Quality control in quantitative microanalysis and reference materials

Emma Bullock

Carnegie Science

Earth & Planets Laboratory

European Microbeam Analysis Society

Introduction

- **What do we mean by quantitative analysis?**
  - Comparing our unknowns against a well-characterized material

- ~~**EDS and WDS quantitative analysis**~~
  - ~~Sample preparation~~
  - ~~Calibrating your spectrometers~~
  - ~~Choosing your working conditions~~

- **Standard and reference materials**
  - What makes a good standard?
  - How to choose good standards

Quantitative analysis

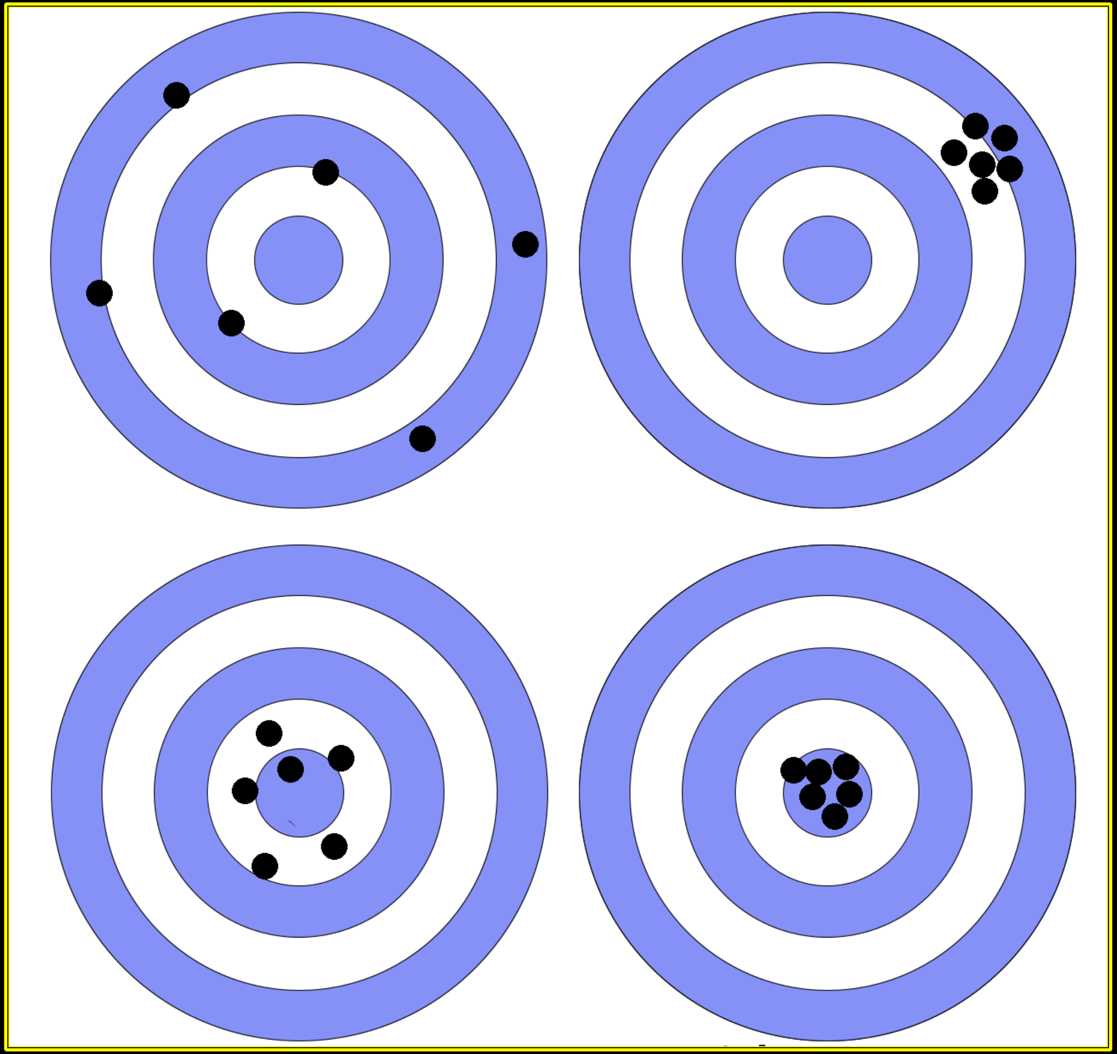
- **Aka Standardized or Standards-based analysis**
  - Comparing the intensity of your unknown material against one of a known composition
  - Wavelength Dispersive Spectroscopy is quantitative
  - Energy Dispersive Spectroscopy may or may not be

- **Compare with Standardless analysis**
  - Uses an in-built factory database
  - Totals are always normalized to 100%
  - This can hide problems with your analysis
    - Missing elements
    - Incorrect valence states

Accuracy versus Precision

Low Accuracy
Low Precision

Low Accuracy
High Precision



High Accuracy
Low Precision

High Accuracy
High Precision

Standards and reference materials

Standards, Reference materials, and Certified Reference Materials

- According to NIST*:
  - Standard = A document establishing requirements, specifications, guidelines, or characteristics for products, processes, or services.

  - Reference Material = A material sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.
    - Reference Materials (RMs): Generic term for materials used in a measurement process.
    - Certified Reference Materials (CRMs): Reference materials with specified properties, characterized by a metrologically valid procedure, and accompanied by a certificate stating their value and uncertainty.

  - NIST Standard Reference Materials (**SRMs**) - A CRM issued by NIST that meets additional NIST-specific certification criteria.

