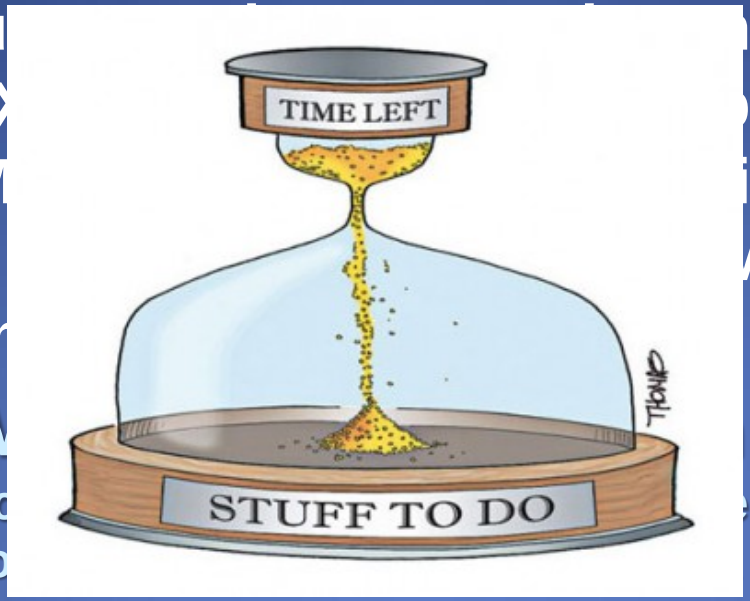
My Assigned Topics

1. Overview of cu ethodology
2. Limitations of X olarized light microscopy (PLM icroscopy (PCM)
3. Advantages of M) methods (SEM, TEM)
4. Methods of mir



M .D.
Ecologic rvices, Inc.
Professor of Geolo @ New Paltz (retired)

How do we measure & characterize the elongate~~X~~ “stuff” in talc products?

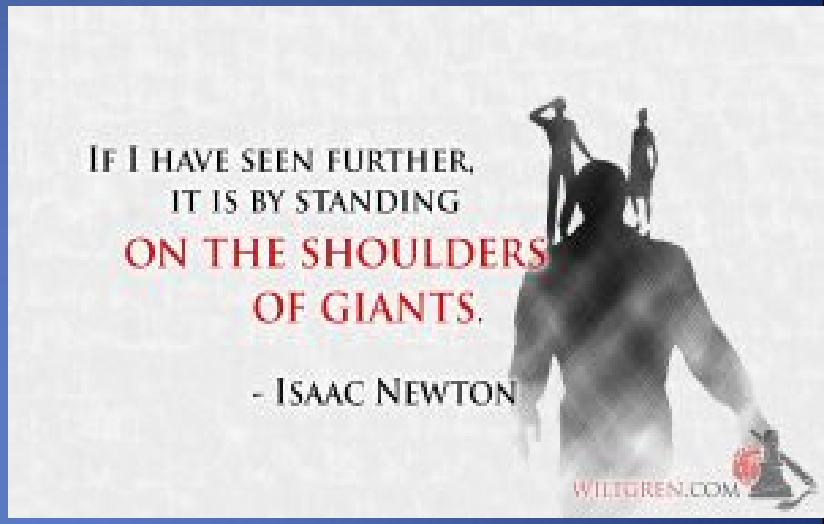
Special thanks to the wisdom of my colleagues on USP's Talc Methods Expert Panels #1, #2

Talc Panel #1

Larry Block*
Detlef Beckers
Jacelyne Ferret
Gregg Meeker
Martin Rutstein
Aubrey Miller
Robert Osterberg
Dilip Patil
Julie Pier
Steven Riseman
Gary Tomaino
Drew Van Orden
James Webber
Jeffrey Medwid (FDA)
Steven Wolfgang (FDA)
Kevin Moore (USP)

Talc Panel #2

Julie Pier*
Martin Rutstein*
Daniel Crane
Sean Fitzgerald
Mickey Gunter
Don Halterman
Kate Houck
Lee Poye
Matthew Sanchez
Alan Segrave
Gary Tomaino
Drew Van Orden
James Webber
Jeffrey Medwid (FDA)
Steven Wolfgang (FDA)
Kevin Moore (USP)

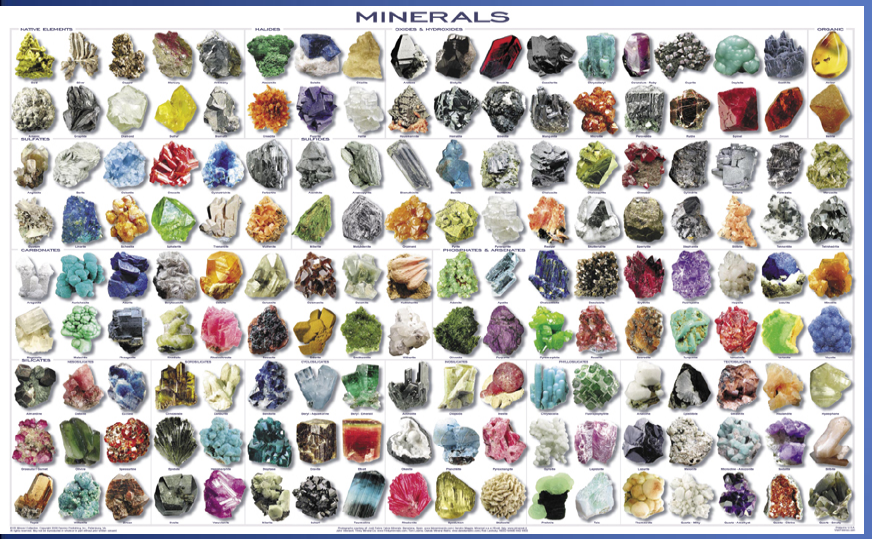


Disclaimer: ***I am speaking in my individual capacity and not on behalf of USP or the USP Talc Methods Expert Panel. All views expressed in this presentation are my own.***

Ref. - See Block *et al*, 2014, USP Talc Panel Stimuli

Topic: Mineral I.D.

