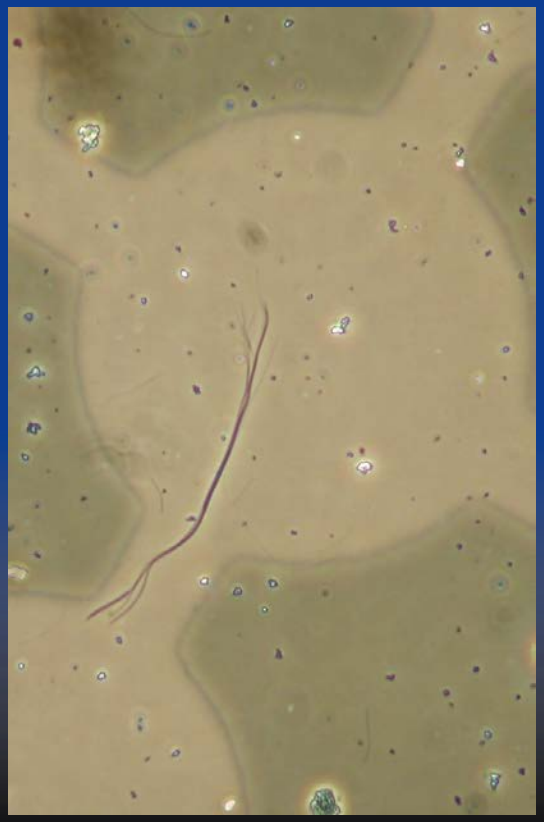
Test Methods: Applicability of reference materials and development of qualified standards



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Courtesy Professor
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Director of Scientific Research
Zefon International, Inc.
CDC/NIOSH - Retired

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General characterization issues

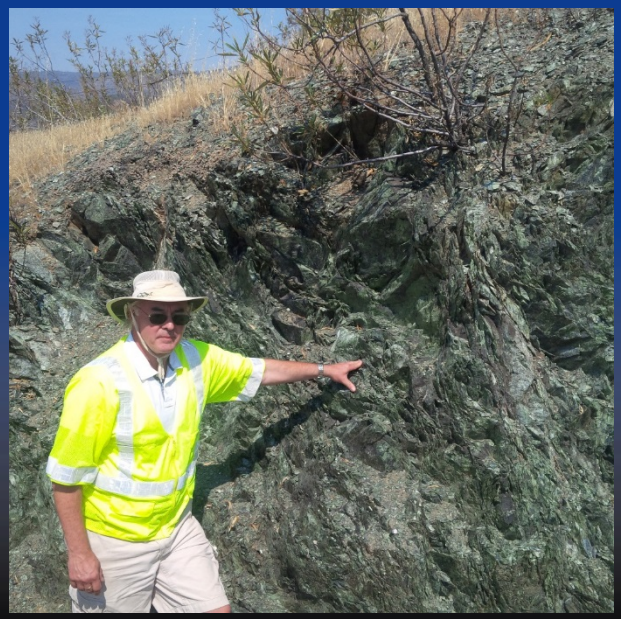
- What is the nature of the “sample”?
  - Air filter, soil, lung tissue, building material, bulk mineral, consumer product
- How much of the sample is representative of the whole sample?
- Can we resolve variation between different laboratories?
- What is the minimal number of particles examined for accurate characterization?
- Analytical calibration, proficiency testing and reference materials

Bulk materials examination

- Examination of bulk materials can take place at several levels of magnification:
- Eyeball to hand-lens
- Stereo-microscope
- Polarized light and phase-contrast microscopes
- Scanning electron microscope
- Transmission electron microscope
- Examination at each level is for different purposes – quality assurance also varies by level

Eyeball and hand-lens

- Characterizing in the field is difficult
- A rock outcrop can contain many different minerals and habits
- “Fibrous” can span a range of fibrosity



What is the appropriate sample to determine “asbestos” component?

- Even commercially exploited asbestos deposits include some material that might not be considered “asbestiform”
- Need to come up with a sampling protocol
- At least in the prior example, you can see some of the material is composed of elongate mineral particles, and some even asbestiform, but what if you cannot?

How many particles to examine?

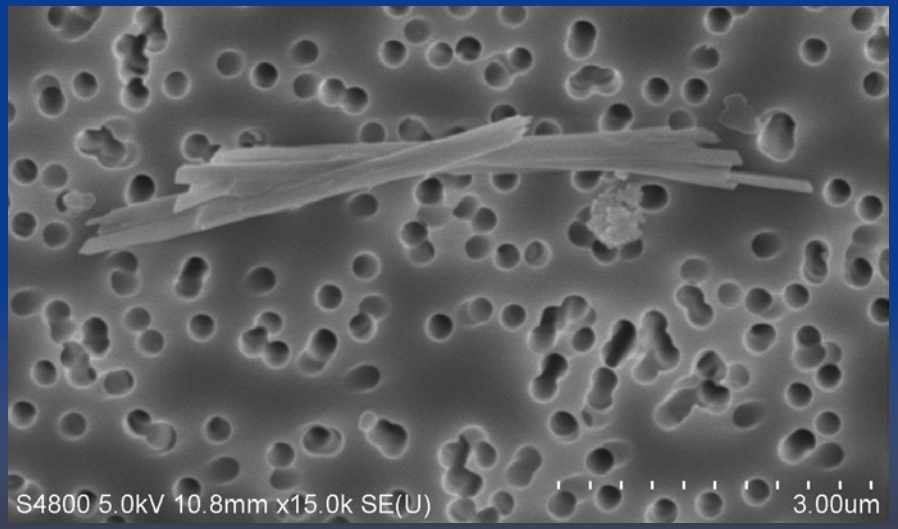
- How many particles do we need for determination of asbestos contamination?
- Example, an analysis of 20,000 fibers in UICC B chrysotile found no amphiboles (Frank et al., 1998)
  - but trace tremolite and Amosite have been reported (Amosite may be contamination)
- How many particles do we need to measure to obtain reproducible distributions?
  - At least 300, preferably 1000
- And for accurate chemistry?
  - At least 30 particles

