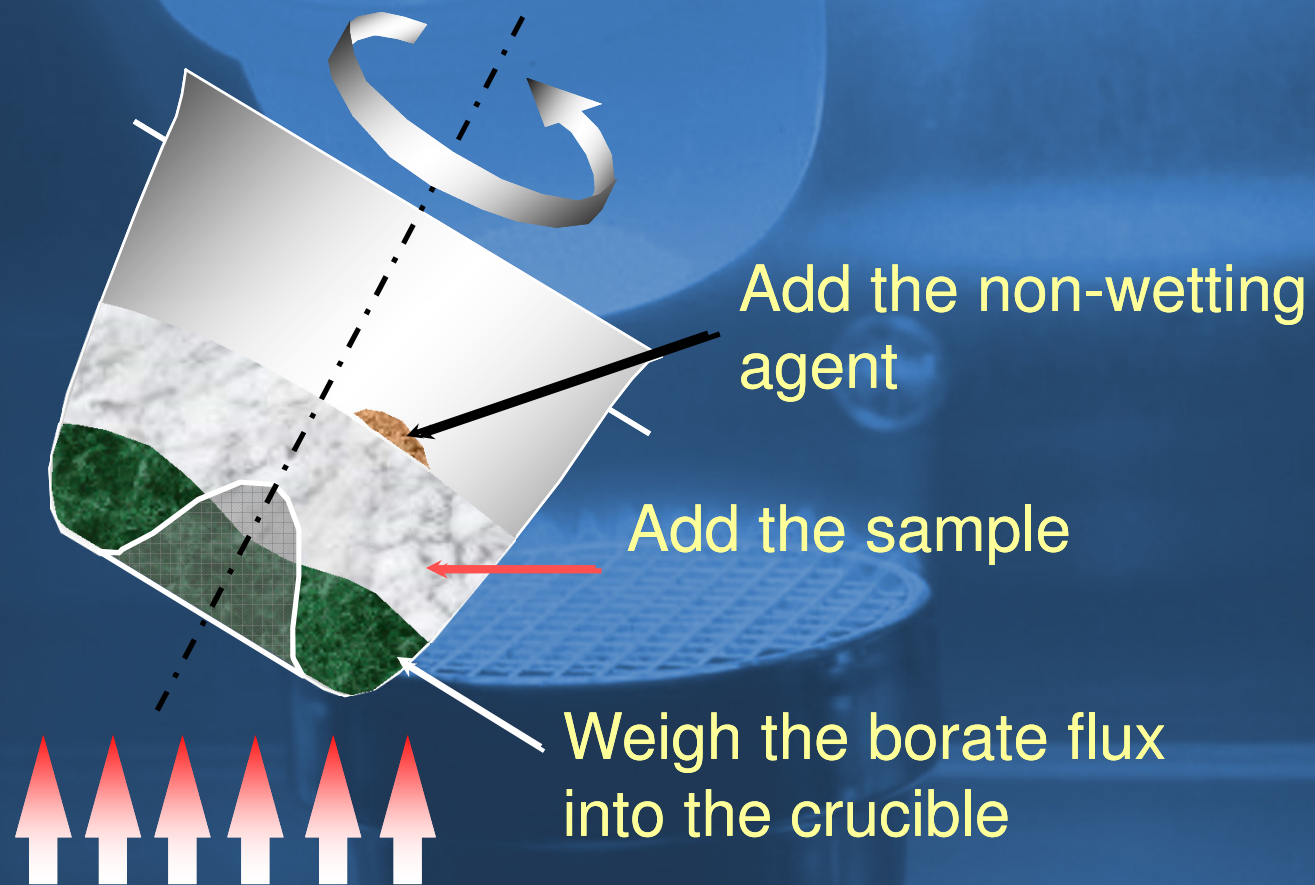
Any sample can be oxidized, but **ONLY** oxides are soluble in molten borate.



**Heat while agitating**



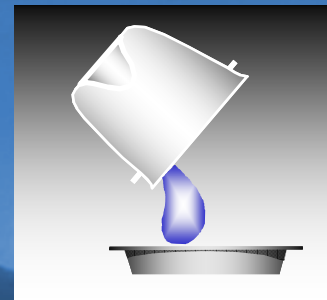
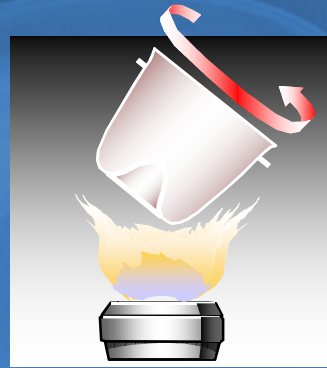
# Typical fusion procedure (glass disk)



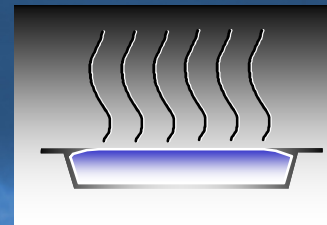
Heat at 900-1000°C while agitating

# Fusion steps

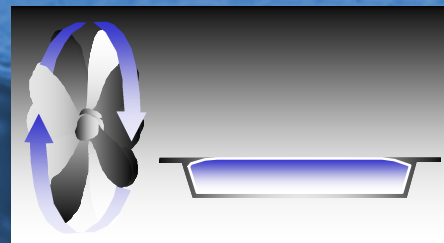
Casting



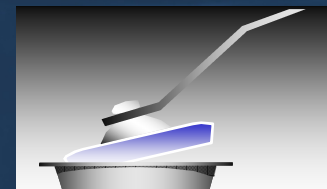
Free cooling



Forced cooling



Bead retrieval

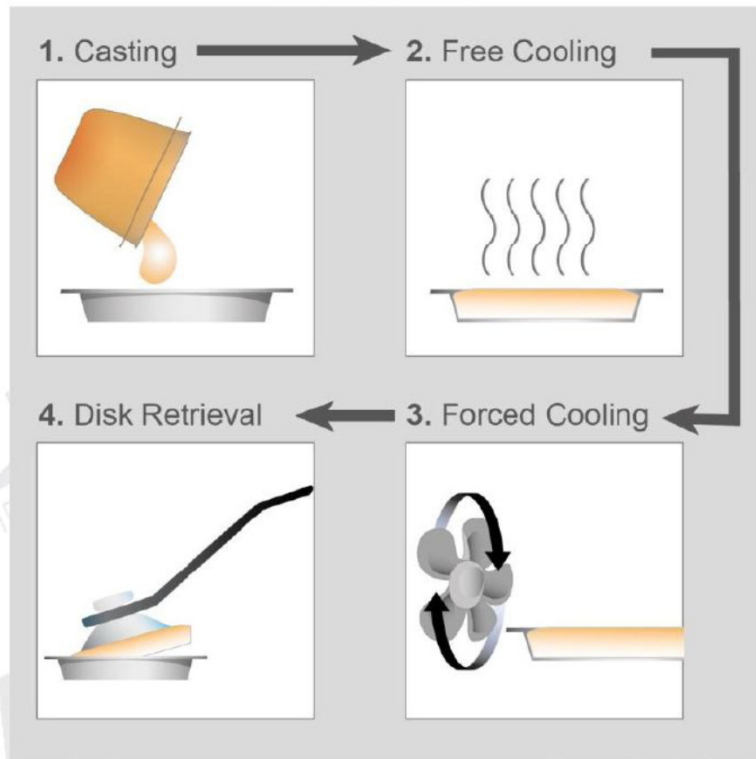




# Sample Preparation by Fusion

8

## XRF Analysis



## ICP and AA Analysis



# Sample Preparation for XRF Analysis:

## Natural – Industrial Solids

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## Benefits of Sample Preparation by Fusion for XRF<sup>10</sup>

The golden rule for accuracy in XRF analysis<sup>1</sup>:

*If the goal is to achieve the highest accuracy possible, it is absolutely necessary to understand the concepts involved. For sure, the XRF technique for quantitative analysis is a comparative technique. That is, by virtue of using calibration curves, the ratio technique, or type standard technique, the closer the standards used are to the mineralogy, particle homogeneity, particle size, and matrix characteristics of the unknown, the more accurate the analysis will be.*

X-ray Fluorescence Spectroscopy, Part II: Sample Preparation, Jul 1, 2014, John A. Anzelmo, Mathieu Bouchard, Marie-Ève Provencher, Spectroscopy, Volume 29, Issue 7, pp. 12-22



## Preparing Samples

- Minerals mining, clays, ores, geological, soils
- Blended cement, polymers with different additives, catalyst, electronic and composite materials, etc.