Classification
Identification
Characterization



“lots” of minerals to make up rocks & ores

Classified on basis of STRUCTURE & COMPOSITION

(Ref.- See Intro. Ch 19, Dyar & Gunter, 2008)

Mineralogy is the study of minerals. So, what is a mineral?

This, of course, involves the nature of definitions and the "problems of cubbyholes and exceptions".

definition of Pruitt (1966): and a commonly cited legal definition is

"Any substance occurring in the earth having sufficient value separated from its sites to be mined, quarried or dug for its own sake or for its own specific use."

NATURAL
DEPLETABLE
EXPLOITABLE

legal definition can cause “problems”

amphibole grunerite (Fe-Silicate)
ruled to be *”amosite” asbestos* in Lake
Superior mining of taconite ores
(iron-oxide-jasper)

One of the most widely accepted definitions is from Berry and Mason (1959):

A mineral is a naturally occurring, homogeneous solid, inorganically formed, with a definite chemical composition and an ordered atomic arrangement.

Advanced reference- the Gold Standard (for now)

ERNEST H. NICKEL, JOEL D. GRICE, 1998,

THE (International Mineralogical Association) IMA COMMISSION ON NEW MINERALS AND MINERAL NAMES: PROCEDURES AND GUIDELINES ON MINERAL NOMENCLATURE, The Canadian Mineralogist, vol. 36, pp. 1-14

Mineralogist's Definitions of a Mineral

Nickel & Grice, 1998, The Concept of a Mineral Species

The IMA Commission on New Minerals and Mineral Names: Nomenclature and Guidelines on Mineral Nomenclature, 1998.

The Nomenclature Debacle, 2004, Rocks & Minerals, v. 79, pp 192-193.

Asbestos by Mineralogy & "Color"

Serpentine

- Chrysotile = "white"

Amphiboles

- "Amosite" = "brown" (cummingtonite-grunerite)
- Crocidolite = "blue" (riebeckite)
- Asbestiform varieties of
  - Tremolite, Actinolite, Anthophyllite

“Asbestos” defined by…

Chemistry & Usage

Shape/Size

(The Regulated “Six”)

>5 µm long, diameter <0.3 µm, aspect ratio >3:1 (LAF)

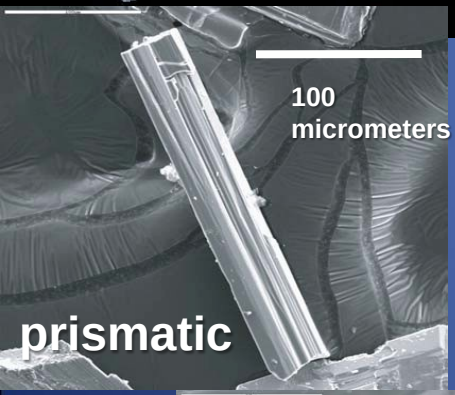
additionally

Medically

Bio-reactivity

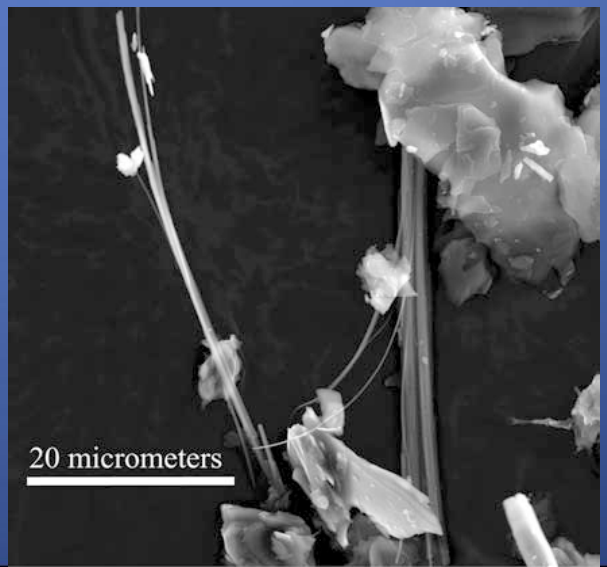
Emotionally

What are these and how do we define and measure?



Van Gosen et al, 2004

Ca-amphiboles



More than 30 analytical methods for “asbestos” (Dodson *et al*, 2007)

The Big Issues

Measurement & regulation of
"elongate" particles (EMP's)
of
talc? tremolite? anthophyllite? c*hrysotile?*
(& some other minerals, esp. sepiolite)

cleavage fragments
(broken crystals)

acicular/prismatic shapes
(long & narrow crystals & fragments)

asbestiform minerals
(fibers formed by crystal growth)

Talc, Asbestos, Amphiboles & Numerous Minerals

One can often find "something" elongate in almost all rocks!

**** Ref. - See**
Gunter et al, 2016
Buzon & Gunter, 2016,
esp. for sepiolite

Building Materials
vs.
Pharmaceutical-Personal Care Products

Building materials relatively much more straightforward

Pharmaceutical products much more complicated!