SEM and TEM characterization of “fibrosity” of bulk materials

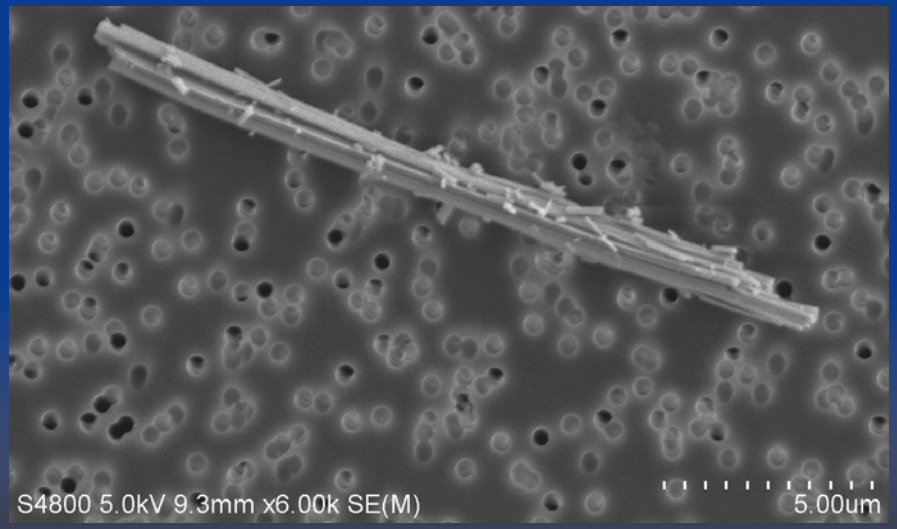
- Popularized by Eric Chatfield and others
- Can be used to compare fiber dimensions
- Preparation procedure is critical; jaw crushing, mortar and pestle grinding, jet milling, sonication, etc. all break up fibers horizontally and vertically, but differently, and energy and time are important
  - *milling procedures not only change the size distribution, but also the particle shape and crystal structure of asbestos fibers. Ultrasonic energy … produces changes in fiber size and fiber concentration*. Spurny, et al., 2010
- “Fibrosity” measurements require standardization

Problems with existing UICC reference materials

- Prepared in jet mill, which shatters fibers
- Tiny particles then attach to longer fibers



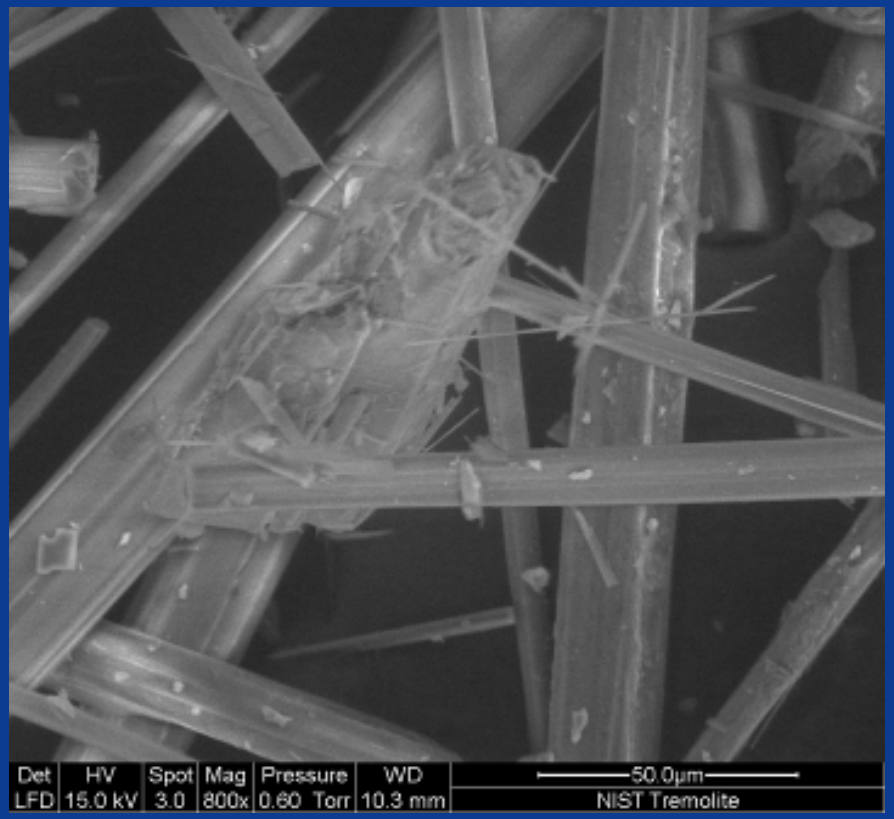
Wittenoom crocidolite, not milled



UICC crocidolite, milled

Reference Materials

- NIOSH Roadmap goal: a reference material repository for minerals
- ISO: *"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"*
- NIOSH has some, prepared by IITRI
- UICC Reference materials, most remaining material landfilled, now hard to obtain
- NIST Common/Uncommon no longer available

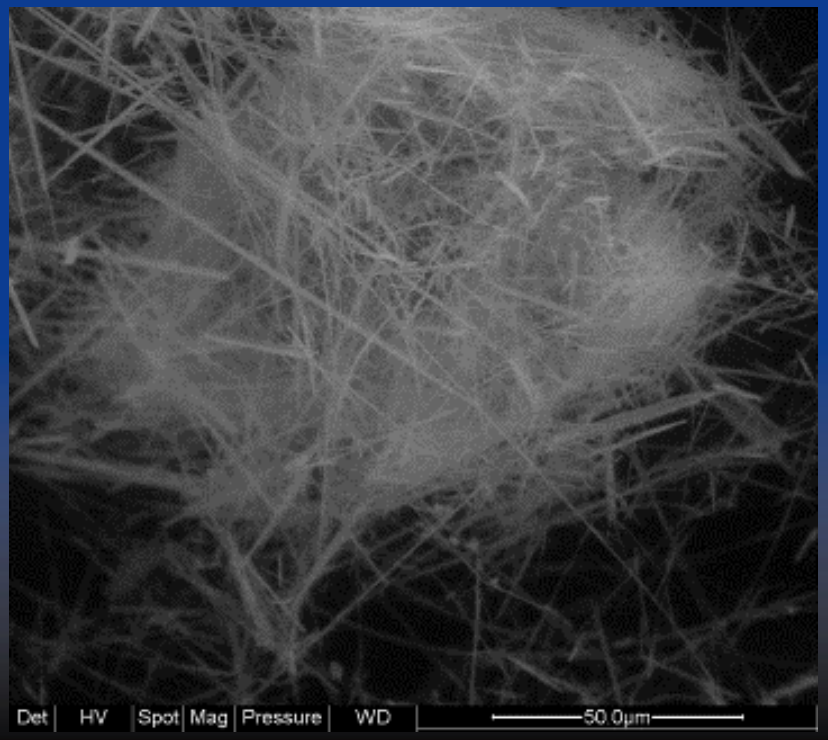


NIST tremolite asbestos also considered not very “asbestiform” (Brown and Gunter, 2003, *Microscope 51*:121–40)