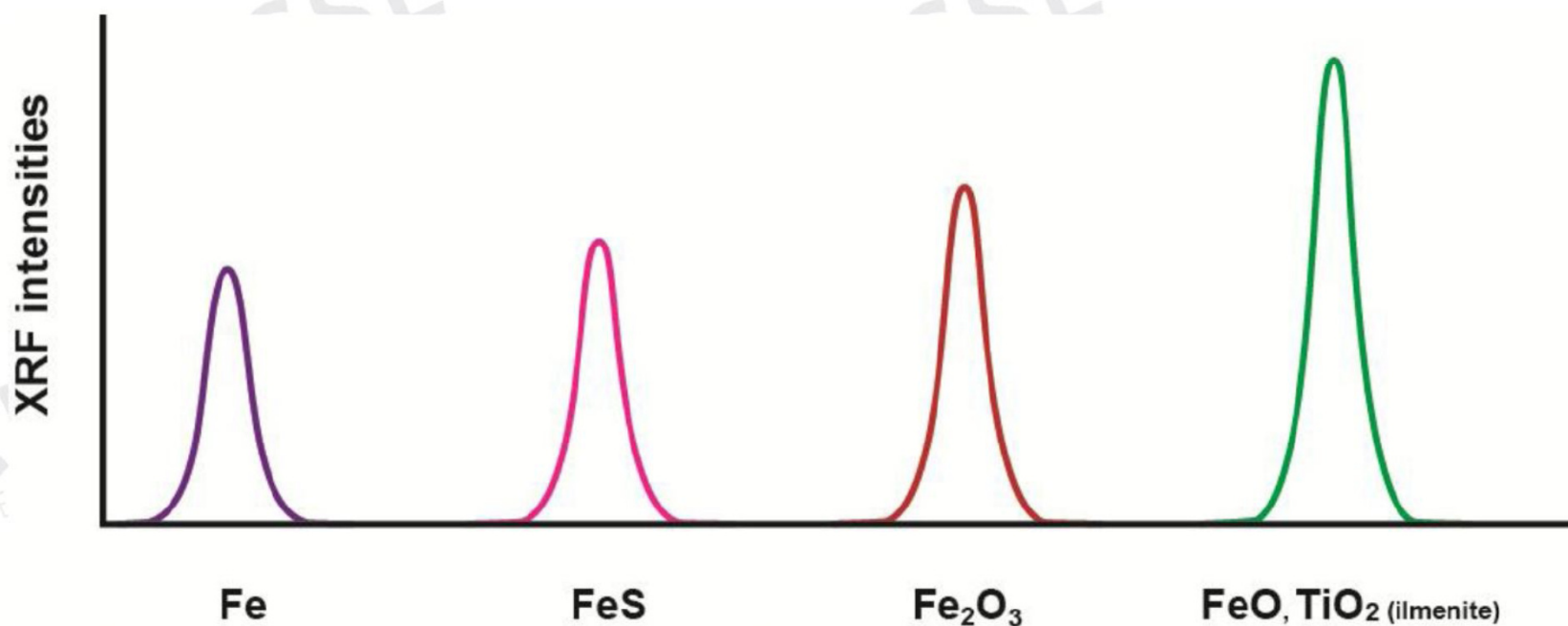
Will the unknown and the standards be matrix matched?

**To solve this issue**  **FUSION**





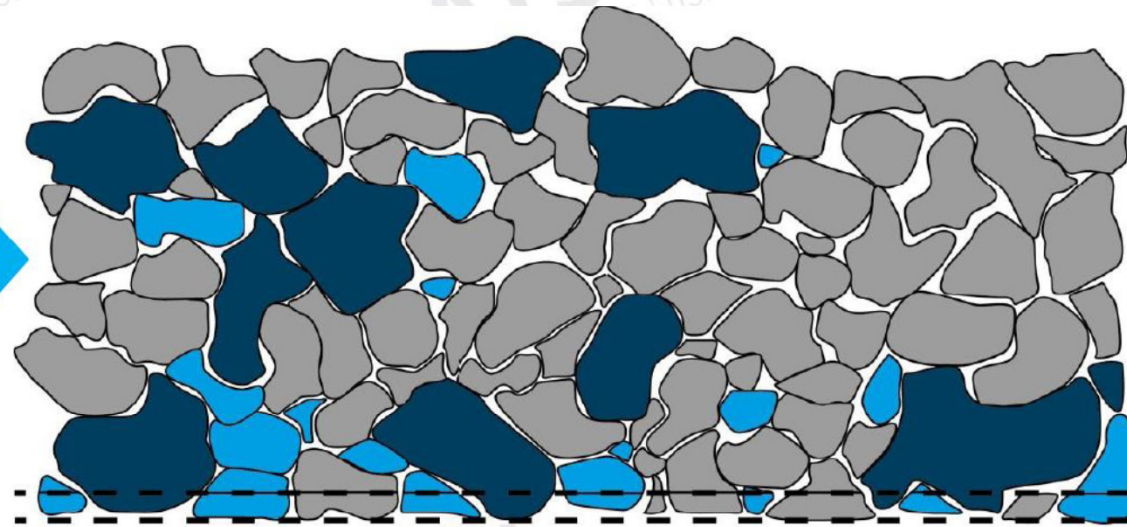
## Mineralogical Effect on XRF Intensities



Fe = same concentration, same particles size but different mineral (densities)

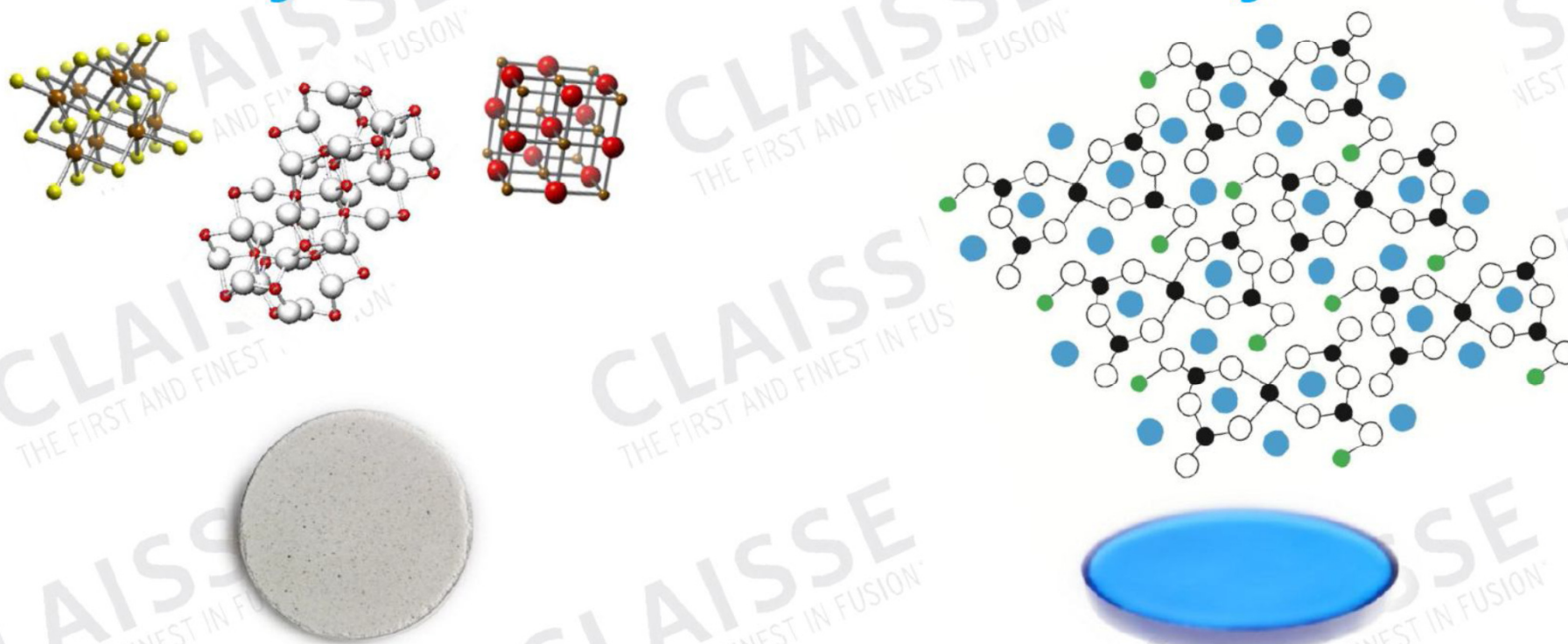
# Homogeneity, Mineralogy and Particle Size Simulated in a Pressed Pellet