Definitional Conundrums

Conflicting definitions: mineralogical, industrial, regulatory & legal

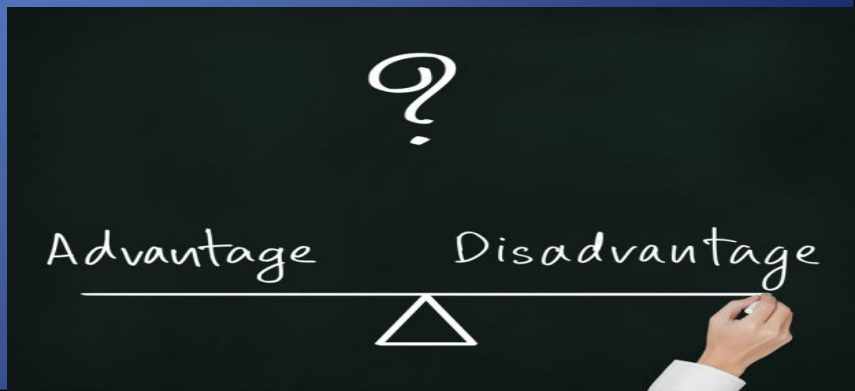
Need agreed-upon protocols to discriminate asbestos from non-asbestos particles

Ref. - See 2014, 2015 papers by Gordon *et al* vs. Lee & Van Orden, re "disagreements"

Analytical Procedures
&
Strategies

Which method is best for all situations/asbestos-talc types?

PLM, PCM, XRD, SEM,TEM-
each has specific
INDIVIDUAL & COLLECTIVE
advantages
and
disadvantages.



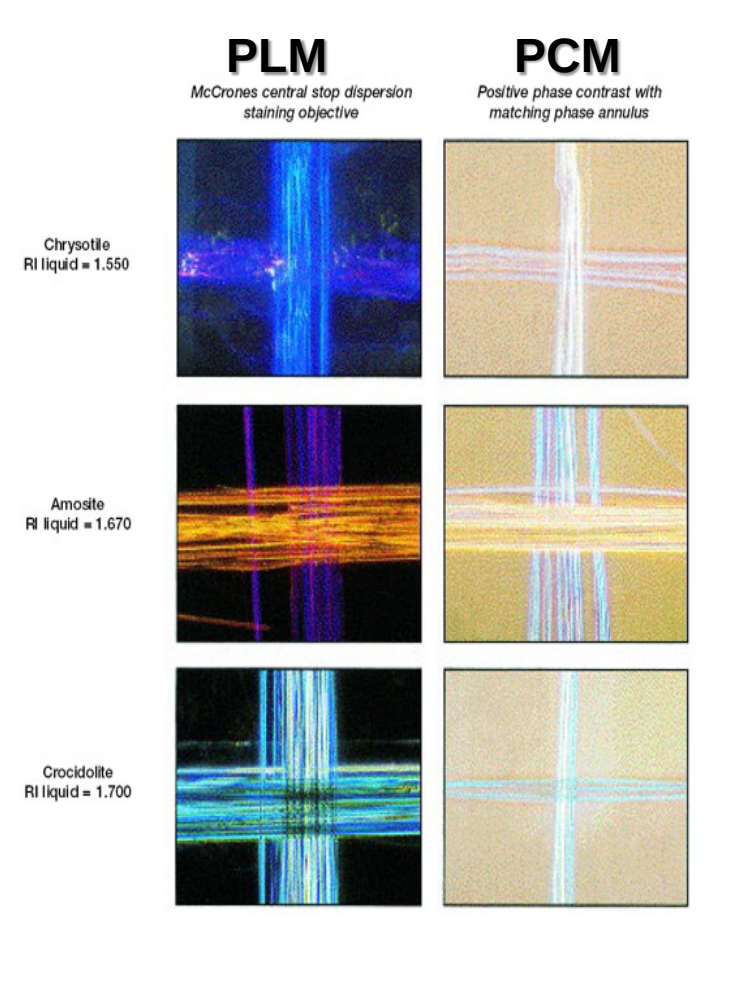
“Eyesight” Observations

Hand lenses (10x) for screening “closer” look

Stereozoom magnification 10x-30x
Good for rapid ID of higher concentrations of elongate particulates

Optical Microscope Observations

PLM- differences in optical properties from structure and composition; especially useful for building "bulk materials".



PCM- minute differences in phase of light to <u>exaggerate</u> phase boundaries; especially useful for "fibers" in industrial site air samples.

Polarized Light Microscopy- (PLM) for Asbestos, talc & “fibers”

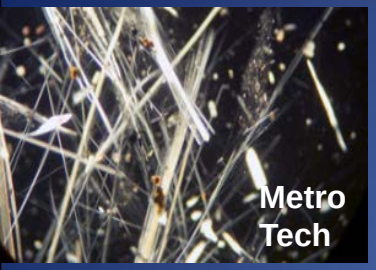
Advantages:

Codified by EPA *
Widespread usage *
Relatively inexpensive
Rapid turn-around
Standardized rules

Dispersion staining
Becke Line

“Sees” larger fiber sizes
Good for building bulk materials *

Polarized Light Microscopy- (PLM) for Asbestos, talc & “fibers”



Disadvantages/ limitations/”issues”:

- Magnification limit ~400x *
- Quantification of small amounts *
  - *improvable by sieving, elutriation*
- Becke Line techniques “harder”
  - *(pleochroism, extinction, RI, …)*
- Variations in chemistry affect RI
- Building materials
  - *non-friable materials opaque*
  - *smaller fibers can be masked by matrix*

Hi-Tech Instrumentation

X-ray diffraction

structural “fingerprint”