Tremolite asbestos: NIST

Both x 800

Tremolite asbestos: HSL →

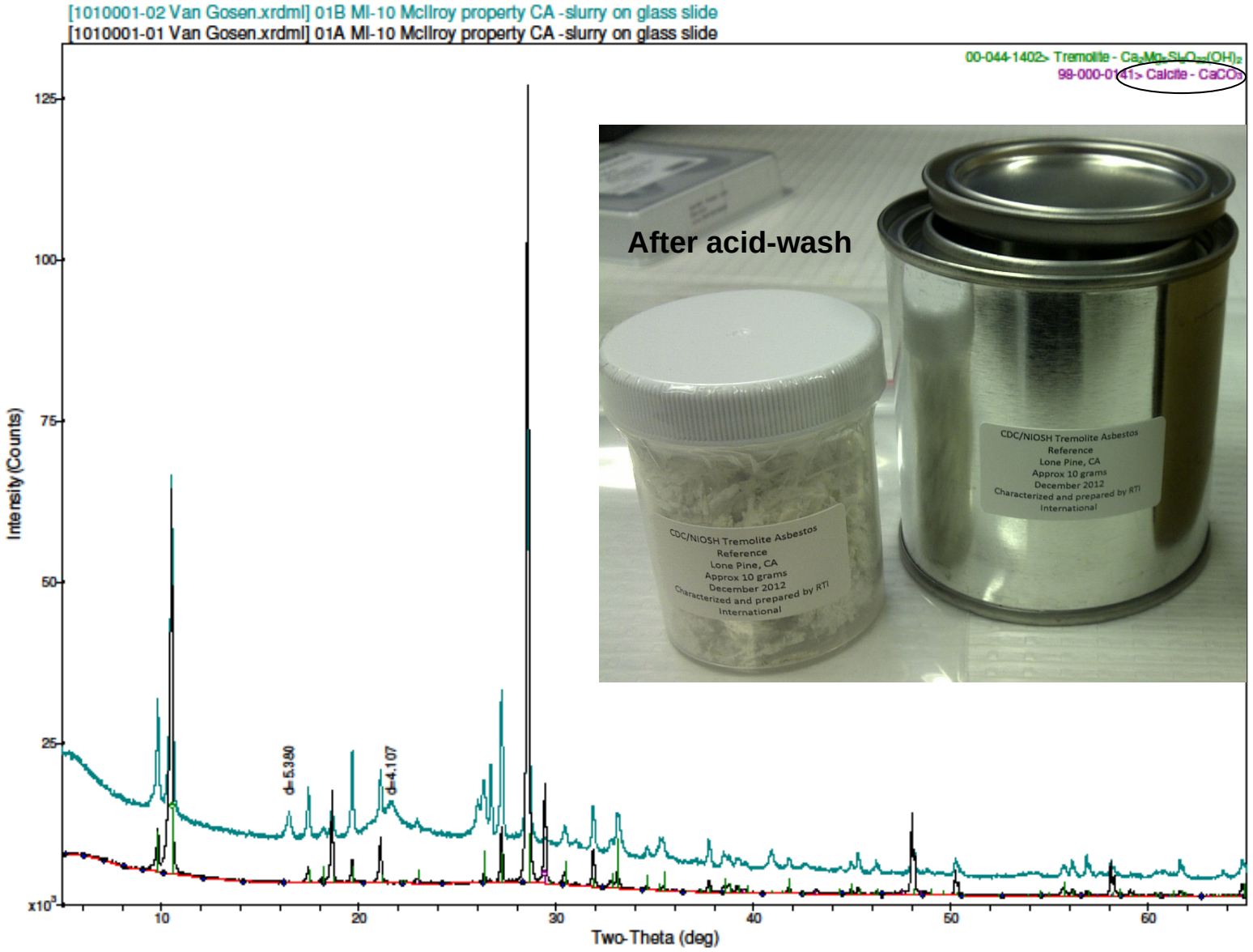


UK HSE Asbestos Reference Materials

- Tylee, et al.,1995, *Ann. Occup. Hyg. 40*:711–4
  - Chrysotile (x2), Amosite, crocidolite, tremolite asbestos, actinolite asbestos, anthophyllite asbestos – quantities diminishing
- Where did the tremolite asbestos come from?
- Company person who donated the material had died and company had changed hands
- “Salt Works” mine in Southern CA was all we had to go on – but not listed in US Gazetteer
- Later found to be listed as “McIlroy Property”

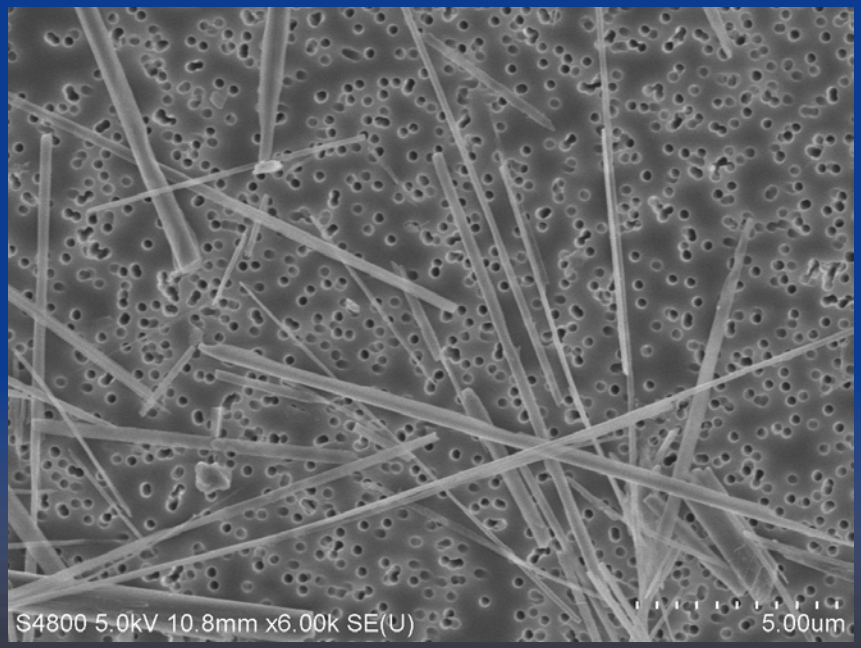
Mine adit and asbestos vein

- Originally perhaps a talc mine
- One major vein of cross-fiber tremolite asbestos inside
- Used for lab-grade asbestos