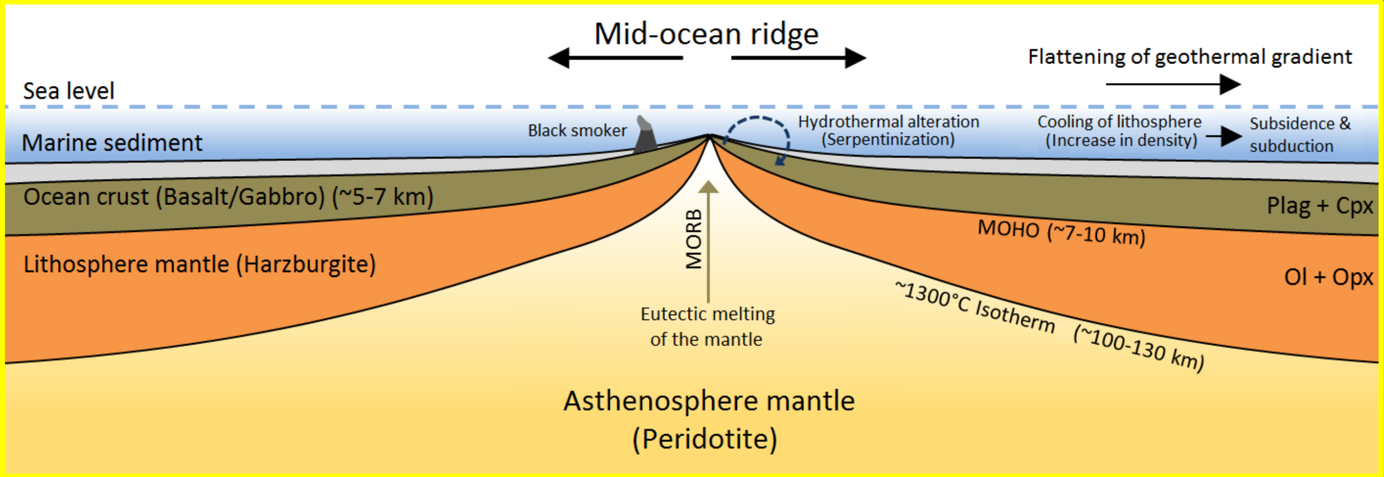
*National Institute of Standards and Technology

...Not all standards/reference materials are created equal....

Why are good standards so important?

Case study: Mid-Ocean Ridge Basalts ("MORBs")

- Rocks that form at divergent plate boundaries:
  - e.g. Mid-Atlantic Ridge
- Geologists care because:
  - Help us understand plate tectonics
  - Important for ocean chemistry
  - Retain evidence for magnetic pole reversals
  - Support ecosystems



Wikipedia

https://earthsci.org/story/mid_ocean_ridge/mid-ocean_ridge.html

Why are good standards so important?

Case study: Mid-Ocean Ridge Basalts (“MORBs”)

- Chemistry determined using ICP-MS and EPMA

- Gale et al., 2013, *“The mean composition of ocean ridge basalts”*

- Global datasets compiled and corrected

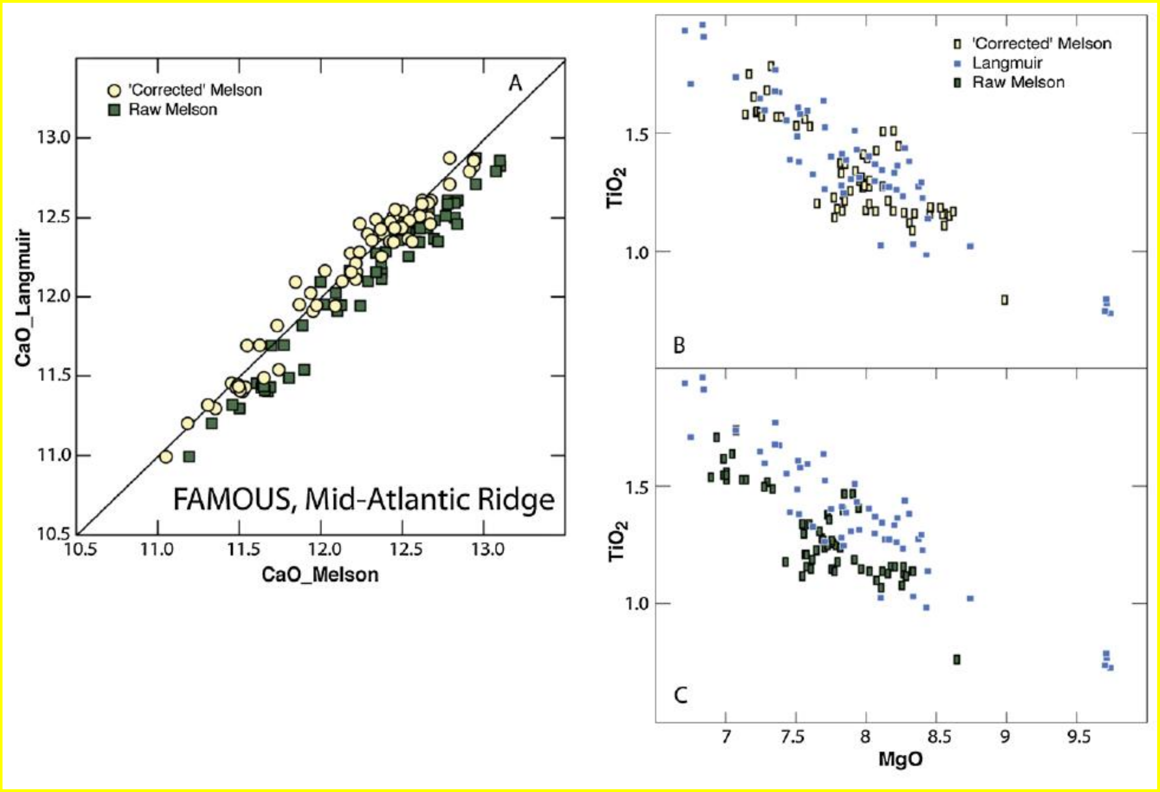


Figure 2. (A) Measurements of CaO (wt. %) from both the Langmuir and Smithsonian laboratories on identical samples from the FAMOUS segment, with a 1:1 line for reference. (B, C) TiO_2 (wt. %) versus MgO (wt. %) data from the Smithsonian and Langmuir laboratories on samples from a selected region of the Central Indian Ridge. The offset between laboratories is eliminated once proper interlaboratory bias corrections are applied. Without the application of such factors, apparent chemical differences in lavas caused simply by analytical procedures could be erroneously interpreted as true differences.

Why are good standards so important?