&

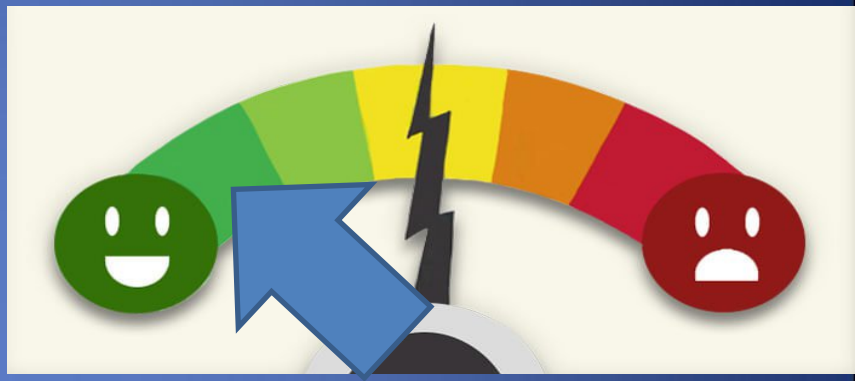
electron microscopy

atomic structure

&

chemical analysis

XRD for Asbestos, talc & “fibers”



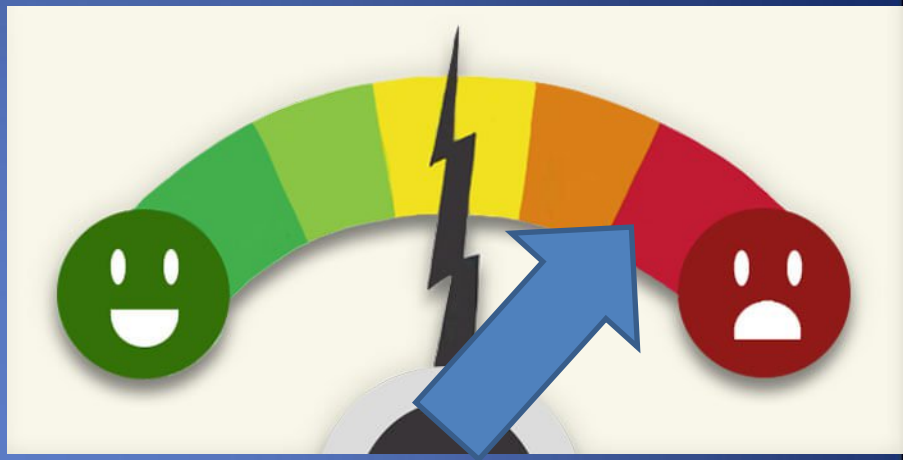
Advantages:

Rapid turn-around *
Standardized procedures
Good for gross phase ID *
Identifies much of mineral assemblage *
Semi-quantitative for amounts *

improvable by concentrating and scan speed

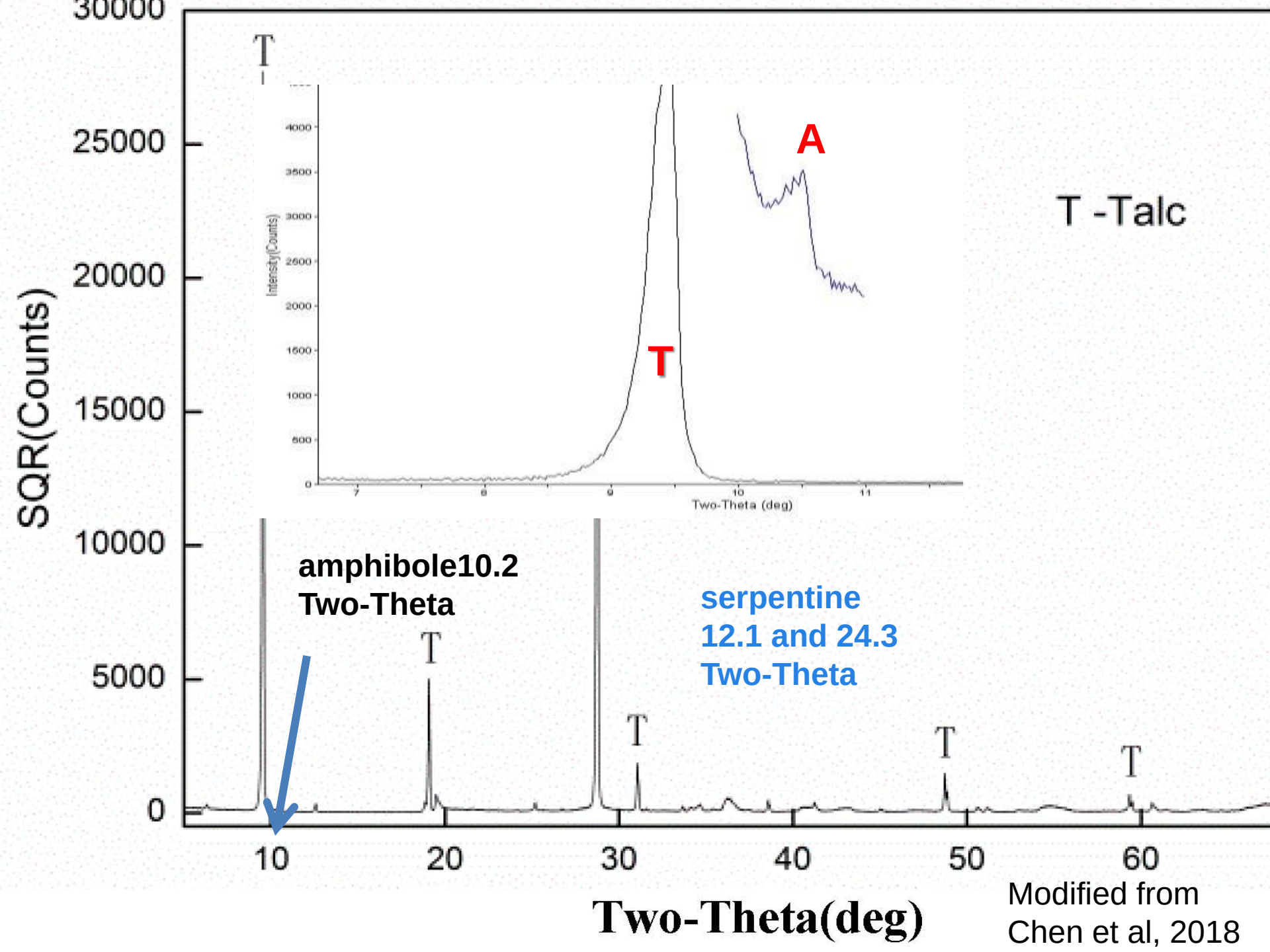
XRD for Asbestos, talc & “fibers”