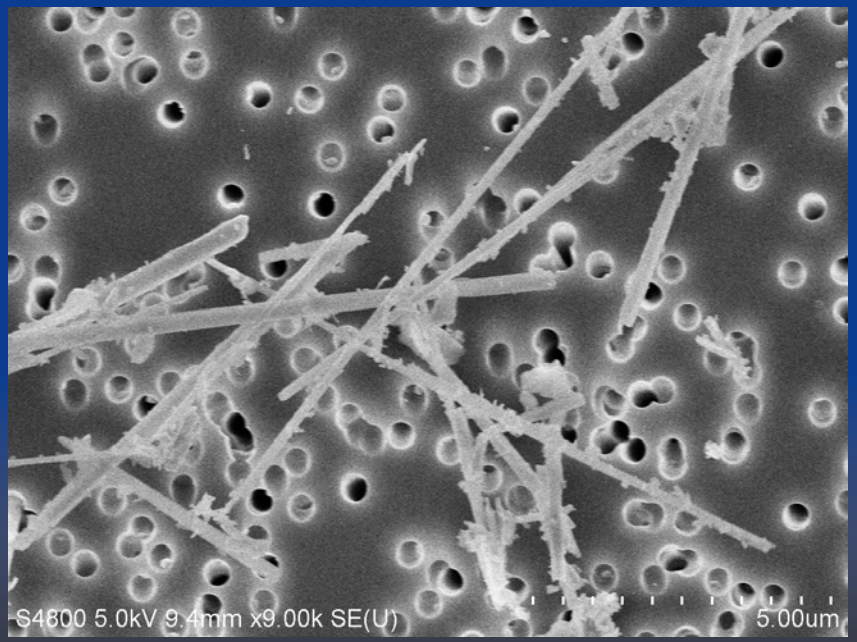

[1010001-02 Van Gosen.xrdml] 01B MI-10 McIlroy property CA -slurry on glass slide
[1010001-01 Van Gosen.xrdml] 01A MI-10 McIlroy property CA -slurry on glass slide
00-044-1402> Tremolite - Ca2Mg5Si8O22(OH)2
99-000-0141> Calcite - CaCO3
After acid-wash
CDC/NIOSH Tremolite Asbestos
Reference
Lone Pine, CA
Approx 10 grams
December 2012
Characterized and prepared by RTI
International
d=5.380
d=4.107
Intensity (Counts)
x10^3
Two-Theta (deg)

