

Preliminary Review of the RTI Report on the “Analysis of Crayons for Asbestos”

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A preliminary review of the RTI report¹ is presented below. The results of the review lead to the conclusion that: 1) RTI failed to use accepted methodologies for preparing and analyzing the samples; and 2) RTI overestimated the abundance of asbestiform fibers because of improper sample preparation, counting and identification techniques in the TEM. Taken alone, without regard to the question of whether transitional fibers are asbestiform, their optical data is in nominal agreement with other results. The main difference in their results is an overestimate of the abundance of fibrous components because of the use of a visual estimation procedure to determine the abundance of components with dramatically different shapes.

RTI's published diffraction patterns indicate their electron microscope is not in calibration and that the SAED pattern identified as anthophyllite in the report is from a transitional fiber. They incorrectly attribute asbestiform characteristics to all transitional fibers. RTI improperly concluded that their data supports the premise that the optical properties of anthophyllite are not understood. RTI found consistent chemical and structural compositions for anthophyllite fibers by TEM, but reached the non-physical conclusion that two particles with the same composition and structure will have significantly different optical properties.

Background and General Commentary

The analysis of talc in crayons has been the center of controversy for about 9 months. As initially reported by the Seattle Post-Intelligencer (SPI), the controversy erupted over the reporting of tremolite asbestos in samples of crayons. This work was discredited by subsequent analysis, as no laboratory using the mineralogical definition of cleavage fragment has reported the presence of tremolite asbestos. Several laboratories have reported tremolite asbestos, but only if they were defining asbestos strictly on the basis of aspect ratio (i.e., a particle had an aspect ratio greater than 3:1 or 5:1). As pointed out by RTI, the photograph of the tremolite particle published by the SPI clearly illustrates the exemplar tremolite particle is a cleavage fragment.

RTI notes that one of the central issues in this controversy is the definition of asbestos used by laboratories. However, in our opinion, RTI did not get it right. They state that cleavage fragments are defined as less than 10:1 in aspect ratio by various standards. This is incorrect. Cleavage fragments, as pointed out in documents cited by RTI elsewhere in their report, are the result of breakage of minerals along preferred planes. There is no natural restriction on the dimensions or aspect ratios of cleavage fragments – the 10:1 limit is one of observation. Asbestos fibers result from the separation of naturally occurring bundles of asbestos that grew as individual fibrils. Further, this growth occurs independently; therefore, the orientation of fibrils in a bundle is random. The dimension of the asbestos fibril has a natural limit of something under 0.5 micrometer diameter.

¹ M. E. Beard, O. S. Crankshaw, J. T. Ennis, and C. E. Moore (2001). Analysis of Crayons for Asbestos and other Fibrous Materials, and Recommendations for Improved Analytical Definitions, Research Triangle Institute, Research Triangle Park, NC.

RTI, like many laboratories, fails to appreciate that the regulated minerals are the asbestos varieties of certain amphiboles and serpentines. This is the material to be counted. The aspect ratio criterion **is a limit on which asbestos particles** are to be counted, not the definition of asbestos. If a particle meets the aspect ratio criterion, but is not asbestiform, it is not to be included in the count of regulated minerals. Meeting the criteria of being a countable asbestos structure means that the structure is not only an amphibole or serpentine mineral, but that it formed as bundles of individual fibrils whose characteristics RTI cite in their report.

The counting confusion is procedural. Many laboratories first decide whether a particle meets the aspect ratio criterion and then determine if it is an amphibole or serpentine before including it in the count. In fact, the laboratory should first decide if the particle is a fibril or bundle of asbestos, then determine whether it meet the aspect ratio criterion. The proper scientific procedure s to first determine if the particle is the asbestos form of the regulated minerals and to then to compare the aspect ratio of the particle to the counting criteria of the analytical method.