Case study: Mid-Ocean Ridge Basalts ("MORBs")

- The magnitude of the correction applied varies by lab

- Without careful correction, "variations" in composition could be misinterpreted

Microscopy and Microanalysis, **29** (Suppl 1), 2023, 243–244
https://doi.org/10.1093/micmic/ozad067.109

Microscopy AND Microanalysis

Meeting-report

The Holy Trinity of Microanalysis: Standards, K-ratios and Physics

John Donovan[1], Aurélien Moy[2], Will Nachlas[2], and John Fournelle[2]

[1]*CAMCOR, University of Oregon, Eugene, Oregon, USA*
[2]*Department of Geoscience, University of Wisconsin-Madison, Wisconsin, USA*

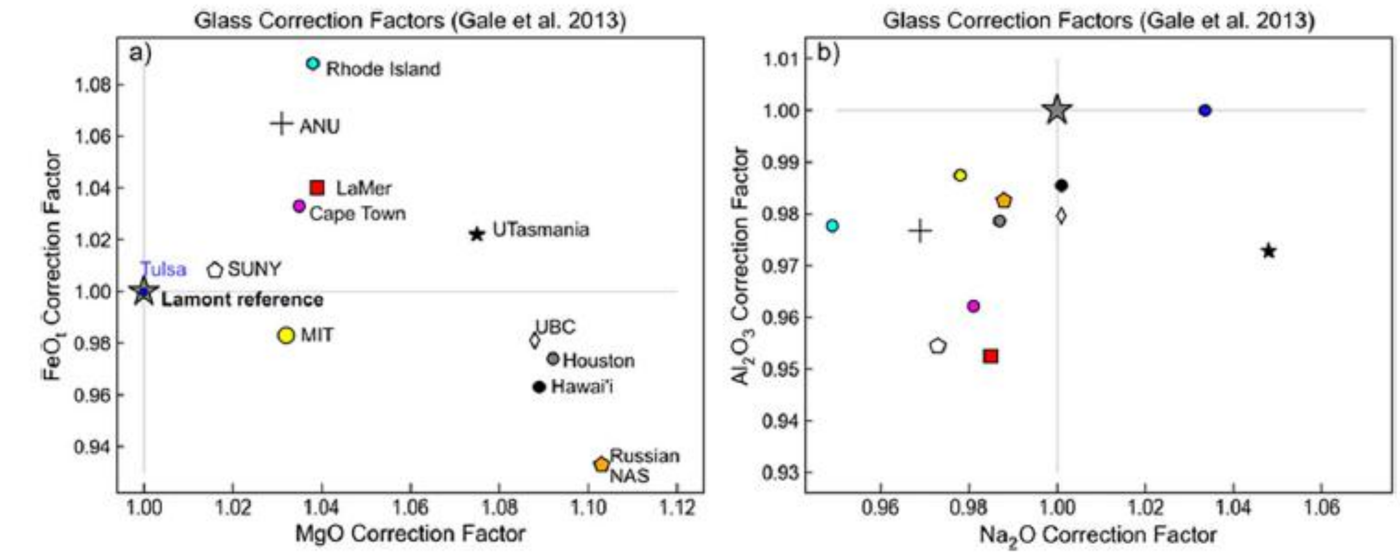


Fig. 1. In part, due to reliance on natural standards with uncertain composition, documented heterogeneity and unknown purity, inter-laboratory comparisons show consistently divergent results for a number of elemental systems.

So…. What makes a good standard?

What makes a good standard or reference material?

- Compositionally homogenous at the scale of the analysis
  - Not zoned
  - No inclusions (or easily-avoidable inclusions)
  - Same composition from grain to grain
- Be well-characterized
- Have an independently verified composition
  - Not just an EDS spectra!

What makes a good standard or reference material?

Mindat.org

<u>San Carlos olivine</u>

- Grains not zoned from core to rim
- USNM 111312-444
  - $Fo_{89.6}$ to $Fo_{90.5}$
  - "Given" $Fo_{90.1}$
- Non-USNM
  - $Fo_{89.2}$ to $Fo_{91.4}$
- Mount multiple grains and characterize them!

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842
doi:10.1017/S1431927611005083
Microsc. Microanal. 17 (Suppl 2), 2011
© Microscopy Society of America 2011

An Investigation of "San Carlos Olivine": Comparing USNM-distributed Material with Commercially Available Material

John H. Fournelle*

ELSEVIER
Chemical Geology
Volume 605, 5 September 2022, 120968

Compositional variability of San Carlos olivine

Sarah Lambart [a], Sarah Hamilton [a], Otto I. Lang [a]

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https://doi.org/10.1016/j.chemgeo.2022.120968
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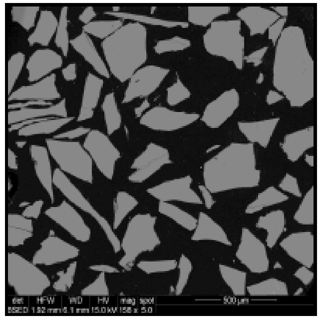
Highlights

- We report the major, minor & trace variability of non-USNM San Carlos olivine

Smithsonian
National Museum of Natural History

Olivine, NMNH 111312-44

SiO_2:	40.81
FeO:	9.55
MgO:	49.42
CaO:	<0.05
P_2O_5:	0.00
MnO:	0.14
NiO:	0.37
TOTAL	100.29



Size fractions available:
0.25 mm - 0.177 mm

Analysis: E. Jarosewich (Jarosewich, *et. al.*, 1980).
Source: San Carlos, Arizona

Standard Specifics:

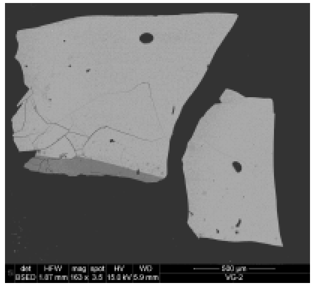
See Fournelle (2011) for detailed compositional variability.

What makes a good standard or reference material?

Smithsonian
National Museum of Natural History

Glass, Basalt NMNH 111240-52 *(VG-2)*

		* preferred values	
SiO_2:	50.81	SiO_2:	50.81
Al_2O_3:	14.06	Al_2O_3:	14.06
Fe_2O_3:	2.23	Fe_2O_3:	2.23
FeO:	9.83	FeO:	9.83
MgO:	6.71	MgO:	6.95
CaO:	11.12	CaO:	11.12
Na_2O:	2.62	Na_2O:	2.62
K_2O:	0.19	K_2O:	0.19
TiO_2:	1.85	TiO_2:	1.85
P_2O_5:	0.20	P_2O_5:	0.20
MnO:	0.22	MnO:	0.22
H_2O^-:	0.02	H_2O^-:	0.02
Total	99.86		100.10



Analyst: E. Jarosewich (Jarosewich et. al., 1980)
Source: Juan de Fuca Ridge

Size fractions available:
1.0 mm - 2.0 mm
> 0.350 mm

Standard Specifics:

*NOTE: It is widely known that the published **MgO** value for VG-2 is low. We suggest 6.95 wt.% is a better working value based on hundreds of analyses of numerous grains from the original material. See Helz et al (2014).