Disadvantages/ limitations/”issues”:



Expensive
Radiation protocols
Instrument calibration
Analyst expertise & skills
Sample “mounts”
powder “packing”
grain orientation
Quantitation standards
“Poor” shape information

Overlap of peaks *
Detection limits *
fast, slow scans

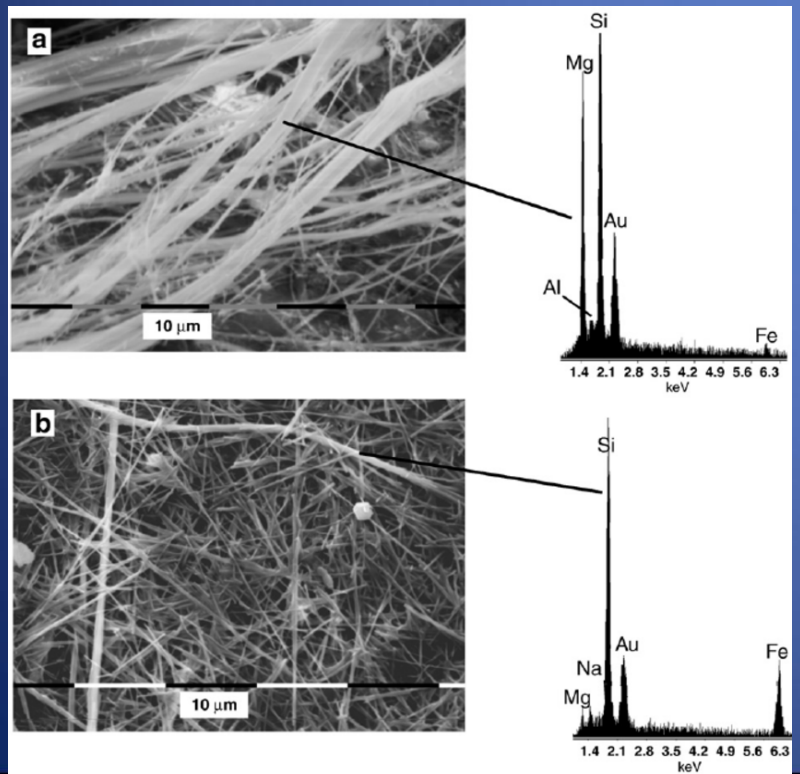


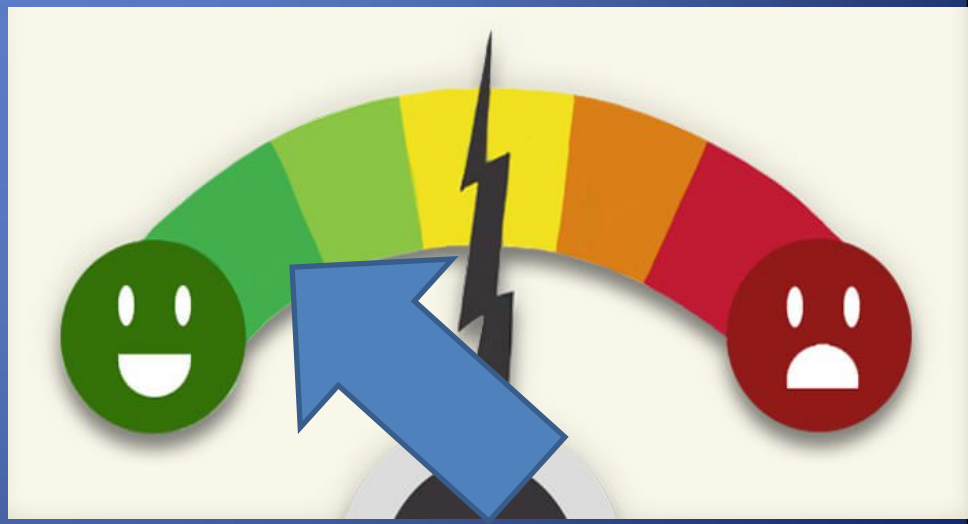
Modified from
Chen et al, 2018

SEM for Asbestos, talc & “fibers”

Advantages:

Visual magnification of shape
Chemistry by EDS





SEM for Asbestos, talc & “fibers”

Disadvantages/ limitations/”issues”:

Versus TEM, the perceived “Gold” standard *
No structural capability *
can’t discriminate some amphiboles *
Interpretation shapes/morphologies *

TEM for Asbestos, talc & “fibers”