RTI, while purporting to present only analytical data, actually present numerous statements which take them out of the analytical realm and into other domains. They suggest that crystal defects are not a likely indicator of biological activity – this simply flies in the face of decades of research. RTI suggests the miners and baggers at the Vanderbilt plant are at high risk – this flies in the face of decades of epidemiological research. RTI suggests that no asbestos mineral is free of “mineral inclusions” – this flies in the face of decades of mineral characterization. RTI speculates that the differences between their optical and TEM results are due to a “convention which restricts the definition of anthophyllite”, not the result of mineralogical standards and evaluation of scientific data.

RTI suggests that the difference between anthophyllite and transitional fibers is the result of “mineral inclusions” of talc. This is incorrect. Mineral inclusions in general do not have a stoichiometric relationship between the inclusion and the host lattice – transitional fibers do. RTI suggests that the “mineral inclusions” give rise to an “extra reflection” in the diffraction pattern. They do not. In fact, the transitional patterns contain two patterns of reflections, one from talc reflections and a second from anthophyllite, as well as reflections resulting from double diffraction between the two lattices. The proper description of this phenomena is that the transitional fibers are comprised of mineraloids that are too small to be defined as crystals or inclusions. In general, they do not evidence fibular construction, splayed ends, or curvature.

RTI’s results differ dramatically from any detailed study which has been performed both in the US and abroad since the controversy began. No other laboratory has reported more than trace quantities of Anthophyllite and no other laboratory has reported as much as 16 percent transitional fibers. No other laboratory has concluded that a significant percentage of the transitional fibers are in fact asbestiform.

We evaluate their methods and likely sources of error in the following. We attribute the differences to: 1) improper interpretation of SAED patterns; 2) improperly prepared TEM samples; 3) lack of appropriate comparison of the optical and TEM images; 4) improper identification of asbestiform particles in the optical microscope; and 5) improper quantification of components.

Review of analytical procedures and results

RTI presents itself as the quality assurance laboratory which reviews the work of commercial laboratories. Perhaps this is the most troubling aspect of the report. As such a laboratory, they should be familiar with and follow recognized methodologies. They failed to do so.

RTI did not Properly Interpret the SAED pattern attributed to Anthophyllite

RTI states repeatedly in their report that “the SAED patterns confirm an anthophyllite pattern as indexed to zone axis 100 and confirms the material to be anthophyllite.” The published pattern (Figure E1) is not a 100 zone axis of anthophyllite. In addition, the pattern suffers from significant distortion, and the apparent spacing of the spots and rows in the pattern vary across the center spot. This is documented in the illustrations attached at the end of this document.

Even so, Figure E1 can be identified as having contributions from both talc and anthophyllite. The base anthophyllite component is a rectangular pattern with a d-spacing of about 2.5 by 8.9 angstroms. The base talc pattern is a pseudo hexagonal pattern near a 100 zone. These patterns shift in position in different areas of the Figure because of distortion in the image and feed-through from adjacent reciprocal lattice planes. Double diffraction between the anthophyllite and talc patterns accounts for the filling in of the patterns to give apparent triplet spots, and in some regions of the pattern, an apparent 100 anthophyllite zone. The majority of the spots originate from talc reflections or double diffraction between the components, not from anthophyllite.

RTI Did Not Properly Prepare TEM Samples

RTI's TEM preparations failed to conform with any accepted method of preparation and this may have led to problems in both diffraction pattern analysis and evaluations of energy dispersive x-ray data. General guidance for TEM preparations to determine mass or fiber count is that a monolayer of particles are deposited on a filter substrate which is then prepared for TEM analysis. RTI used a "mircodrop" technique which was recognized in ASTM studies over twenty-five years ago to be suitable only for qualitative evaluation and unsuitable for quantitative determination of fiber count or mass.

RTI's published photographs show significant numbers of overlapping particles and a particle loading which is unacceptable in any current TEM method. This particle overlap prevented RTI from being able to determine whether the electron diffraction patterns were from single or multiple particles. It is an even more serious problem for energy dispersive x-ray analysis, a technique used by Datachem to distinguish between anthophyllite, talc, and transitional fibers in an independent study performed for CPSC.