Trace elements: see Jenner and O'Neill (2012) for a large suite of trace element analyses by LA-ICP-MS.

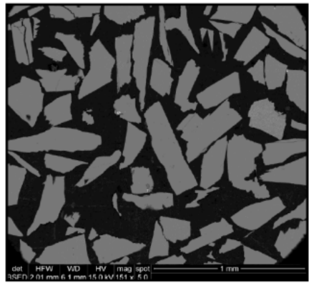
Sulfur and Cl content: see the next page for information about the S and Cl content.

Impurities: tiny olivine crystals; common
plagioclase; large crystal (on one grain)

Smithsonian
National Museum of Natural History

Hornblende (Kakanui) NMNH 143965

SiO_2:	40.37
Al_2O_3:	14.90
Fe_2O_3:	3.30
FeO:	7.95
MgO:	12.80
CaO:	10.30
Na_2O:	2.60
K_2O:	2.05
TiO_2:	4.72
P_2O_5:	0.00
MnO:	0.09
H_2O:	0.94
TOTAL	100.02



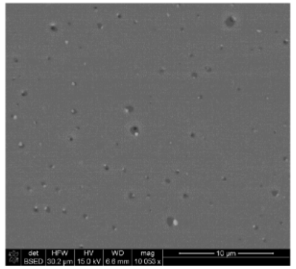
Analyst: E. Jarosewich (Jarosewich *et. al.*,1980)
Source: Kakanui, New Zealand

Sizes available:
0.590 mm - .420 mm,
> 0.420 mm
0.420 mm - 0.297 mm
0.420 mm - 0.250 mm
0.297 mm - 0.177 mm
0.250 mm - 0.177 mm
0.250 mm - 0.177 mm
0.177 mm - 0.125 mm

Standard Specifics:

Impurities: FeTi oxide: complex melt (?) inclusions with tiny oxide crystals; abundant (see image)

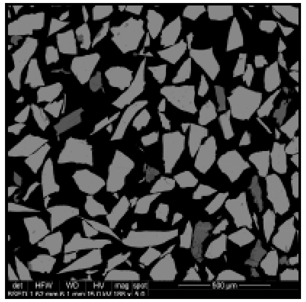
Impurities: FeTi oxide: larger individual crystals; rare



Smithsonian
National Museum of Natural History

Fayalite, NMNH 85276

SiO_2:	29.22
Fe_2O_3:	1.32
FeO:	66.36
TiO_2:	0.04
MnO:	2.14
H_2O:	0.10
TOTAL	99.18

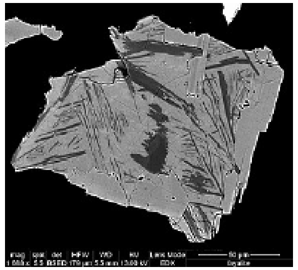


Analyst: J. Nelen (Jarosewich et. al., 1980).
Source: Rockport, Massachusetts

Size fractions available:
Tiny grains, see image.

Standard Specifics:

Impurities: This material is known to contain approximately 10% amphibole, probably grunerite, commonly associated with the Fayalite from this locality (visible in image above). Some Fayalite grains are intergrown with impurities. Other complex grains such as the image below remain largely unstudied.



What makes a good standard or reference material?

- NMNH datasheets found at:

https://naturalhistory.si.edu/research/mineral-sciences/collections-overview/reference-materials/smithsonian-microbeam-standards

Smithsonian
National Museum of Natural History

Hornblende (Kakanui) NMNH 143965

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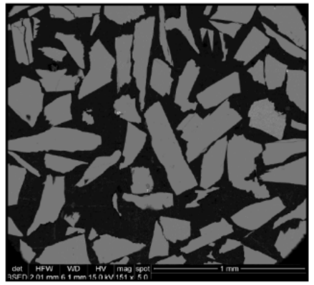

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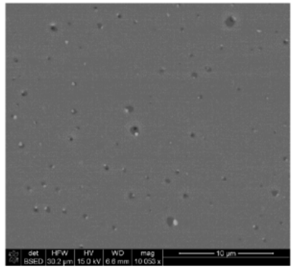

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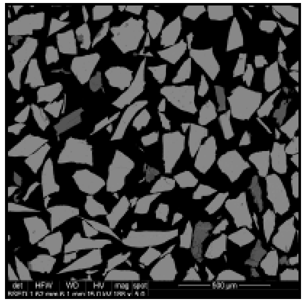

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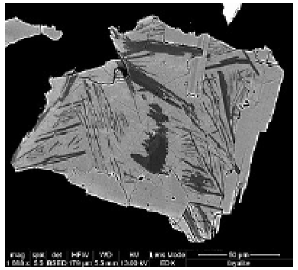

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- Stable under the electron beam
- Easy to mount and (re)polish
- Available in sufficient quantity to allow comparison with other labs