And just to remind you about jet-milling …

- Jet-milled in NIOSH laboratory to show effect

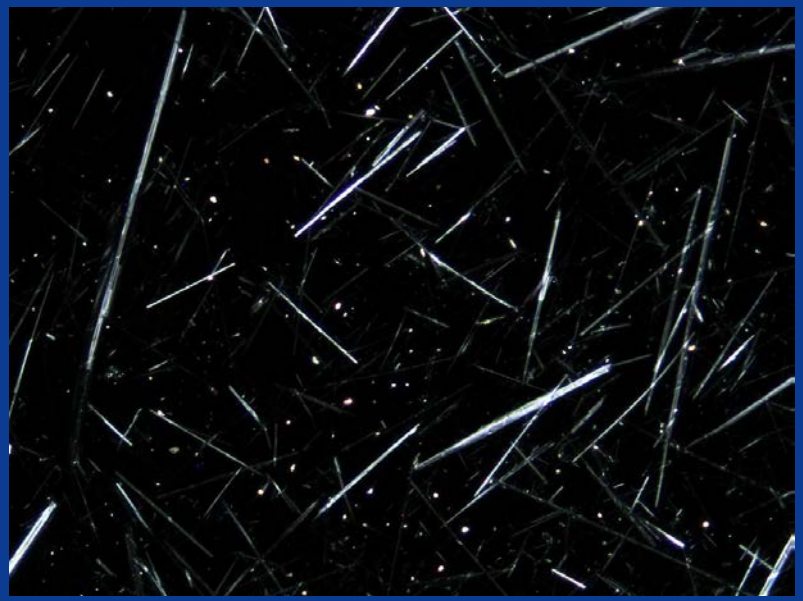


Lone Pine tremolite, not milled

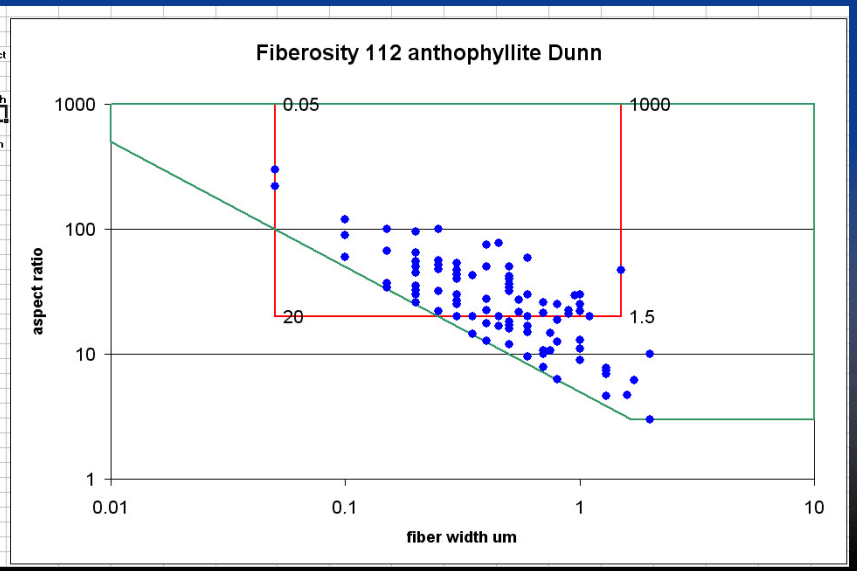


Lone Pine tremolite, milled

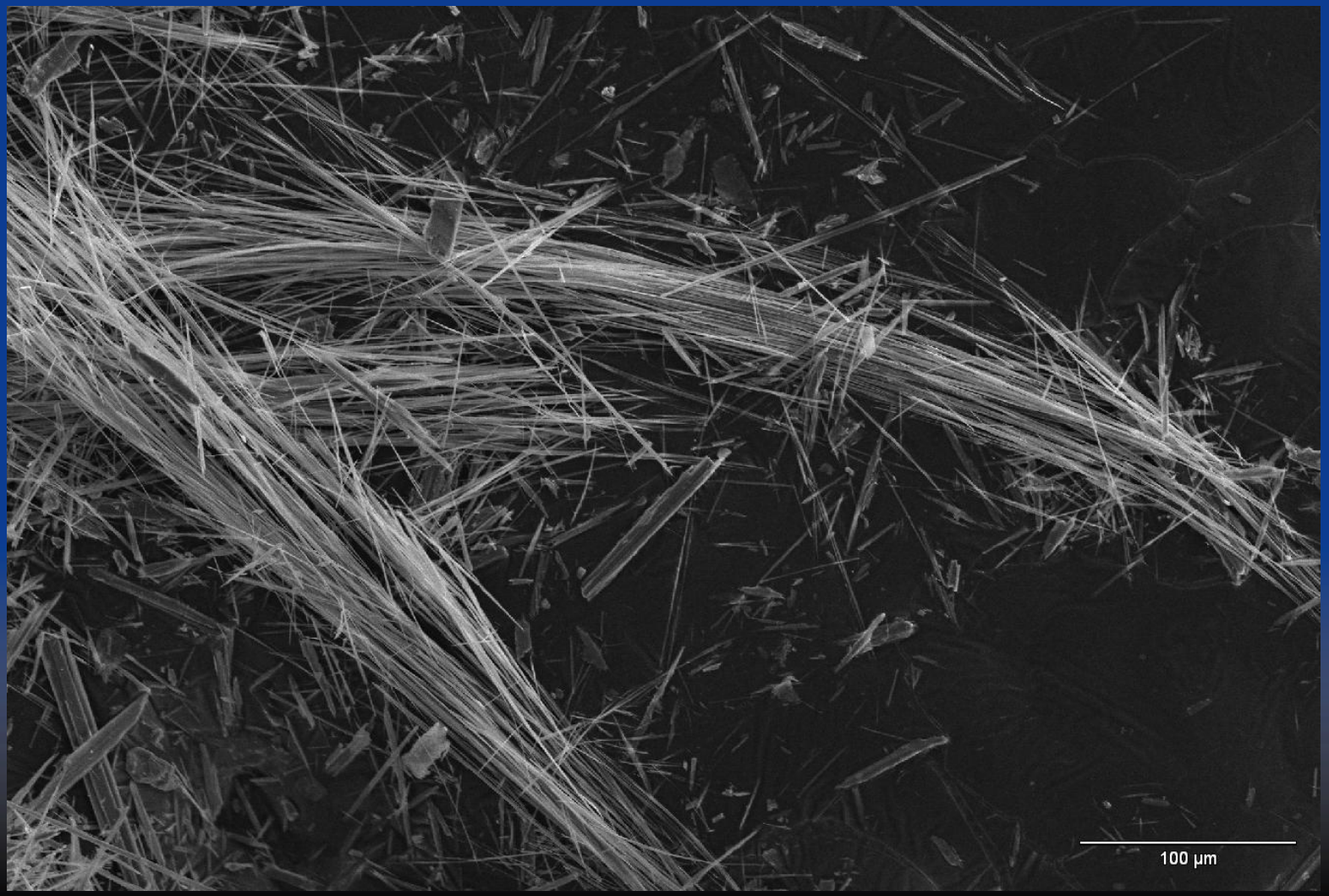
Percival-Dunn Mines, CA



A.Index %
62
Avg Aspect
33
Ave Length
12.9
Ave Width
0.60



Alabama anthophyllite



Cleavage fragments and fine, prismatic crystals

- Massive, non-asbestiform amphiboles and serpentine minerals can split along cleavage planes to produce elongate particles with aspect ratio > 3:1 (and length > 5 µm)
- Amphiboles can also crystallize as prismatic crystals that meet the same criteria
- Although neither exhibits nano-fibrillar structure under TEM, under PCM both of these can look like asbestos fibers in air samples

NIOSH Recommended Exposure Limit (REL)

- NIOSH believes discriminatory counting should be avoided if possible and that there is insufficient evidence of safety to exclude cleavage fragments
  - EPA: "it is prudent at this time to conclude equivalent potency for cancer" Report on the Peer Consultation Workshop to Discuss a Proposed Protocol to Assess Asbestos-Related Risk, Final Report, 2003, page viii
- OSHA included cleavage fragments in its initial 1986 standard, but removed them in 1992 (57 FR 24310) – practices discriminatory counting
  - ASTM Standard D7200 was an attempt to codify discrimination, but it needed to confirmed

Non-asbestiform amphibioles

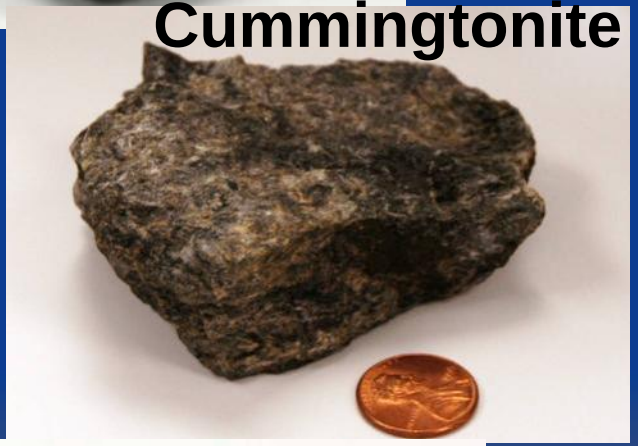
- Obtaining quantities of coarsely crystalline amphiboles was not easy – amphibole minerals are not collector's dream items
- Not always what they say they are – e.g. anthophyllite that turned out to be enstatite, tremolite that turned out to be inesite
- Riebeckite was collected with USGS assistance
- Five good materials: actinolite, tremolite, grunerite (amosite), riebeckite and anthophyllite
- All samples of anthophyllite contained fibrous talc
- Currently using actinolite from Wrightwood, CA, NIEHS tremolite (NY), grunerite from Tras os Montes, Portugal, and riebeckite from Colorado Springs, CO