Magnification, PLUS
energy dispersive analysis
&
selected area electron diffraction

Advantages:

Perceived as AHERA “Gold” standard *
Relatively widespread usage
Morphology, Chemistry, Structure *
distinguish amphibole species

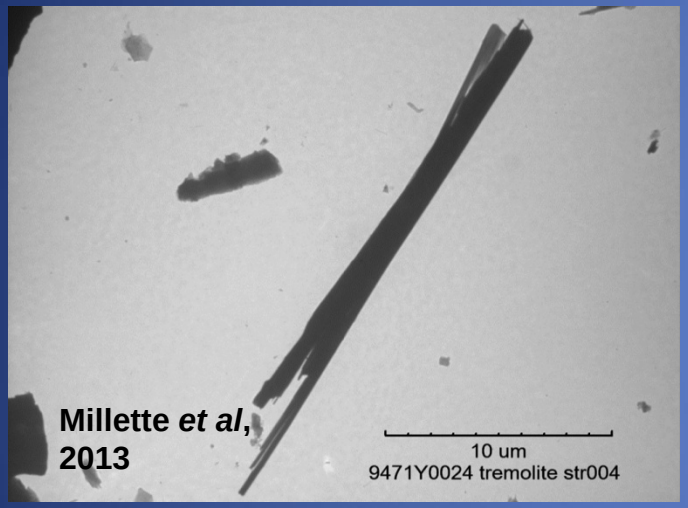
TEM for Asbestos, talc & “fibers”

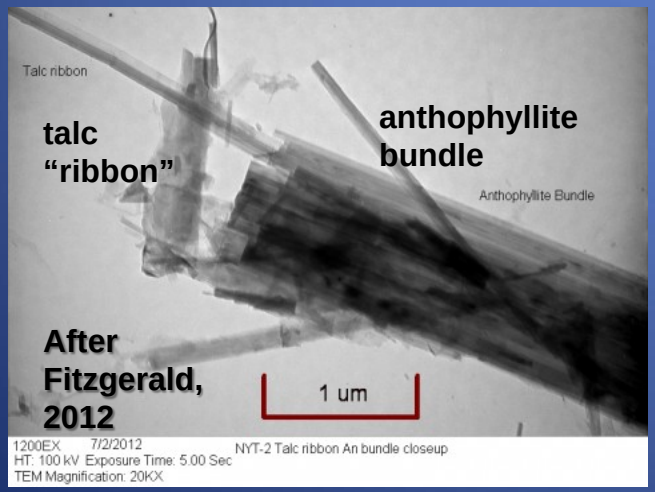
Disadvantages/ limitations/”Issues”:

“Sees” mostly smaller size particulates
Expensive
Need reference standards
Analyst expertise
Instrument calibration
Interpretation shapes/morphologies *
sample preparation (grinding, milling)
Population and amounts *
detected/not-detected; confirmed/not-confirmed
Talc vs. anthophyllite - Twisted talc ribbons/fibers *
“kinky” talc *

TEM Limited Population Issues

Unequivocal ID from a single "fiber" can be VERY misleading!





It's "likely" to be (regulatory) asbestos on basis of:

- Aspect ratio
  - population
- Parallel sides
  - bent/flexible
- Terminations
- Surfaces
- Nomenclature
  - unit cell
  - chemistry

Litigation

TEM CHEMISTRY "ISSUES"
Talc-Tremolite-Anthophyllite

anthophyllite $Mg_7Si_8O_{22}(OH)_2$

Ca:Mg:Si = zero:7:8

talc $Mg_3Si_4O_{10}(OH)_2$

Ca:Mg:Si = zero:3:4

tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$

Ca:Tc & An = infinity

tremolite readily distinguishable by Ca
anthophyllite often takes "work"
to distinguish from talc!

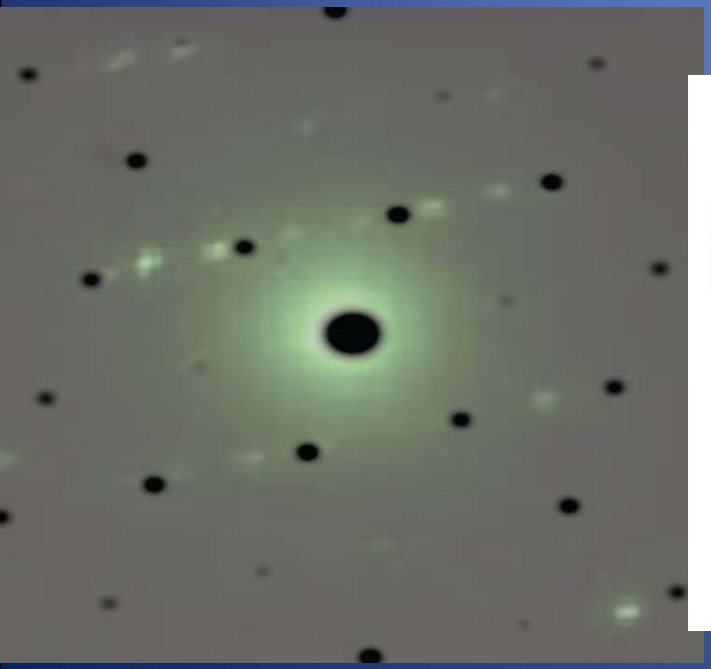
Ref. - See Millette, 2015, p. 17;
disc. "Fibers with kinks"