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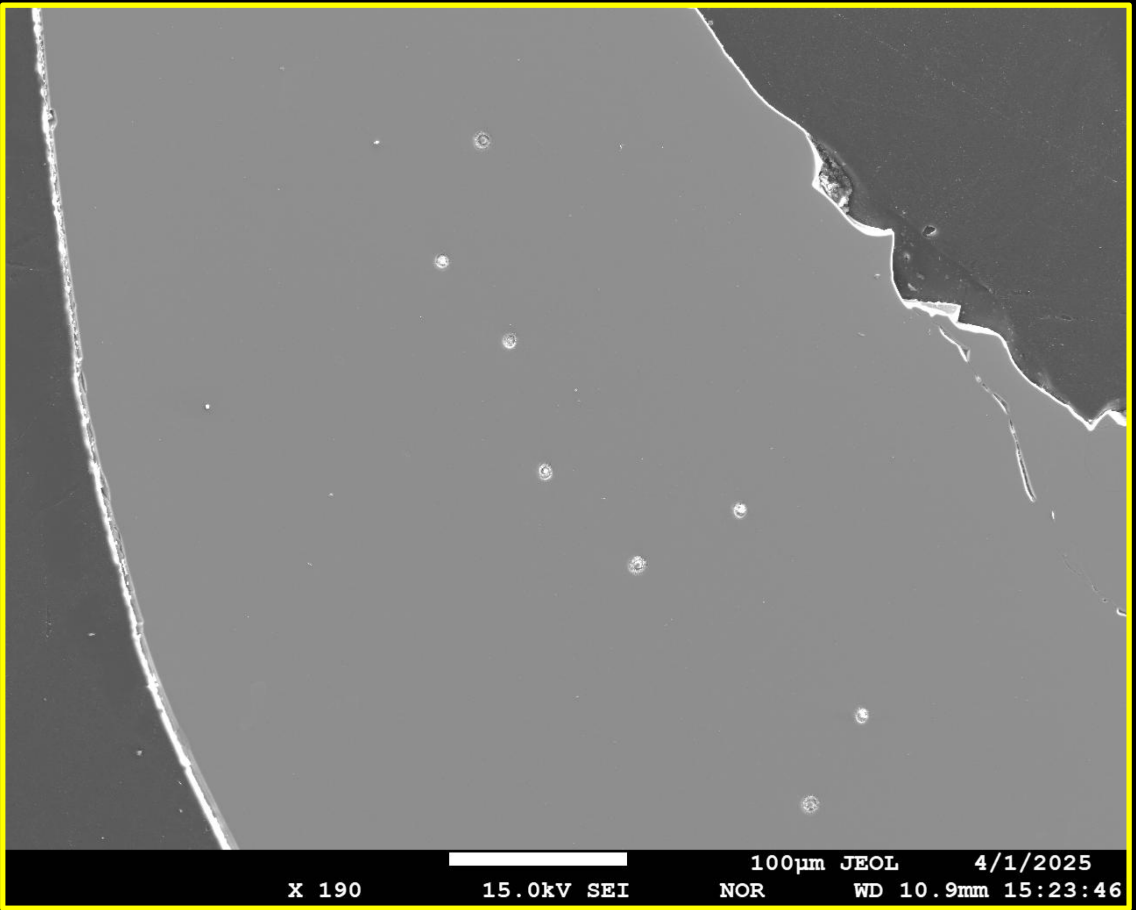

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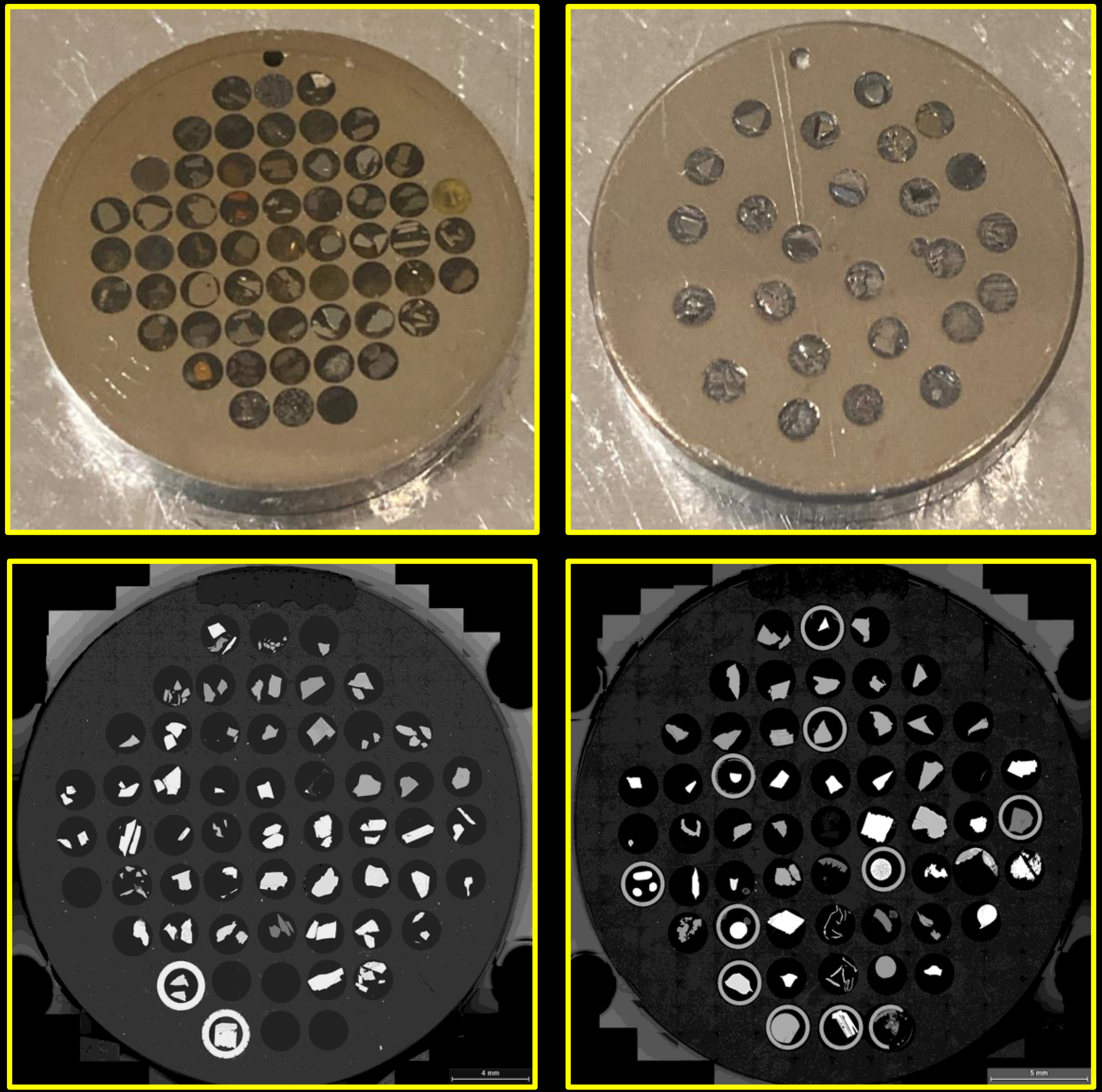

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So…. Where can I find good standards?