Pressed pellet



Segregation and different density distribution

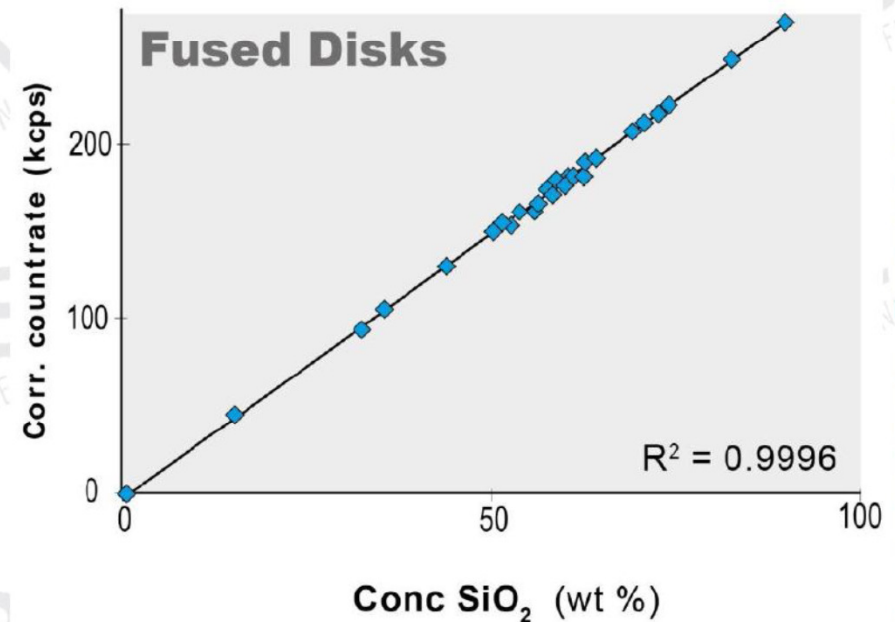
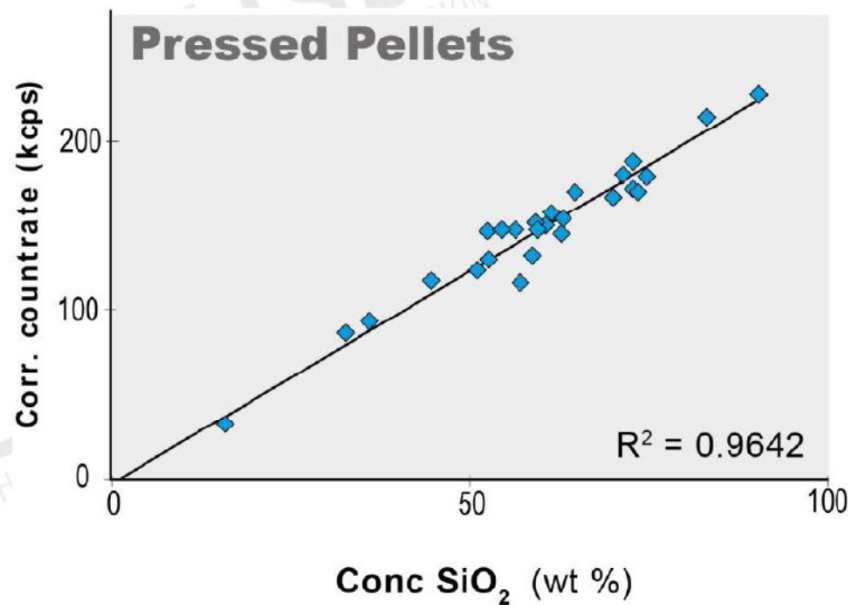
# Eliminates the Mineralogical Effect from the Crystal Structure to the Glassy Matrix





# Facilitating the Calibration

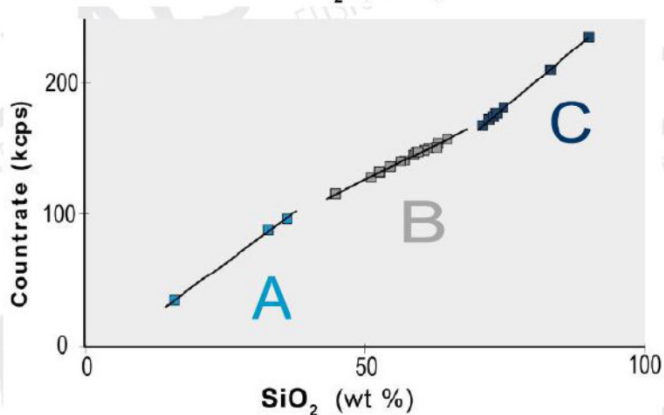
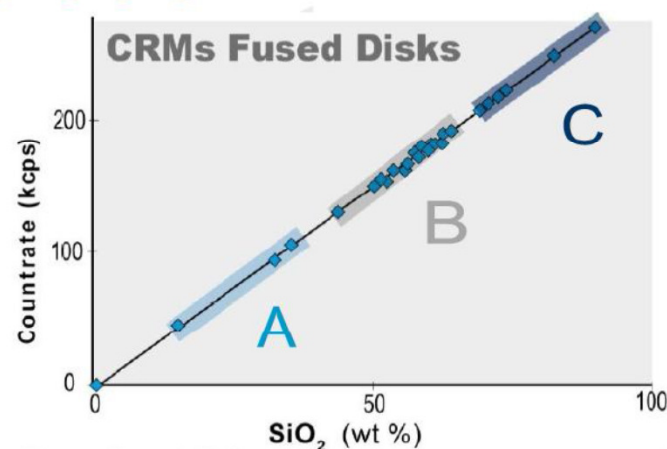
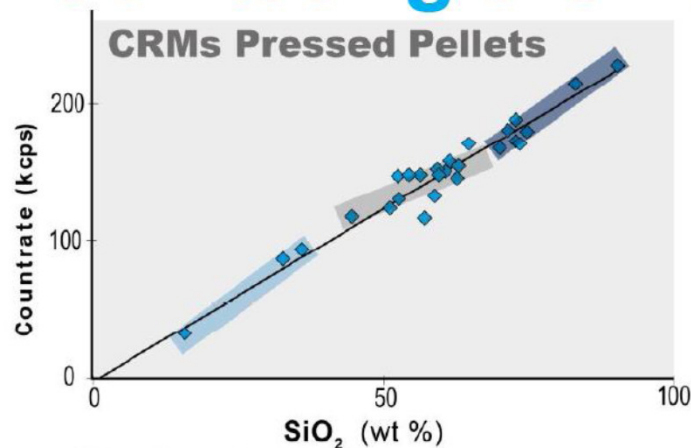
15