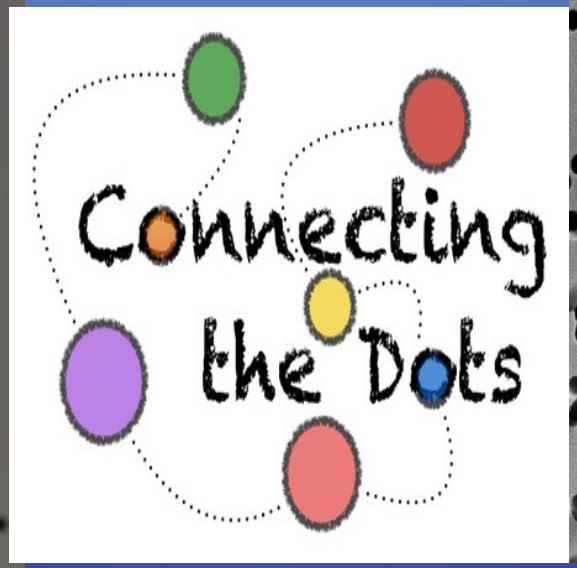
SAED ID “ISSUE”

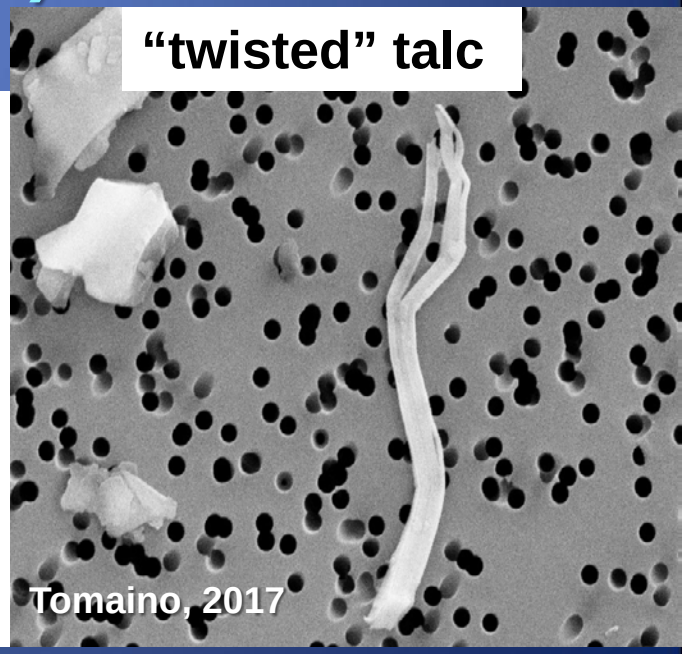
characteristic unit cell dimensions

tremolite	a = 9.84Å	b = 18.02Å	c = 5.27Å
talc	a = 5.27Å	b = 9.2Å	c = 18.85Å
anthophyllite	a = 18.55Å	b = 18.03Å	c = 5.28Å

NOT ALWAYS CORRECT TO USE JUST 5.27Å (~0.53 nm)







The 5.27Å Factor!

Same crystal cell dimensions for a & c

Different crystal cell dimensions

So, need 2 dimensions & 1 angle for correct identification

Summary of Limitations & Advantages of a Single Method

THERE ARE NO
"ONE-SIZE-FITS-ALL"
SOLUTIONS

Goal for Talcs:
"prove" absence of relevant amphiboles and chrysotile

CONCLUSIONS

Need a full spectrum of analytical tools, applied in context of a common analyte definition, to assert problematical levels of concern!

Levels of concern determined by producer/user

CONCLUSIONS

PLM will remain primary technique given its simplicity and widespread availability.

SEM useful supplement.

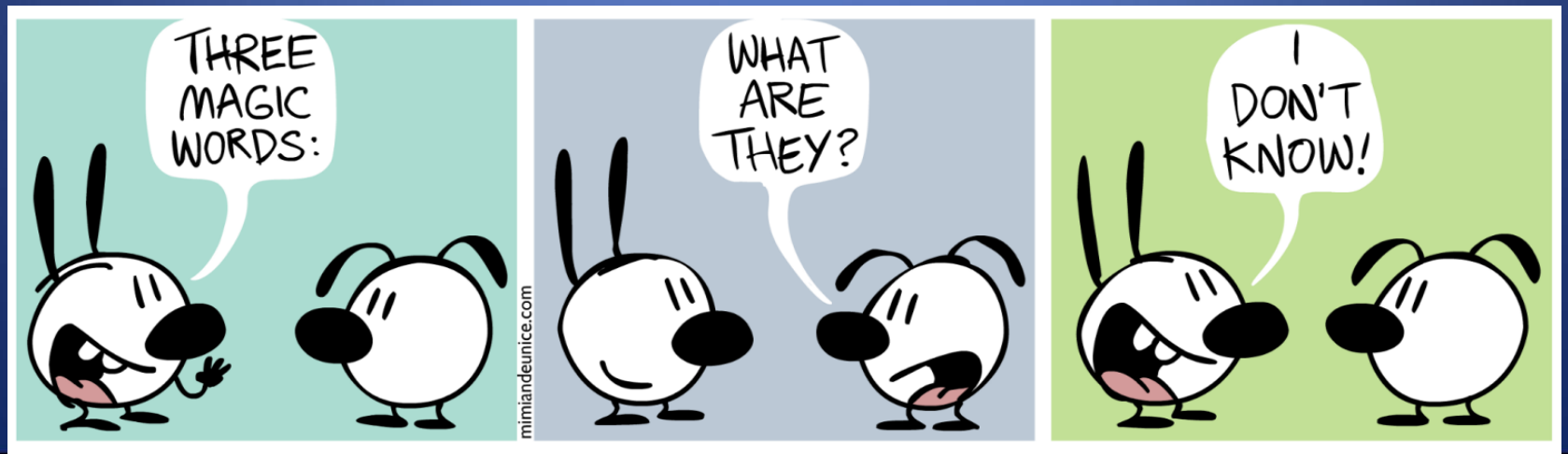
XRD especially useful to confirm presence of amphiboles.