Obtaining standards

- **From national collections**
  - (e.g. Smithsonian, NIST, USGS…)
- **Companies:**
  - MAC standards (Electron Microscopy Sciences)
  - Geller standards (Agar Scientific, Avantor ScienceCentral)
- Other labs…
- **BUT:**
  - Standards unavailable, or only in tiny quantities
  - Trust but verify materials

USGS science for a changing world

Smithsonian

NIST

Electron Microscopy Sciences

agar scientific A CALIBRE SCIENTIFIC COMPANY

CARNEGIE SCIENCE

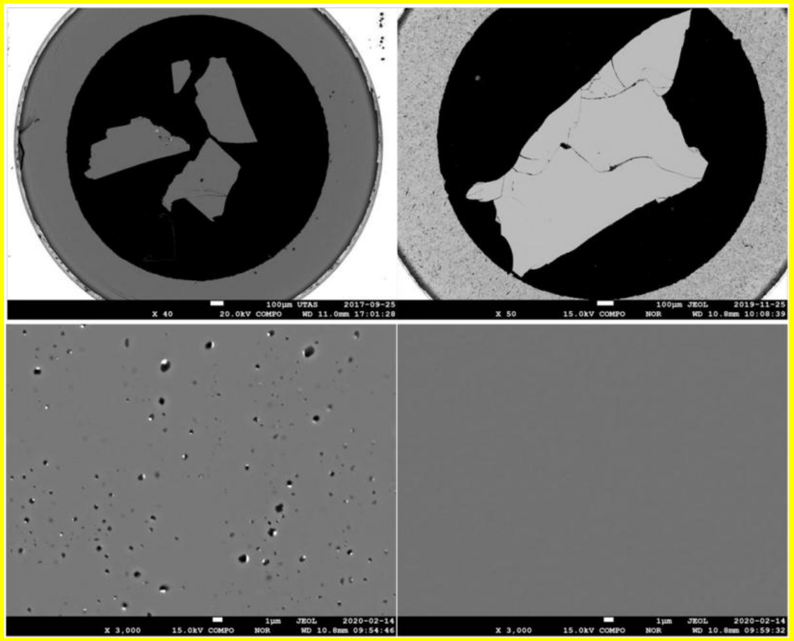
And others….

Finding new standards

- **Microanalysis community identifying new materials**

Anette von der Handt, Round robin of materials

John Fournelle, Kakanui hornblende



Vol. 47 — N° 4 12/23 p. 907–929

GEOSTANDARDS and GEOANALYTICAL RESEARCH

A New Albite Microanalytical Reference Material from Piz Beverin for Na, Al and Si Determination, and the Potential for New K-Feldspar Reference Materials

Julien M. **Allaz** (1)*, Marcel **Guillong** (1), Lorenzo **Tavazzani** (1), Georg **Spiekermann** (1), Lydia **Zehnder** (1), Emma **Bullock** (2), Joel **DesOrmeau** (3), Michael J. **Jercinovic** (4), Joachim **Krause** (5), Felix **Marxer** (6), William O. **Nachlas** (7) and John **Spratt** (8)

Finding new standards

- K-ratio database:
  - Ratio of the X-ray intensity in the standard versus unknown
  - A universal quantity, independent of the instrument or detector
    - when measured under the same conditions
  - Deviations in the k-ratio may indicate instrument instability
    - Avoid MORB-like issues in the future….

Finding new standards

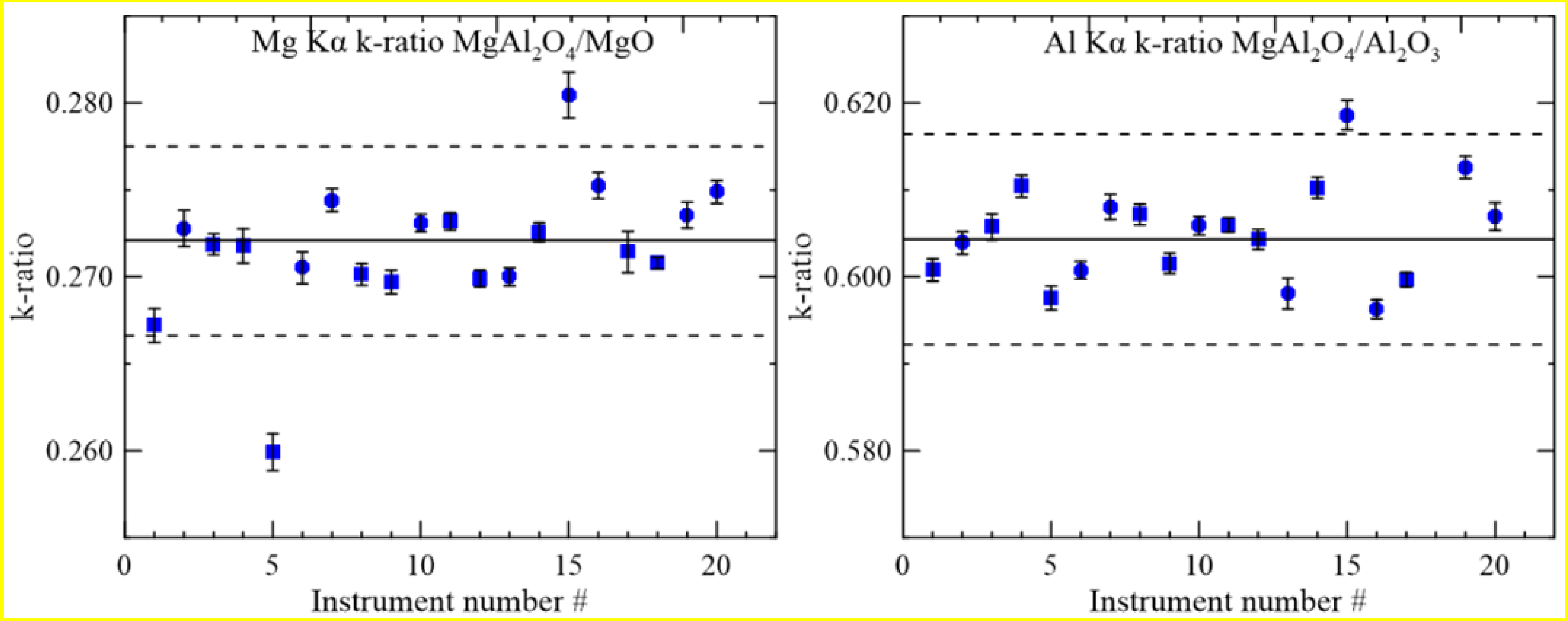
- K-ratio database:
  - The k-ratio obeys the transitive property:
    - If one thing is related to a second thing, and the second thing is related to a third thing, then the first thing is also related to the third thing
  - The k-ratio of material A with respect to material B can be determined through an intermediary material C
    - If: there is agreement about material C
    - Then: Lab 1 can measure k_{AC}
    - Lab 2 can measure k_{BC}
    - And Lab 1 can determine k_{AB} without ever having material B in their lab