# Facilitating the Calibration

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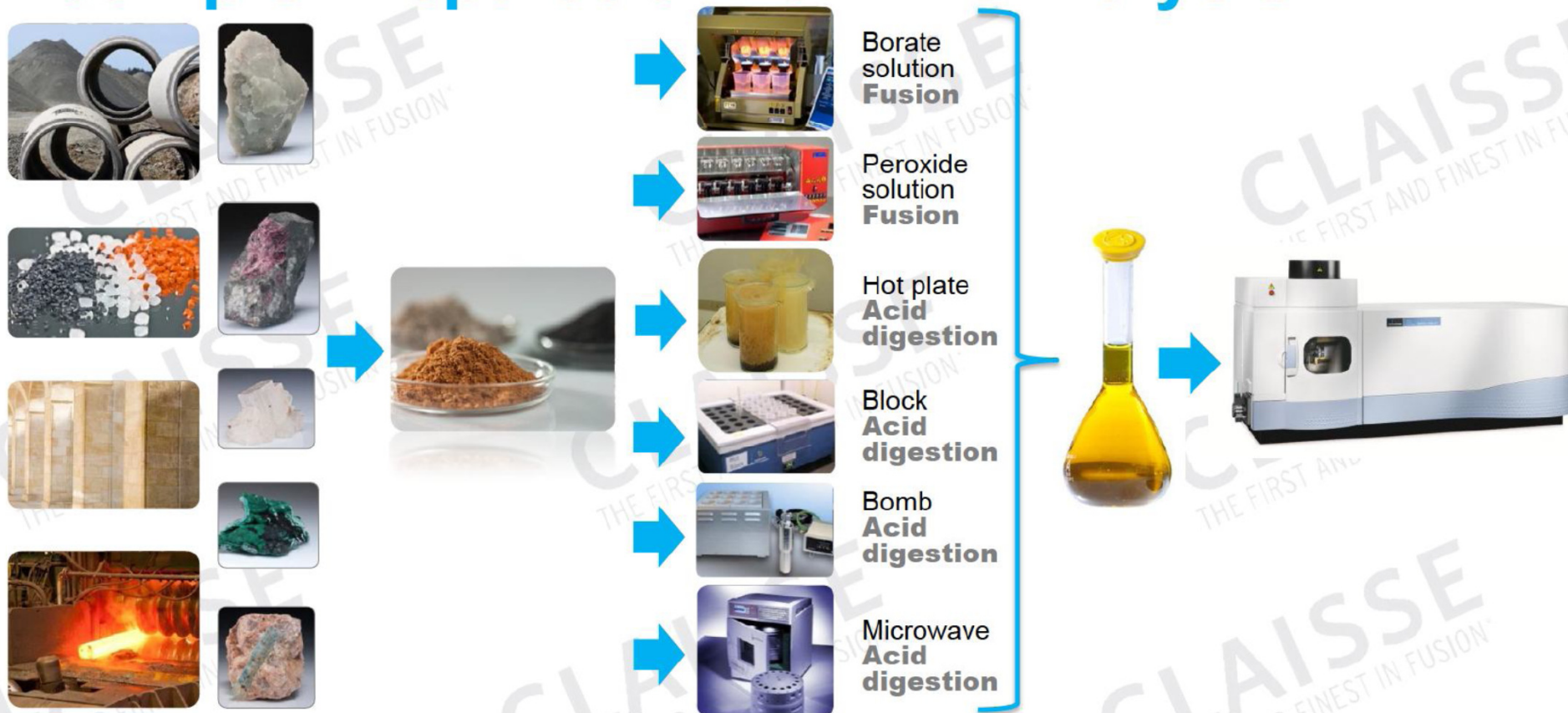
# Pressed Pellet Technique vs Fusion Technique



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|                                           | Pressed pellet<br><b>Pressing</b> | Glass disks<br><b>Fusion</b> |
|-------------------------------------------|-----------------------------------|------------------------------|
| Affected by mineralogy                    | Yes                               | No                           |
| Affected by particle size                 | Yes                               | No                           |
|                                           |                                   |                              |
| Desirable size of powder (microns)        | 5 - 30<br>(DIFFICULT)             | 50 - 100<br>(EASY)           |
| Accuracy                                  | ≤10%                              | ≤1%                          |
| Easy calibration with synthetic standards | No                                | Yes                          |
| Application of matrix correction          | No                                | Yes                          |

# Sample Preparation for ICP Analysis



# Microwave digestion

Alpha-Alumina



{ Acids :  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$   
Time: 50 min

Tungsten oxide  $\text{W}_2\text{O}_5$



{ Acids :  $\text{HF}$  and  $\text{HNO}_3$   
Time: 40 min



# Microwave digestion

## (Chromite ore)

### Step 1

Acids:  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$   
Time: 60 min

### Step 2

Acids:  $\text{HNO}_3$  and  $\text{HF}$   
Time: 35 min

### Step 3

Acid:  $\text{H}_3\text{BO}_3$   
Time: 30 min

Time: 2hrs 5 min  
5 different acids

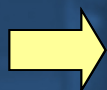
# Advantages over hot plate acid digestion

- Complete dissolution of the sample



**High analytical  
accuracy**

- Easy to use
- Quick dissolution of the sample



**Time  
savings**

**12 to 20x  
Faster**

**Money  
savings**



# Examples of Fusion Solutions



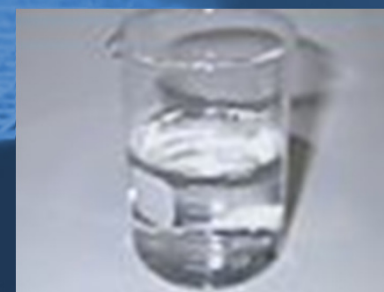
Bauxite



Catalyst



Copper



Ceramics



# Peroxide Fusion

Peroxide fusion **transforms powders of pure metals, alloys, noble metals and highly refractory samples into acids solutions.** These solutions are analysed by ICP or AA.

**Sodium peroxide is typically used**, but a wide variety of fluxes can also be used.

These fusions are usually made in **zirconium (Zr) or nickel (Ni) crucibles.**

Here are the steps of the chemical reactions:

- Oxidation made on the Peroxide Fluxer instrument: 
$$\text{Na}_2\text{O}_2 + E \xrightarrow{T \geq 460^\circ\text{C}} \text{Na}_2\text{O} + EO$$
- Reaction with water in solution: 
$$\text{Na}_2\text{O} + EO + \text{H}_2\text{O} \rightarrow 2\text{Na}^+_{(aq)} + EO + 2\text{OH}^-_{(aq)}$$
- Acidification: 
$$EO_{(s)} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{E}^{2+}_{(aq)}$$



# Peroxide fusion

- [https://www.youtube.com/watch?feature=player\\_detailpage&v=OCji1uEoktk](https://www.youtube.com/watch?feature=player_detailpage&v=OCji1uEoktk)

## Benefits of Using Peroxide Fusion

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|                                       |                                |
|---------------------------------------|--------------------------------|
| Complete dissolution of samples       | Versatile                      |
| Fast method - quick turnaround        | Simple protocols               |
| Safe (no health risks)                | Only dilute acids are required |
| Very cost-effective - low labor costs | Simple waste management        |
| Repeatable results                    | Method is not matrix-dependant |
| Clean method                          | Uses zirconium crucibles       |

## Benefits of Using Borate Fusion

Only dilute HCl or HNO<sub>3</sub> is used

- No HF, no aquaregia and no HClO<sub>4</sub> required
- No large waste quantities
- No endless paperwork to fill for strong acids disposal

Dissolves within 12 minutes even the most refractory samples such as chromites, zeolites, silica, zircons and titanium oxides

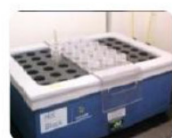
Highly pure fluxes (99,995+%) allow to do some trace analyses

# Benefits of Using Borate Fusion

|                                                                                     |                                                   |
|-------------------------------------------------------------------------------------|---------------------------------------------------|
| Complete dissolution of even the most refractory samples (Zr, Cr, Si and Al oxides) | Versatile                                         |
| Fast method - quick turnaround                                                      | Simple protocols                                  |
| Safe (no health risks) - No HF                                                      | Only dilute acids are required                    |
| Very cost-effective - low labor costs                                               | Simple waste management                           |
| Repeatable results                                                                  | Method is not matrix-dependant                    |
| Completely automatic                                                                | Possible to identify some trace elements          |
| Clean method                                                                        | Reusable and recyclable labware                   |
| Automatic pouring of fused sample in dilute acid                                    | Ultra high purity fluxes are available (99,995+%) |