Actinolite

Tremolite

Grunerite

Cummingtonite



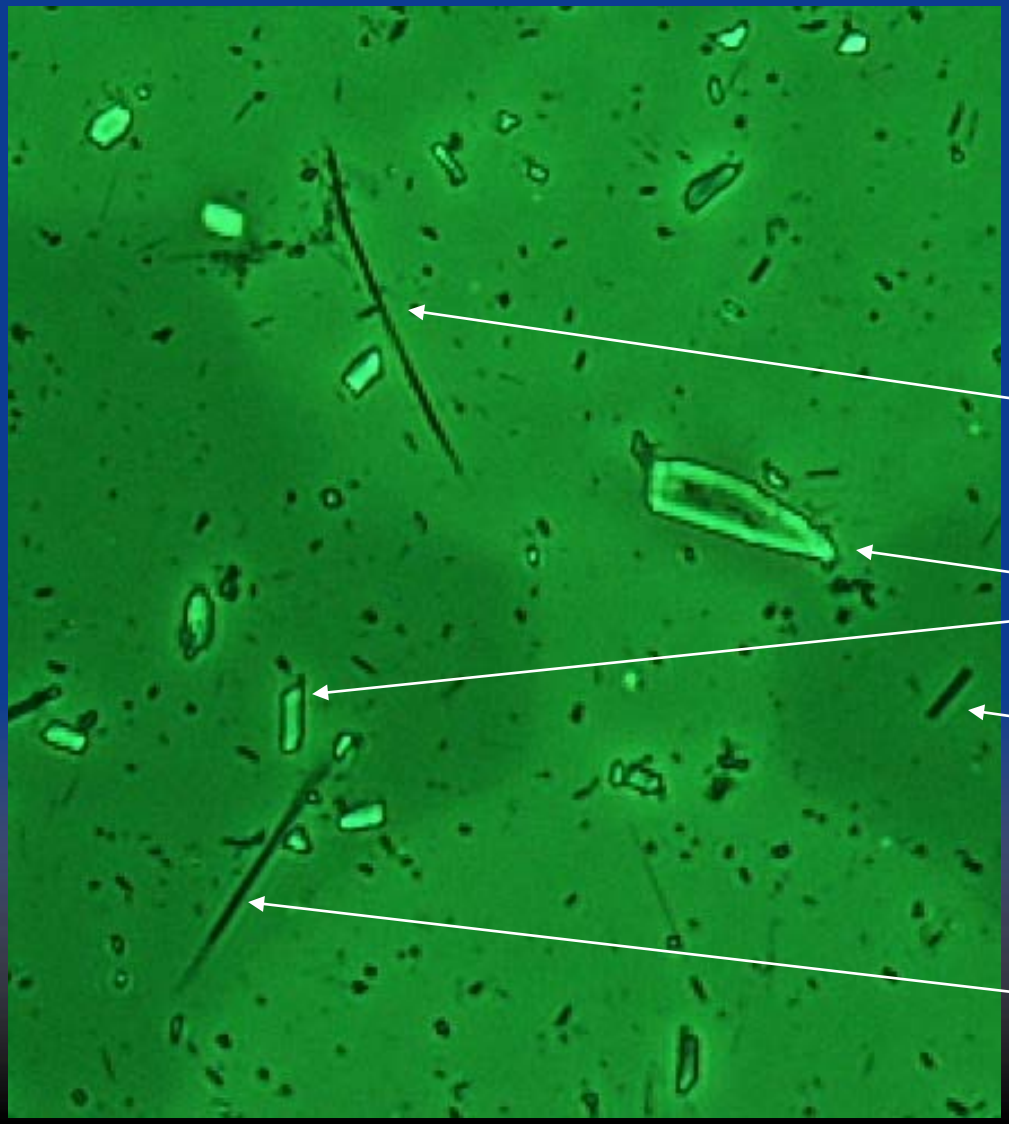
Anthophyllite

Riebeckite

Cleavage fragment reference materials

- Grinding massive non-fibrous amphiboles does NOT produce a lot of fiber-like cleavage fragments – about 1% of particles meet the dimensional criteria
- Cannot use a 1% fraction for tests
- RTI worked out a procedure to concentrate the fiber-like fraction; they were able to make 100-150 mg quantities with about 50% “fibers”
- Tremolite (NIEHS), actinolite, grunerite and riebeckite were used for PCM round-robin
- Tremolite/riebeckite also being used in tox. tests

Fibers and cleavage fragments



OSHA and MSHA do not include cleavage fragments as asbestos

Crocidolite fiber with curvature

Riebeckite cleavage fragments

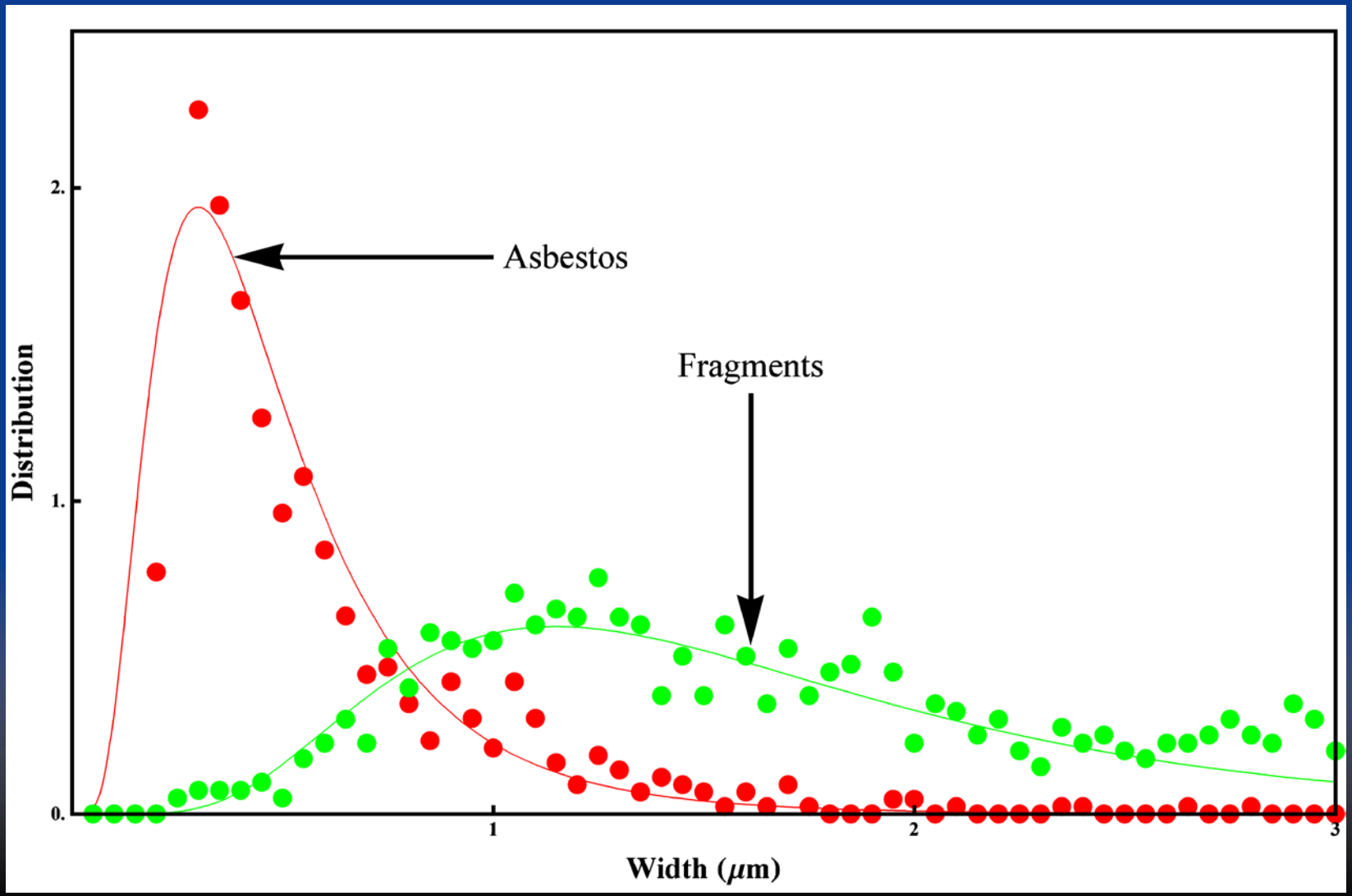
Cleavage fragment or short fiber bundle? Not always obvious!

Crocidolite fiber with fuzzy split ends

Asbestos by Class 1 (morphology)

	100% asbestos fibers				0% asbestos fibers			
Lab #	CR	AG	TR	AC	CR	AG	TR	AC
1	25	6.2	2.2	0	2.3	5.9	6.7	4.5
2	9.9	11	13	8.9	34	34	71	85
3	14	2.0	2.9	0.4	1.4	0.9	1.3	1.1
4	9.5	3.7	1.7	1.8	0.9	4.1	1.0	1.0
5	52	19	8.2	2.6	11	11	8.1	1.0
6	18	0.5	9.3	1.7	1.4	1.6	16	23
7	39	13	-	-	17	13	-	-
8	46	24	15	28	8.8	4.5	20	5.8
9	46	36	29	32	73	57	71	85
10	-	-	90	96	-	-	11	0.6
11	-	-	3.5	10	-	-	7.9	2.4