Finding new standards

- K-ratio database:
  - If labs have a common set of materials, they can compare k-ratios
    - Determine instrument stability
    - Compare materials via k-ratio rather than directly measuring them
  - Will Nachlas, Nicholas Ritchie et al are working on a “Universal Standard Mount”
    - Ultra-high purity synthetic materials
    - Covering elements commonly analyzed in geology
    - Create a community “Consensus” database of k-ratios

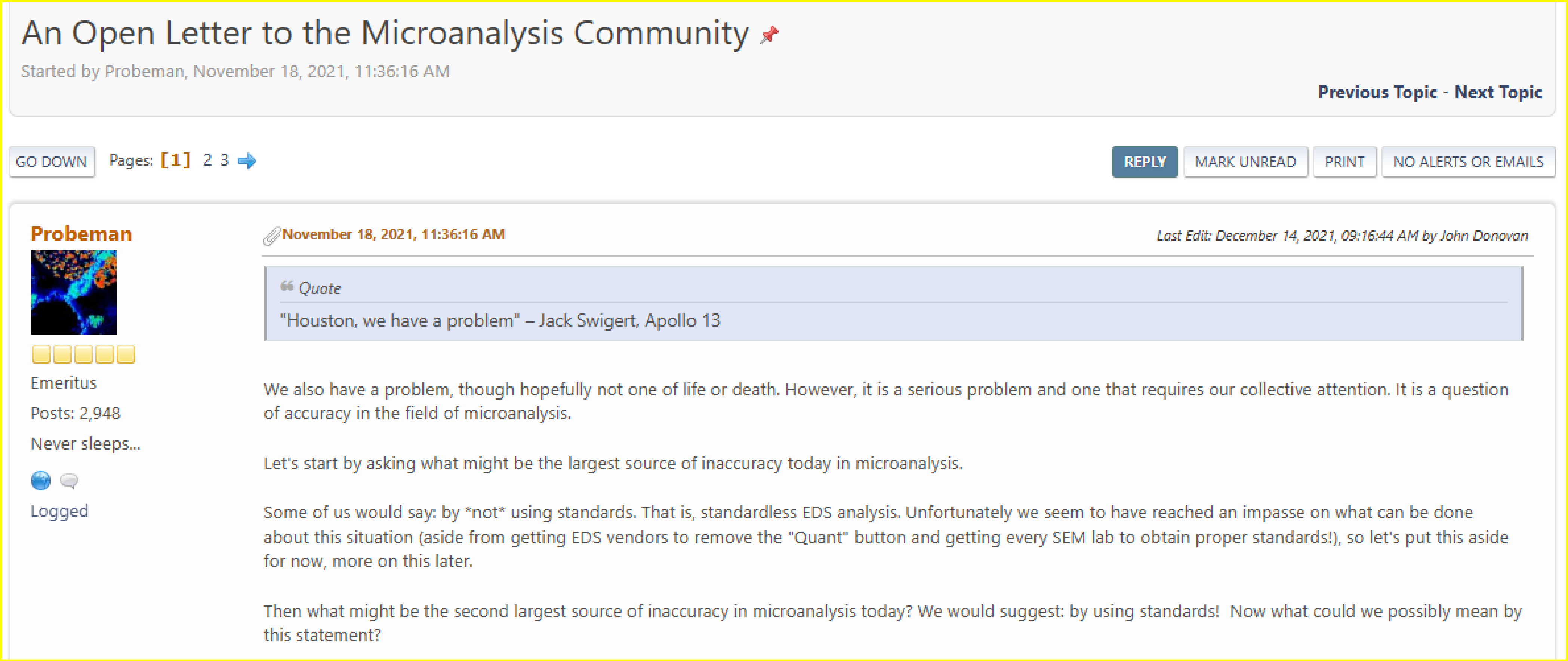
Finding new standards

- Round robin of MgO, Al_2O_3 and $MgAl_2O_4$
- Specific instructions given on how/what to measure



Finding new standards

- John Donovan call to action:



An Open Letter to the Microanalysis Community

Started by Probeman, November 18, 2021, 11:36:16 AM

Previous Topic - Next Topic

GO DOWN   Pages: [1] 2 3

REPLY   MARK UNREAD   PRINT   NO ALERTS OR EMAILS

Probeman

Emeritus

Posts: 2,948

Never sleeps...

Logged

November 18, 2021, 11:36:16 AM

Last Edit: December 14, 2021, 09:16:44 AM by John Donovan

> *Quote*
>
> "Houston, we have a problem" – Jack Swigert, Apollo 13

We also have a problem, though hopefully not one of life or death. However, it is a serious problem and one that requires our collective attention. It is a question of accuracy in the field of microanalysis.

Let's start by asking what might be the largest source of inaccuracy today in microanalysis.

Some of us would say: by *not* using standards. That is, standardless EDS analysis. Unfortunately we seem to have reached an impasse on what can be done about this situation (aside from getting EDS vendors to remove the "Quant" button and getting every SEM lab to obtain proper standards!), so let's put this aside for now, more on this later.

Then what might be the second largest source of inaccuracy in microanalysis today? We would suggest: by using standards! Now what could we possibly mean by this statement?

Finding new standards

- **Microanalysis Society (MAS) making funds available to purchase and analyze material**
  - $10k per year (5 years)
  - $15k per year (following 5 years)

- **Part of the MAS Strategic Initiative**

- **Funding provided for purchasing, synthesizing, analyzing, characterizing etc potential new standard material**

Microanalysis Society

Finding new standards

- Which materials?
- Where can we get them?
    - Synthetic/natural?
- How do we characterize them?
- Which techniques do we locate standards for?
- How/where do we store them?
- How do we distribute them?
- Do we charge for them?
    - If so, how much?