# ICP Sample Preparation Method Comparison



|                                                       | Hot plate<br><b>Acid<br/>digestion</b> | Block<br><b>Acid<br/>digestion</b> | Microwave<br><b>Acid<br/>digestion</b> | Bomb<br><b>Acid<br/>digestion</b> | Peroxide<br>solution<br><b>Fusion</b> | Borate<br>solution<br><b>Fusion</b> |
|-------------------------------------------------------|----------------------------------------|------------------------------------|----------------------------------------|-----------------------------------|---------------------------------------|-------------------------------------|
| Safe (no use of HF or perchloric acids )              |                                        |                                    |                                        |                                   | ++                                    | ++                                  |
| Complete digestion/ dissolution of refractory samples |                                        |                                    |                                        |                                   | ++                                    | +                                   |
| Big batches                                           | ++                                     | +                                  | +                                      | +                                 |                                       |                                     |
| Fast throughput                                       |                                        |                                    | +                                      | +                                 | ++                                    | ++                                  |
| Simple protocols                                      |                                        |                                    |                                        |                                   | +                                     | ++                                  |
| Temperature monitoring and some control               |                                        |                                    | +                                      | +                                 | ++                                    | ++                                  |
| Automatic                                             |                                        |                                    | +                                      |                                   | +                                     | ++                                  |
| Clean                                                 |                                        |                                    | +                                      | +                                 | +                                     | ++                                  |
| Even heat distribution                                |                                        | +                                  |                                        |                                   | ++                                    | ++                                  |
| Cheap                                                 | ++                                     | +                                  |                                        |                                   |                                       |                                     |
| Low labor costs                                       |                                        |                                    | +                                      | +                                 | ++                                    | ++                                  |
| Methods are not matrix dependant                      |                                        |                                    |                                        |                                   | ++                                    | +                                   |

# Basics of Sample Preparation by Fusion

Keys to success:

1. Sample oxidation
2. Flux selection
3. Flux / sample ratio
4. Particule size
5. Fusion temperature
6. The quality of the platinumware surface
7. Cooling rate (specific to XRF application)
8. Other special keys for ICP



Keys to success: **1. Sample Oxidation**

Sample must be in its oxidized form in order to dissolve in the molten lithium-borate flux.

**Three possibilities** to develop a fully operational method :

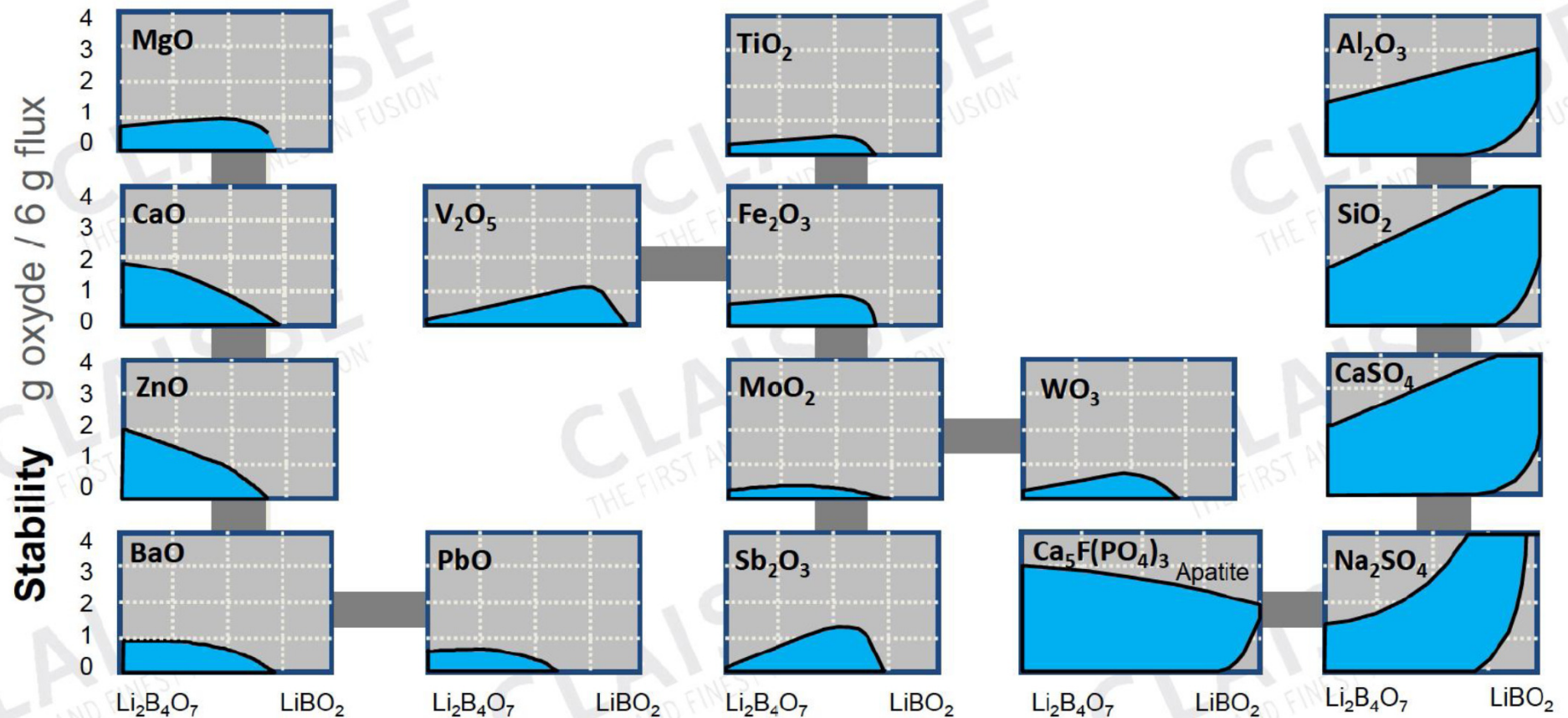
1. High temperature ventilated furnace
2. Wet oxidation ( $\text{HNO}_3$ ,  $\text{LiOH}$ ...)
3. Solid dry oxidation on Fluxer





## Keys to success: 2. Flux Selection

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# Fluxes

## Two Main Products:

1. Lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ )
2. Lithium metaborate ( $\text{LiBO}_2$ )

## Two Types of Fluxes:

1. Powder
2. Pre-fused



## Reminder: Lithium Tetraborate ( $\text{LiT}$ , $\text{Li}_2\text{B}_4\text{O}_7$ )

- Acidic flux
- Melting point:  $920^\circ\text{C}$
- Makes stable glass beads
- Best choice for the fusion of pure alkaline oxides
- Slightly hygroscopic
- Viscous



## Reminder: Lithium Metaborate ( $\text{LiM}$ , $\text{LiBO}_2$ )

- Basic flux
- Melting point:  $849^\circ\text{C}$
- It will definitely crystallize if fused alone
- It will produce vitreous beads with highly acidic oxides
- Perfect to prepare solutions





## Reminder: Mixture of Lithium Borates

- Lowers the melting point
- Higher fluidity = less sticking
- Stable glass beads
- Concentrations vary from 90% LiT / 10% LiM to 20% LiT / 80% LiM

**It is the BEST option for most samples.**



## Non-wetting Agents

- Are also called releasing agents
- Are halides (Br, I...)
- Can be added as salt and solution or are already pre-fused with flux or pills
- Affect the tension of the surface
- Decrease the tendency to stick



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## Basic Concept

You can predict the best choice of flux by using a basic chemical model:

### The acidity / alkalinity equilibrium

An **ACIDIC** sample requires an **ALKALINE** flux  
and  
an **ALKALINE** sample requires an **ACIDIC** flux

# Calculating the Acidity Index

$$\text{Acidity index} = \frac{\text{X}}{\text{Y}} \quad \begin{array}{l} \text{Oxygen atoms} \\ \text{Other atoms} \end{array}$$

**Lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$  ACIDIC)**

$$\text{Acidity index} = \frac{7}{6} = 1.17$$

**Lithium metaborate ( $\text{LiBO}_2$  ALKALINE)**

$$\text{Acidity index} = \frac{2}{2} = 1.00$$



## Calculating the Acidity Index of a Mixture

$$\text{Overall acidity index} = \frac{\text{Qty}_A \times \text{AI}_A + \text{Qty}_B \times \text{AI}_B}{\text{Qty}_{\text{tot}}}$$

**Flux mix, e.g. 67%LiT / 33%LiM**

$$\frac{0.67 \times 1.17}{1.0} + \frac{0.33 \times 1.00}{1.0} = \boxed{1.11}$$

# Important parameters to consider during fusion

## 1. Flux selection

Cement

**LiT**  
(Acidic)

**LiT/LiM**  
**67/33**

**LiT/LiM**  
**50/50**

**LiM**  
(Basic)

# Examples of How to Calculate the Acidity Index

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## Calcium oxide (CaO ALKALINE)