Width distributions



Separation by width

% asbestos	CR		AG		TR		AC	
	≤0.85 µm	≤1 µm	≤0.85 µm	≤1 µm	≤0.85 µm	≤1 µm	≤0.85 µm	≤1 µm
0%	14	21	12	22	16	22	7.3	18
20%	21	31	18	25	35	38	39	41
60%	50	59	44	56	65	69	74	79
100%	90	93	63	72	90	91	93	95

D7200 Standard Practice for Sampling and Counting Airborne Fibers … *in Mines and Quarries …* currently includes width criterion (1 µm)

Proficiency testing

- NVLAP, AIHA BAPAT, HSL AIMS – asbestos etc., in building materials – generally targeted to identification, and quantification > 1%
  - AIMS Round 62 included a sample with 0.1% chrysotile and Amosite, which were not detected by several labs, and a crushed marble with wollastonite where many saw asbestos: 23 labs by PLM-only, 6 with EM
- HSL Low Asbestos Content Scheme (LACS)
  - Round 2 of LACS was a sample of talc containing wollastonite (no asbestos) – 18% of labs incorrectly reported presence of asbestos
- Note: if you join AIMS you can purchase HSL reference asbestos

“New” ASTM Standards

- ASTM WK30024 Test Method for Polarized Light Microscopy (PLM) Analysis of Cosmetic and Pharmaceutical Talc for Asbestos
  - New work item initiated August 13, 2010
  - Technical contact: Sean Fitzgerald, SAI
  - Ann Wylie will assist with current draft (#9)
- ASTM WK30352 Test Method for XRD Analysis of Talc for Asbestos
  - Reported on by Gary Tomaino, Minteq
  - Spikes are 1% and 0.5% of anthophyllite, and 0.5% and 0.25% of tremolite, asbestos to be sent out this Quarter
  - 0.1% spikes to be sent out in 2019
  - Also will include non-asbestiform amphibole and serpentine
- ASTM TEM Method withdrawn temporarily
  - 10 negatives and no resolution within a year

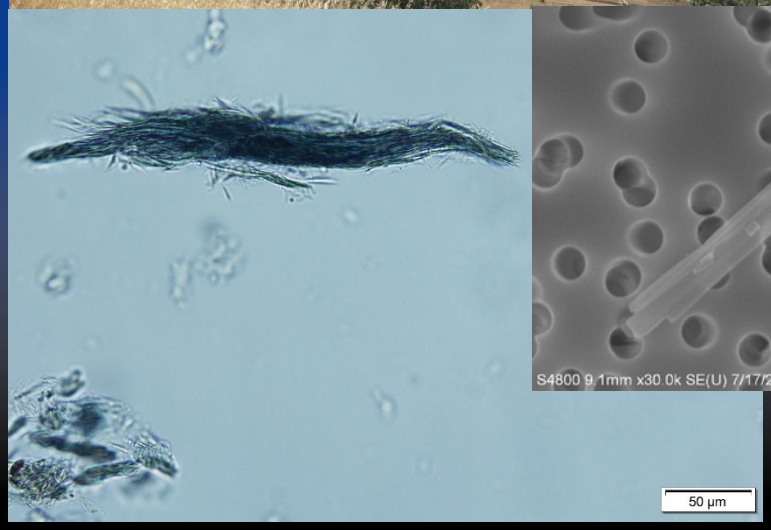
TEM Round-Robin

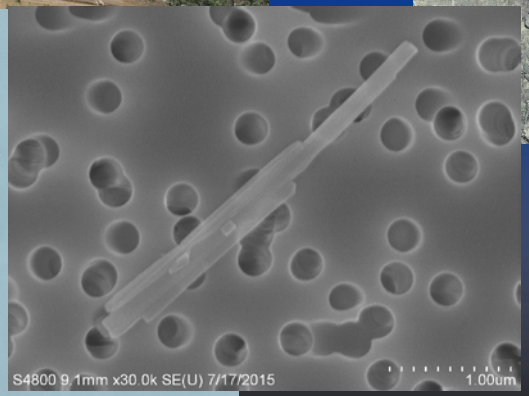
- Reported on by Sean Fitzgerald:
  - Many grids prepared from a single suspension of a talc sample containing tremolite (presumably asbestos)
  - (Used latest version of draft ASTM TEM method)
  - Grids sent to 10 laboratories specifically for analysis by ISO 10312 counting rules
- “Tremolite was consistently found by TEM, but not by PLM or XRD”
- “Chrysotile and anthophyllite were not found consistently” (unclear if actually present)
- Results will be presented at April ME Beard Conf.

Future work

- Extend the number of materials available
- Include zeolites, clay minerals, etc.
- Characterize those we already have
- Make them available as analytical standards
- Use them in identification round-robins
- Use them in hypothesis-driven toxicological studies to determine if our theories of disease induction and progression are correct
- Use the results to derive mineral-specific risk assessments