Focused Interest Group on Microanalytical Standards (FIGMAS)

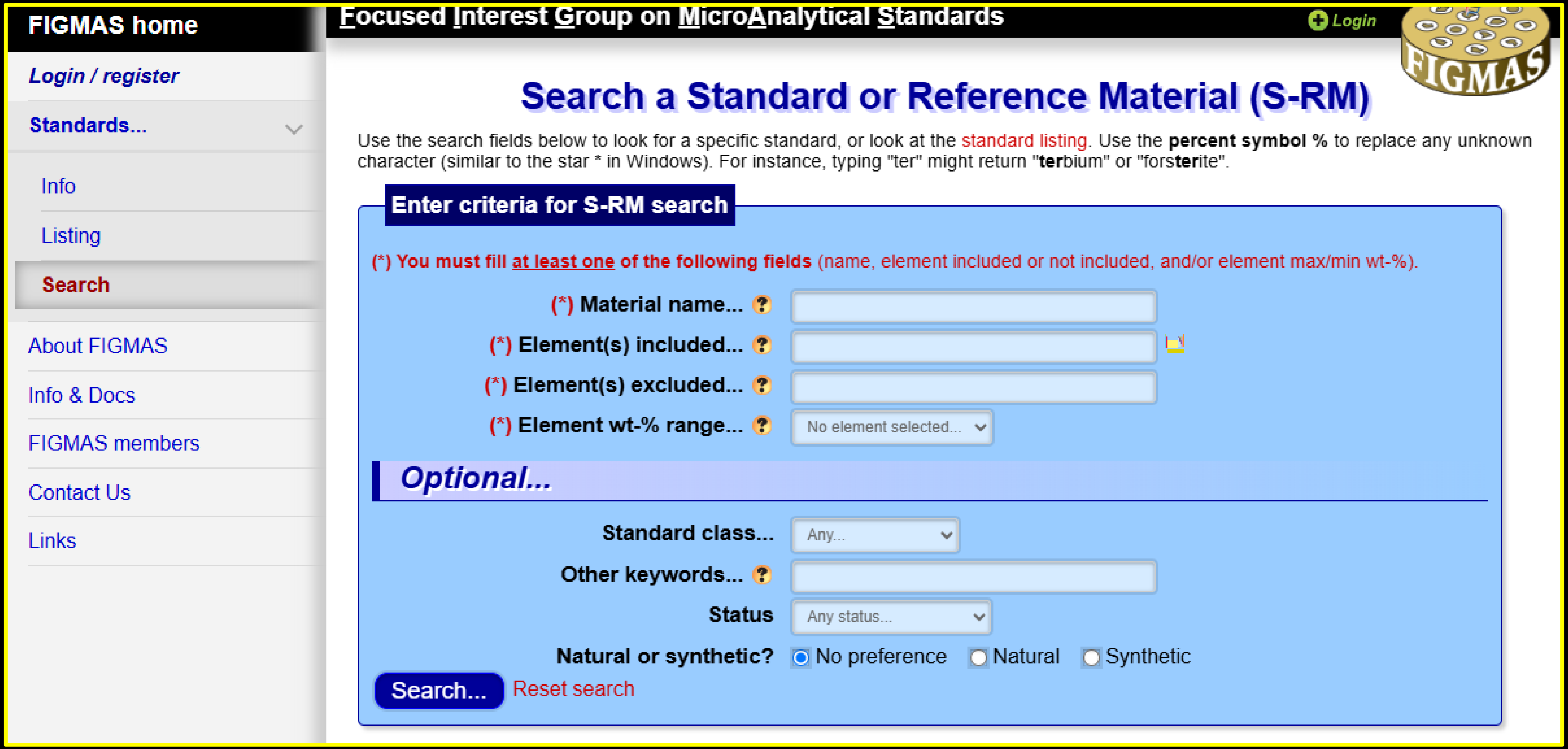
**The Focused Interest Group on MicroAnalytical Standards (FIGMAS) aims to evaluate and catalogue microanalytical standards and reference materials (S-RM) and to facilitate accessibility of these materials to the microanalysis community (EPMA, SEM, LA-ICP-MS…). It is the first group to have been created and approved with the joint support of both MSA and the Microanalysis Society (MAS)"*

Current Leader: Abby Lindstrom (NIST)

https://figmas.org/index.php

Focused Interest Group on Microanalytical Standards (FIGMAS)

*



In summary:

- Quality quantitative microanalysis takes time, care, and patience
- High-quality standards and reference materials are crucial
- As old standards run out, or prove to be lacking, we need to find new sources of material
- Community input will be vital in this endeavour

Questions?
Comments?
Thoughts?
Opinions?

Some resources and links

Gale et al., 2013 "The mean composition of ocean ridge basalts" https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2012GC004334

Donovan et al., 2023 "The Holy Trinity of Microanalysis: Standards, K-ratios and Physics" https://academic.oup.com/mam/article/29/Supplement_1/243/7228584

Lambert et al., 2022 "Compositional variability of San Carlos olivine" https://www.sciencedirect.com/science/article/pii/S0009254122002625

Fournelle, 2011 "An Investigation of "San Carlos Olivine": Comparing USNM-distributed Material with Commercially Available Material" https://academic.oup.com/mam/article-abstract/17/S2/842/6947679

Smithsonian Data sheets: https://naturalhistory.si.edu/research/mineral-sciences/collections-overview/reference-materials/smithsonian-microbeam-standards

Allaz et al, 2023 "A New Albite Microanalytical Reference Material from Piz Beverin for Na, Al and Si Determination, and the Potential for New K-Feldspar Reference Materials" https://onlinelibrary.wiley.com/doi/full/10.1111/ggr.12515

Ritchie et al, 2020 "Proposal: Let's Develop a Community Consensus K-ratio Database" https://www.nist.gov/publications/proposal-lets-develop-community-consensus-k-ratio-database

Nachlas et al, 2023 "Evaluating Consensus in Experimental K-ratios from over 40 WDS and EDS Measurement Systems" https://academic.oup.com/mam/article/29/Supplement_1/225/7228643

John Donovan Call to Action: https://smf.probesoftware.com/index.php?topic=1415.0

Microanalysis Society: https://the-mas.org/