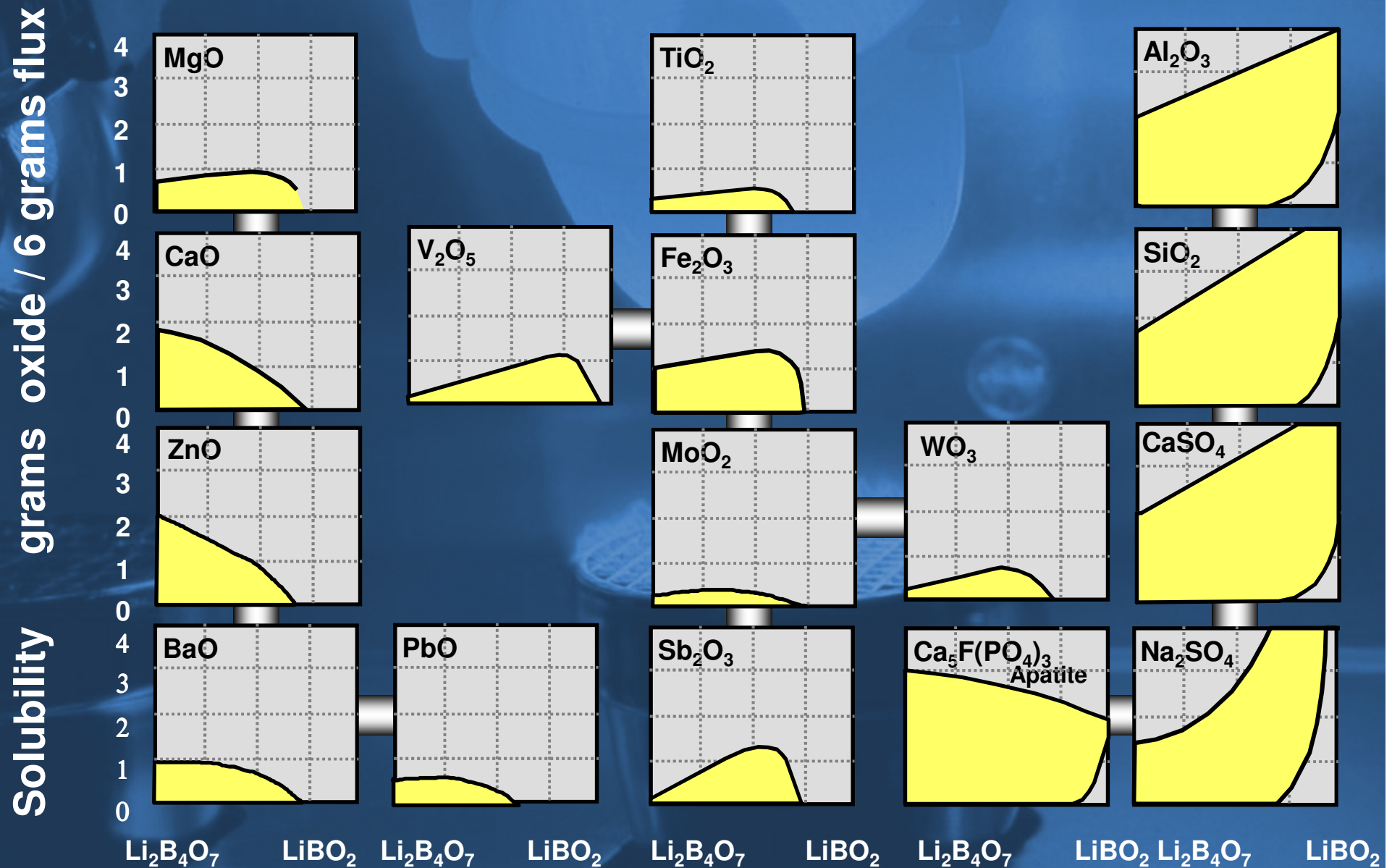
$$\text{Acidity index} = \frac{1}{1} = \boxed{1.00}$$