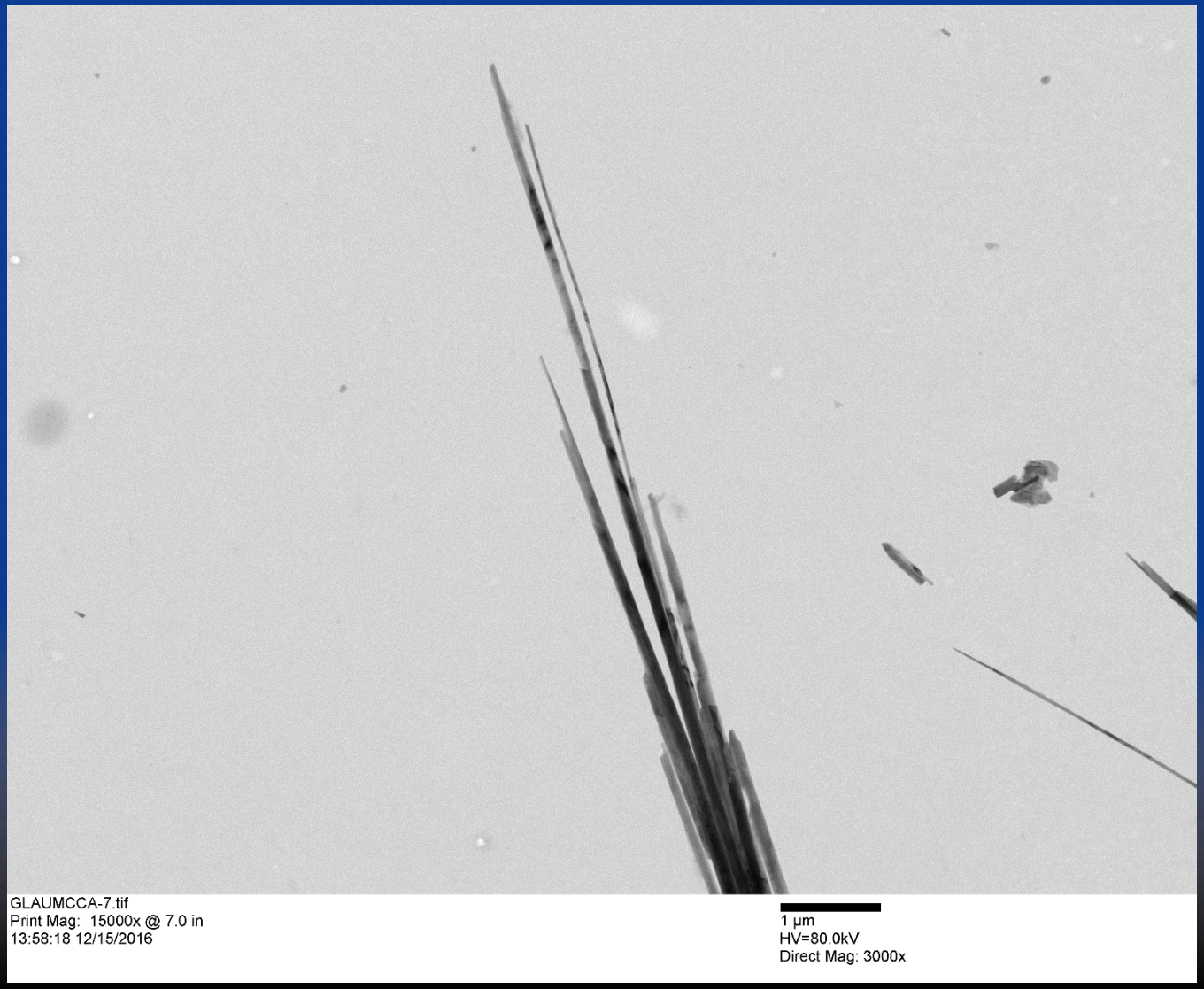
Fibrous glaucophane, CA





- Neither eyeball nor handlens tells you this is an EMP

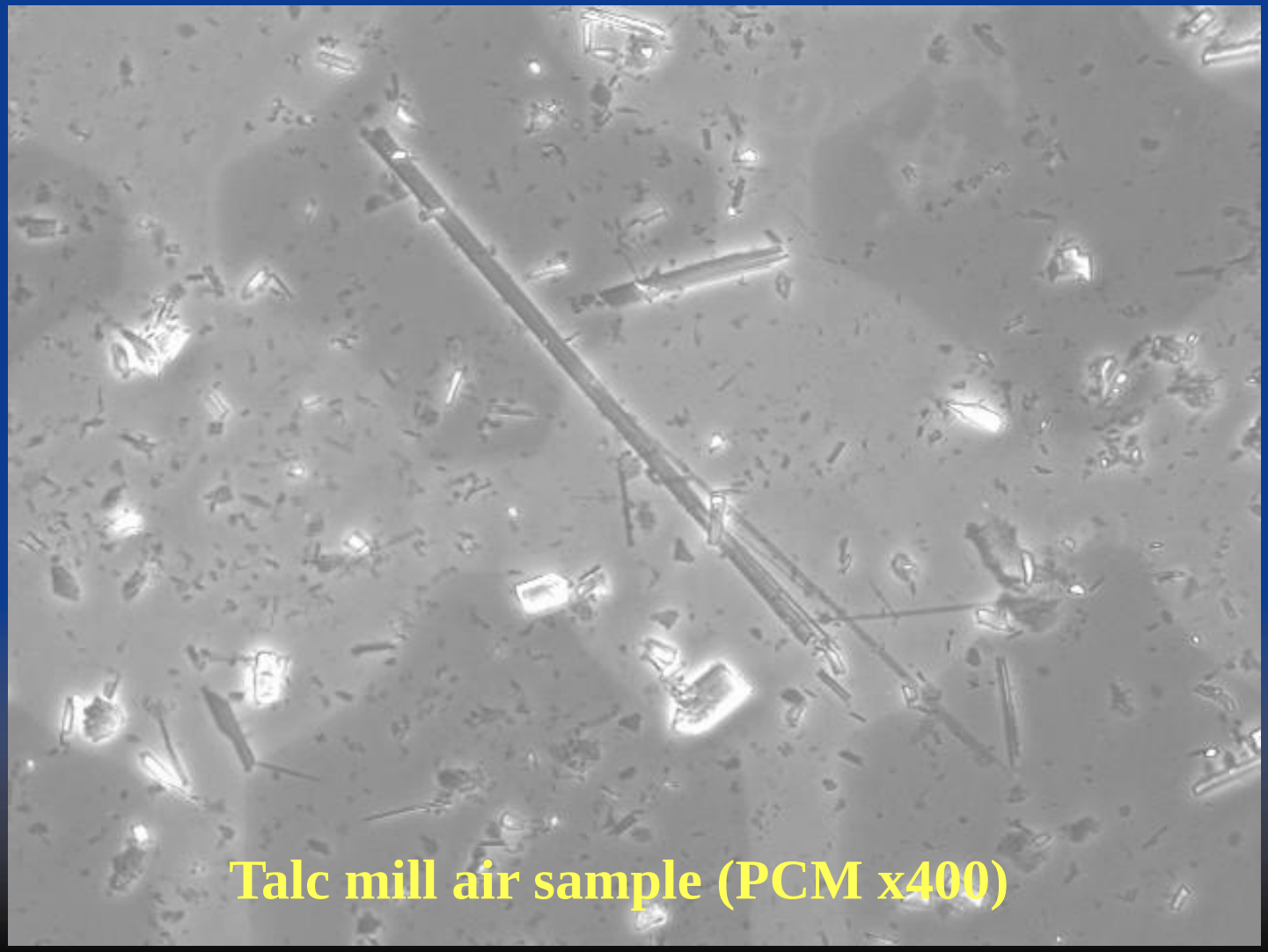
Glaucophane



Full mineral characterization

- Fibrous glaucophane, Marin Co., CA
  - Bulk X-ray powder diffraction and high-resolution synchrotron powder diffraction: Mineralogy
  - Polarized light microscopy: Optical properties
  - SEM and TEM: Fiber sizing, morphology, SAED
  - Electron microprobe: Chemistry; supplemented by ^{27}NMR spectroscopy, Mössbauer spectroscopy, FTIR spectroscopy
  - X-ray photoelectron spectroscopy: surface chemistry
  - ICP-MS: Trace element chemistry
  - Specific surface area, ζ-potential, biodurability
- Subtle disagreements between techniques points to the need for full characterization
- Potential toxicity can be calculated from model

So, what else is “asbestiform”?



Talc mill air sample (PCM x400)

Acknowledgements, because it takes a village …

NIOSH: Eun Gyung Lee, Catherine Beaucham, Patrick Hintz, Gerald Joy, Alan Dozier, Bruce Pacolay, John Nelson, Daniel Farcas, Diane Schwegler-Berry, Taekhee Lee, Anna Shvedova, and many others

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OSHA: Dan Crane and Don Halterman

CA State Geological Survey: Ron Churchill and John Clinkenbeard

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And dedicated to the Memory of Michael. E. Beard

Questions?

Bird’s nest of tremolite asbestos, McIlroy Property