TEM likely to be “ultimate” analytical tool!

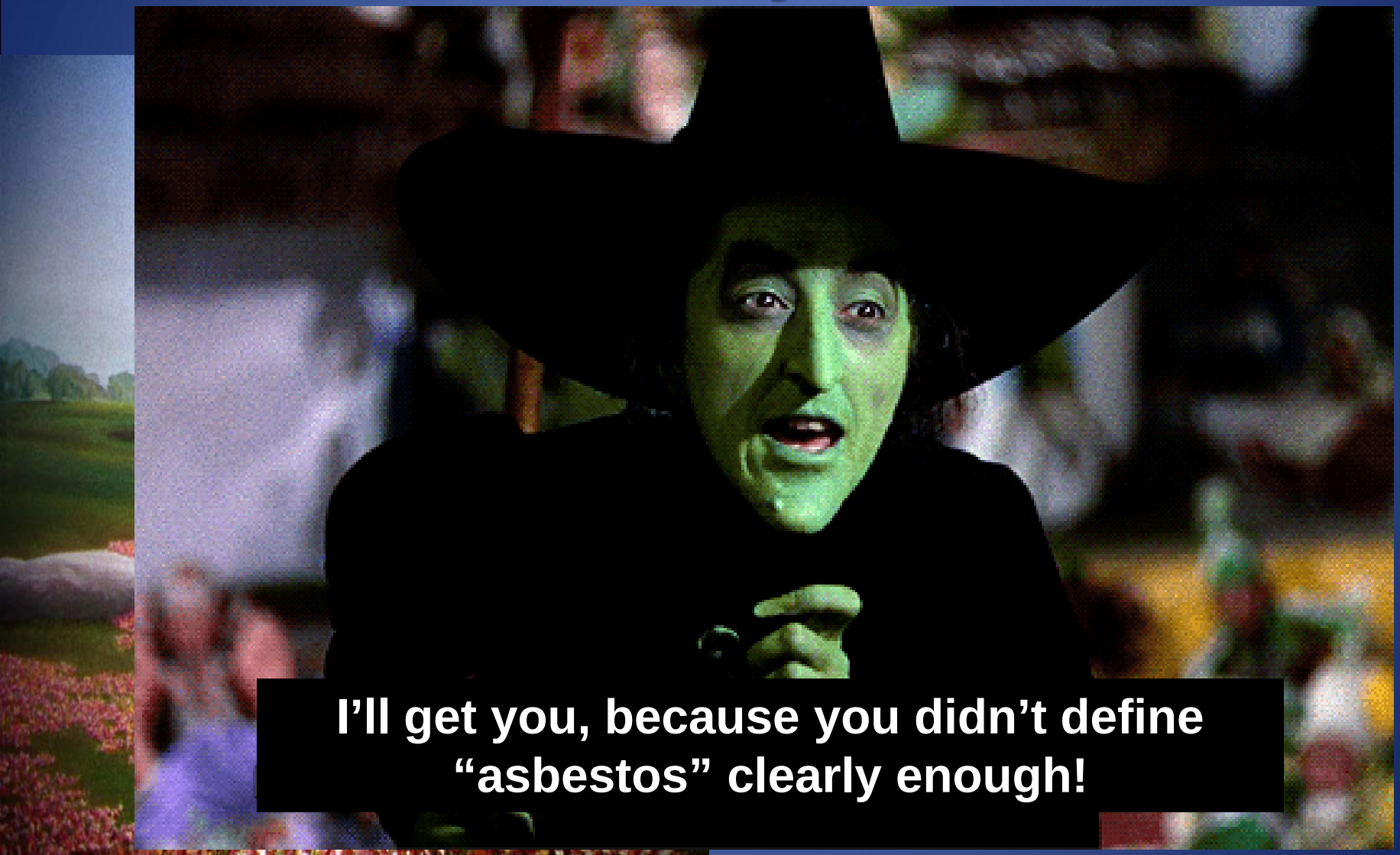
But
ONLY IF
we agree on definitions of names
and
relevant shapes!

And in the absence of unanimity of definitions, methods and results….

Remember that AHERA TEM method allows for “Ambiguous” & “Indeterminate”



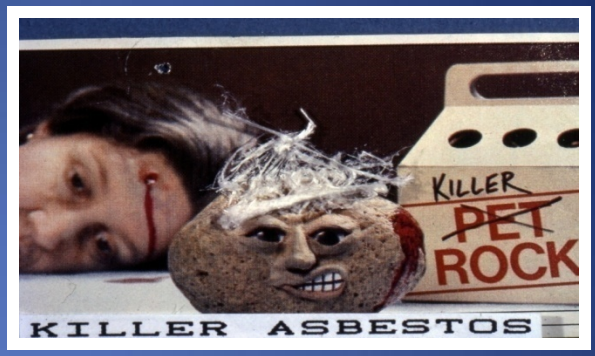
As we seek the “perfect method” and chase after “analytical zero’s”…



Looking back….

You can't tell how deep a puddle is until you step in it.

So, if asbestos is really as dangerous as many perceive…



Is it logic or bias that leads us to be concerned about EMP's?

Geologist trapped in asbestos-mud at Johns-Manville asbestos quarry


Question
Time!