## Iron oxide (Fe<sub>2</sub>O<sub>3</sub> ACIDIC)

$$\text{Acidity index} = \frac{3}{2} = \boxed{1.50}$$

# Important parameters to consider during fusion

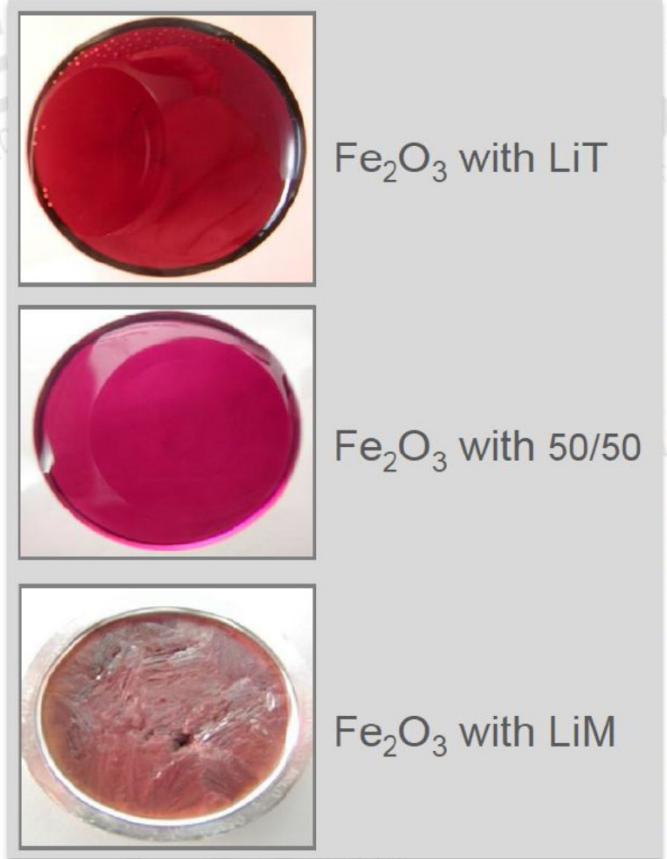
## 1. Flux selection





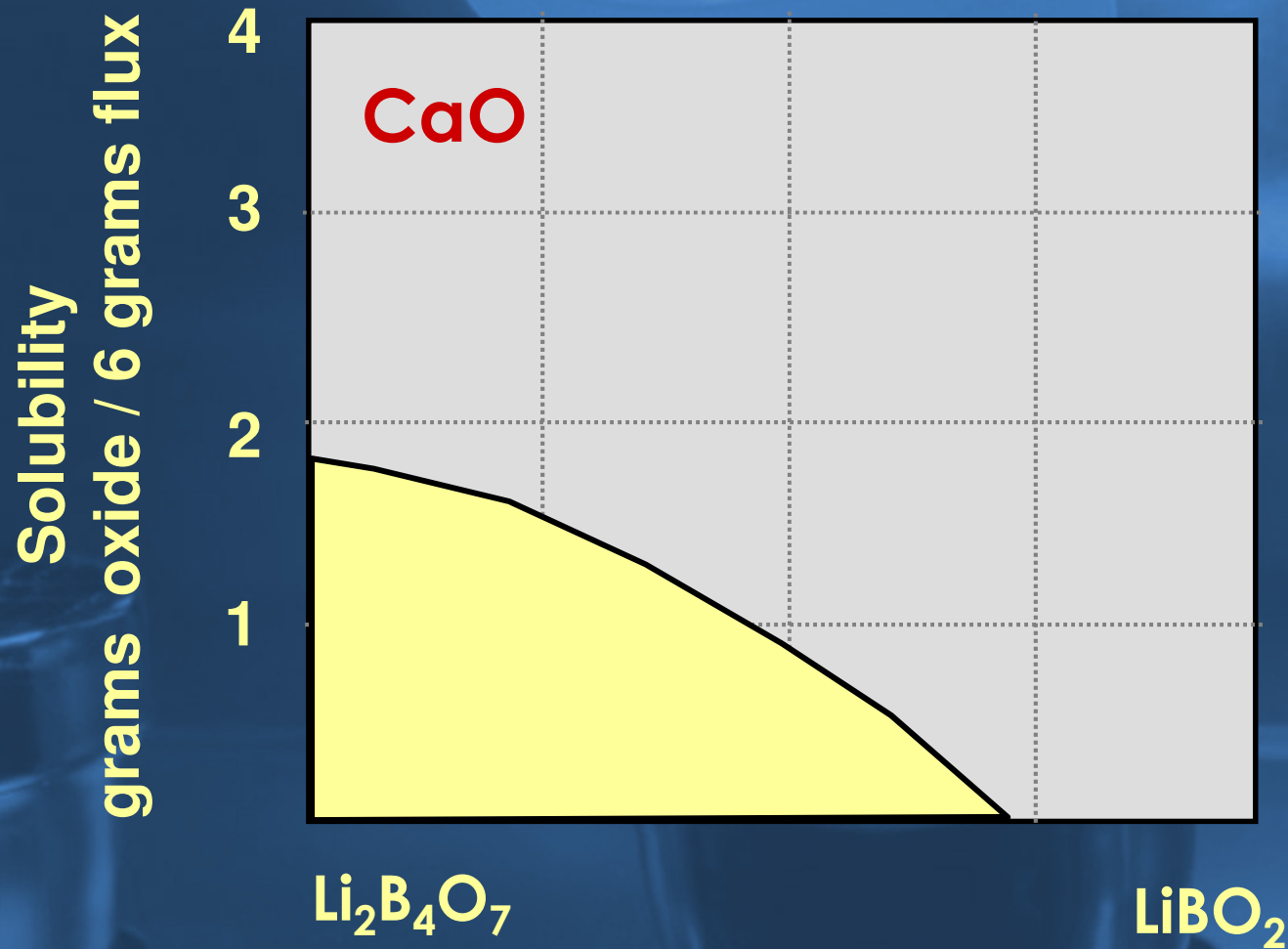
Keys to success: **2. Flux Selection**

- Optimizes solubility of the sample
- Glass disk stability
- Appropriate melting point
- Better fluidity
  - Accelerates dissolution
  - Better pouring
  - Less sticking on the platinum
  - Retains less bubbles



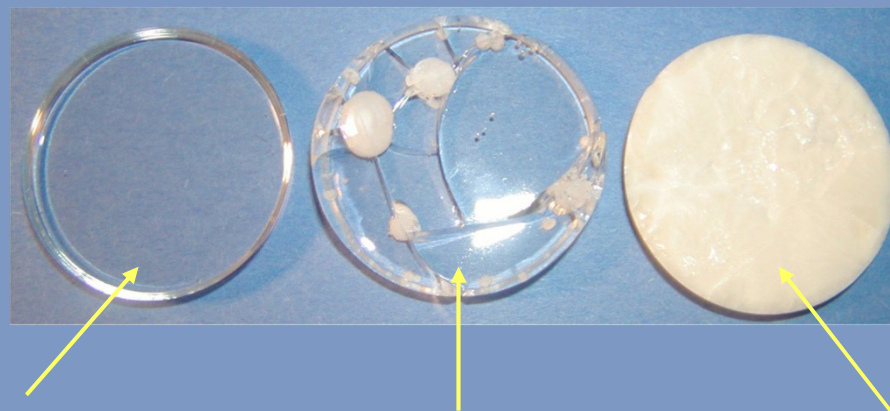
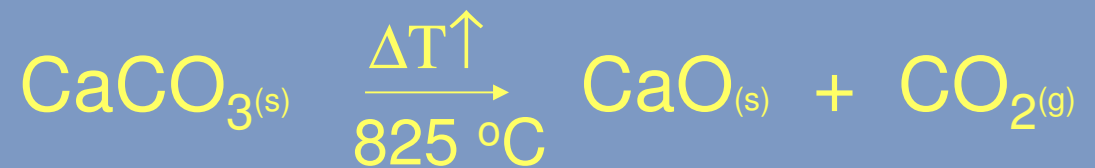
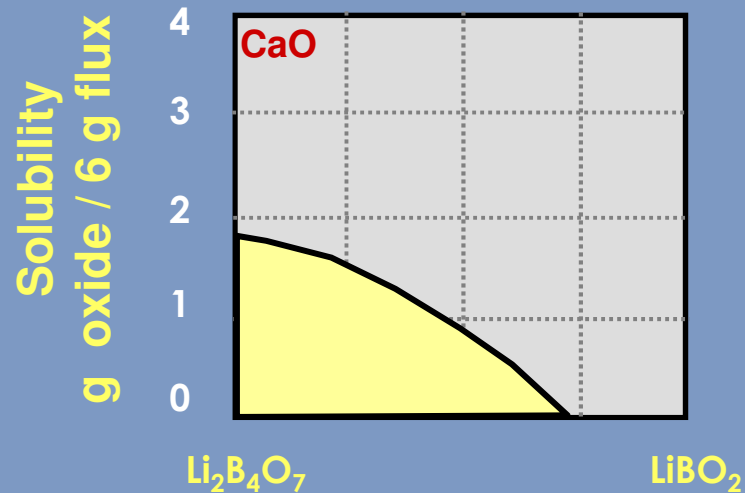
# Important parameters to consider during fusion

## 1. Flux selection



# Important parameters to consider during fusion

## 1. Flux selection



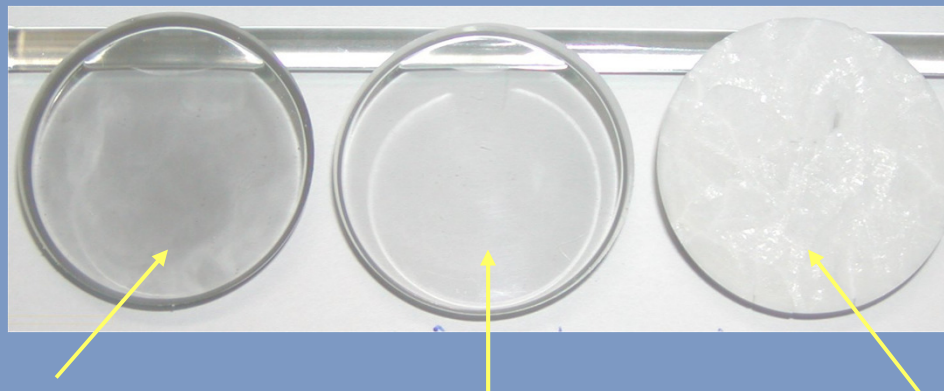
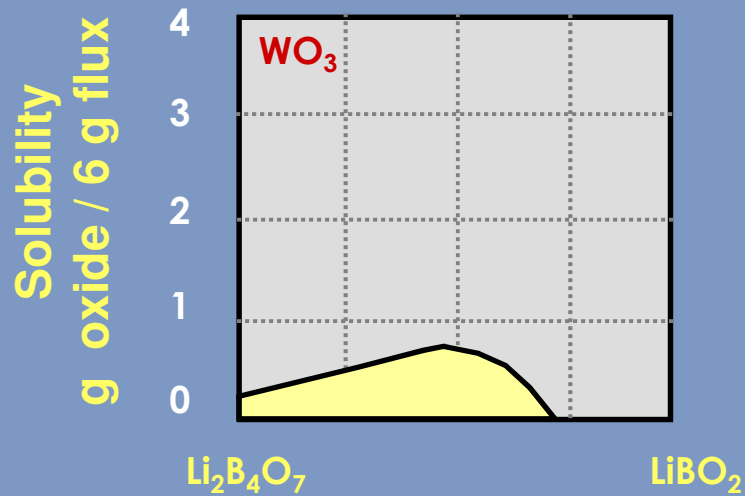
$\text{CaCO}_3$  with LiT

$\text{CaCO}_3$  with 50/50

$\text{CaCO}_3$  with LiM

# Important parameters to consider during fusion

## 1. Flux selection



$\text{WO}_3$  with LiT

$\text{WO}_3$  with 50/50

$\text{WO}_3$  with LiM



## We Recommend

|           |   |                |
|-----------|---|----------------|
| Cement    | → | 67/33 or 50/50 |
| Ceramic   | → | 50/50 to 35/65 |
| Catalyst  | → | 67/33 to 35/65 |
| Limestone | → | 67/33          |
| Iron ore  | → | 50/50          |
| Alumina   | → | 35/65          |

Keys to success: **3. Flux / Sample Ratio**

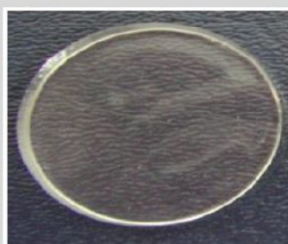
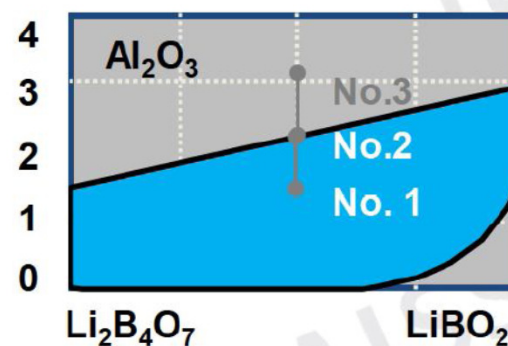
Same sample but different ratios

SAMPLE: 1.0 - 3.0 g

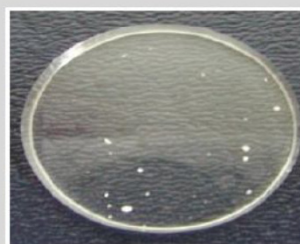
FLUX: 6.0 g

Stability

g oxide / 6 g  
flux



1 g  $\text{Al}_2\text{O}_3$



2 g  $\text{Al}_2\text{O}_3$



3 g  $\text{Al}_2\text{O}_3$

Keys to success: **4. Particule Size**

Smaller particles are easier to oxidize and are dissolved faster

**Coarser** than 100µm



Incomplete oxidation + Cracking

**Finer** than 100µm



Complete oxidation and dissolution



Keys to  
success:

## 5. Fusion Temperature

Melting and dissolving are two different phenomena:

In a fusion context, the flux must **MELT** before the sample can **DISSOLVE** into the molten flux

### Importance of fusion temperature

#### HIGH temperature (>1050°C)

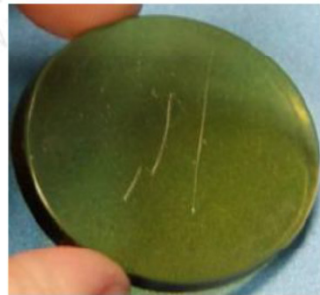
- Loss of volatile elements (Na & SO<sub>3</sub>) and non-wetting agent
- Loss of flux by volatilization
- Platinum deterioration

#### LOW temperature (<1050°C)

- Negligible loss of material
- Higher accuracy
- Retention of SO<sub>3</sub> & Na



## Keys to success: 6. The Quality of the Platinumware Surface



**Influences the distance travelled by the X-rays**

**Affects: elemental intensities**



**Sticking on the platinum crucible wall**

**Affects: Affects melt homogeneity and fusion success rate**

# Important parameters to consider during fusion

## 7. Quality of the mould surface



**%CaO**

64.07  
64.22  
64.18  
63.96  
64.07  
64.18  
64.11  
64.16  
64.04

**%CaO**

63.62  
63.72  
63.72  
63.58  
63.50  
63.54  
63.74  
63.43  
63.59

**%CaO**

63.22  
63.05  
63.05  
63.15  
63.42  
63.16  
63.17  
63.14  
63.19

Average

**64.11**

**63.60**

**63.17**

Std

**0.08**

**0.11**

**0.11**

RSD%

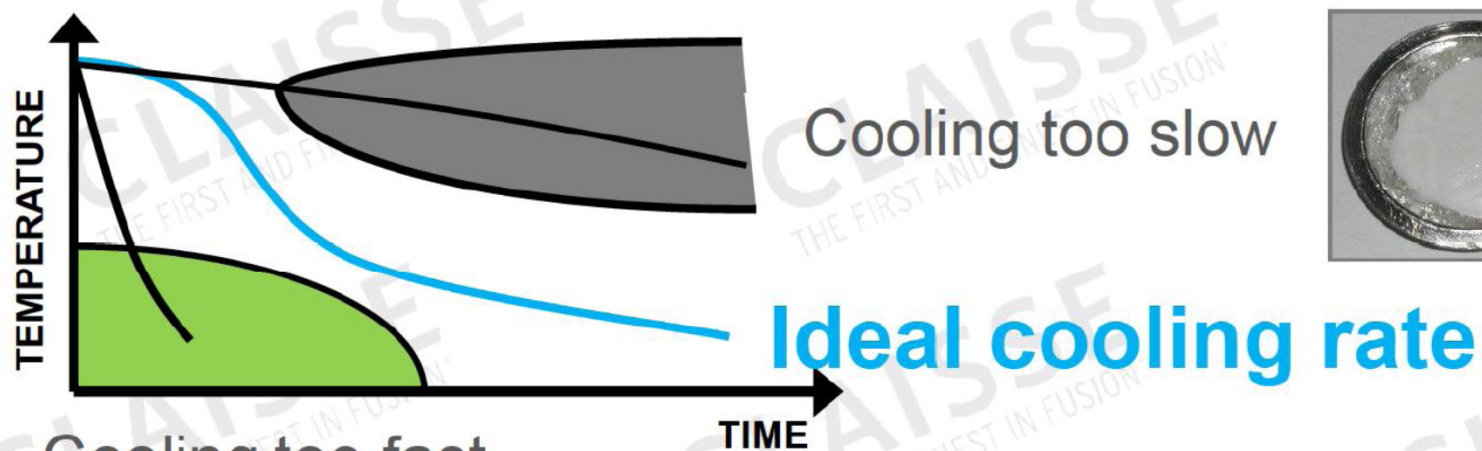
**0.13**

**0.17**

**0.17**



Keys to success: **7. Cooling Rate (Glass Disk)** Specific to XRF Application



## Keys to success: 8. Other Special Keys for ICP Analysis

- TDS must be lower than 1 % on an optical ICP and lower than 0,2 % on an ICPMS– Dilution is necessary
- Reduction of the sample residence time in the plasma
- Use a high energy plasma to avoid deposits on the ICP-OES torch
- Increasing the argon flow rate
- Decreasing the sample flow rate
- Selection of proper sample introduction components:
  - Cyclonic spray chamber
  - Meinhard nebulizer



## Conclusion

- Sample preparation by fusion is a fast and reliable method
- Many different samples can be processed with a single sample preparation method
- Automated method leads to repeatable and precise results
- Possible use of synthetic or pure oxides for calibration

## Sample Preparation by Fusion Allows a Quick ROI

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- Facilitate routine analysis
- Increase analysis throughput
- Improve the quality of results
- Save time and resources
- Save money



# Fluxes

## Two Main Products:

1. Lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ )
2. Lithium metaborate ( $\text{LiBO}_2$ )

## Two Types of Fluxes:

1. Powder
2. Pre-fused



## Powder Flux

- Fluffy
- Low density (0.3 to 0.5 g/cm<sup>3</sup>)
- Segregation possible when LiT and LiM are mixed
- More hygroscopic
- Lower cost



## Pre-fused Flux (Fused Vitreous Beads)

- Uniform glass beads
- High density (1,4 g/cm<sup>3</sup>)
- No segregation, uniform mixture
- Anhydrous, non-hygrosopic
- Available with NWA (non-wetting agent)
- Stable over time

**It is the best option for sample preparation by fusion.**

## Purity

- Pure: 99,98%
- Ultra pure: 99,995+%



# Fluxes Available at Claisse

|                           | Types of Fluxes              | Details                                                                            | Benefits for Customers   |
|---------------------------|------------------------------|------------------------------------------------------------------------------------|--------------------------|
| Regular Product           | Integrated non-wetting agent | Fused vitreous beads with fused non-wetting agent                                  | High fusion success rate |
|                           | Vitreous beads               | LiT – LiM<br>Mixtures of LiT / LiM: 12/22 – 50/50 – 67/33                          | Low water, higher purity |
|                           | Powder fluxes                | LiT – LiM<br>Mixtures of LiT / LiM: 12/22 – 50/50 – 67/33                          | Cheaper                  |
| Customizable              | Prewriteghed vials           | Can be powder, vitreous, integrated NWA and integrated oxidizers, weight per vials | Productivity             |
| Created for the Customers | Special                      | Internal standard                                                                  | Customized               |
|                           | Integrated oxidizers         | Physical mixture between fused vitreous beads and powder oxidizers                 | Productivity             |

# Benefits of Using the Fluxes Offered by Claisse

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- Made of vitreous beads
  - Available with or without NWA
  - Anhydrous
  - Stable
  - Non-hygroscopic

They have a:

- High density
- Controlled granulometry