RTI Did Not Properly compare the optical and TEM Images

RTI pointed out that the fibers seen in the optical microscope and TEM have similar dimensions. The transitional fibers in the optical microscope have dimensions between two and five micrometers. The talc bundles have dimensions less than 2.5 micrometers. Visual comparison of the asbestiform and blocky structures in the TEM leads to the conclusion that the transitional fibers are the opaque, blocky structures, and that the thin curved structures in the TEM images

are identified as talc fibers in the optical microscope. The thick, wide structures in the TEM images show no evidence of fibular structure, no splayed ends, and no curvature.

This leaves the reported trace quantities of “anthophyllite” identified optically in question. The image shown in the optical photograph (Figure A8) has evidence of being a bundle, has apparent fibular components and shows evidence of curvature. It is possible that a rare asbestiform structure in the TEM will meet the definition of “anthophyllite”. Other than that, the obvious asbestiform components in the TEM must be considered as having the optical properties of talc.

RTI Did Not Properly Identify Asbestiform Particles in the Optical Microscope

RTI treats all transitional fibers as asbestiform. This is incorrect. RTI cited a 1992 EPA document which describes the characteristics of asbestiform fibers. The fibers shown in Figures A-4 to A-7 of the RTI report do not meet the asbestiform criteria listed in the EPA document they reference. The fibers shown do not demonstrate splayed ends, very thin fibular structure, or curvature. There is some indication of internal structure in two of the images suggesting these particles could be bundles, but equally well, the observation could be of a ribbed intergrowth which is typical of transitional fibers when observed in the SEM. If these are considered to be bundles, the individual parts do not have a 20:1 or greater aspect ratio; only one image meets this criteria – Figure A4. In the two images which show no evidence of internal structure, the diameters are between 5 and 7 micrometers, too large for an individual asbestiform fibril. The ends of all the structures show blunt terminations which are inconsistent with an asbestiform bundle structure.

In contrast, the fibrous talc bundles, presented in Figures A9 to A14, do exhibit the properties of asbestiform fibers cited by the EPA document. These talc particles clearly show the presence of very fine fibrils, splayed ends, curvature and bundles. Visual comparison of the fibrous talc images and transitional fiber images demonstrate the dramatic difference between the two populations, leading to the conclusion that RTI's assumption that the transitional fibers are asbestiform is incorrect.

RTI's table of optical properties also supports the conclusion that the transitional fibers are not asbestiform. The upper limit on the aspect ratio of the transitional fibers is 20:1. Any asbestiform population must have some portion of the population with aspect ratios greater than 20:1, and **according to EPA and other references – a mean aspect ratio greater than 20:1.**

RTI Did Not Properly Quantify the Components

RTI used visual estimates to quantify the abundance of different components in the samples. This procedure is inappropriate for anthophyllite in the PLM because of the extremely low observed concentration. It is also inappropriate for the TEM analysis because of the morphological similarities between the minerals in question. Visual estimates of fibrous components in mixtures of platy and blocky material have been shown to result in overestimates of the percentage of fibrous material. In addition, in this case, the separation into talc fibers, transitional fibers, and any potential Anthophyllite is complicated by the similar morphologies involved and the need to identify each particle separately. ASTM, the EU and ISO have published validated methods for making estimates of the mass fraction which permit a known mass of material to be deposited, then the size and dimension of each fiber is estimated and the mass fraction computed.

In this case, area estimates or size measurements which do not account for the thickness of the particles, or treat the cross-section as equiaxed can lead to overestimation of the mass fraction by orders of magnitude. The thickness of the asbestiform talc and transitional fibers in this system is generally between 0.05 and 0.25 micrometers. The diameters are often in the range of 1.0 micrometer or larger. If the thickness of these particles is assumed to be equal to the width, the mass is **overestimated by a factor of 4-20 or even more.**

RTI's Optical and TEM data are Inconsistent, Incomplete, and Contain Apparent Errors

The scale factors used to convert the TEM data in Table 3 of the report from the analysis of the residue to the original talc product are not consistent, ranging from 7.6:1 to 8.1:1. This is not possible. Something is wrong with the data, but without access to the underlying data, the reason for this cannot be determined.

RTI reports 3-5 percent transitional fibers in the crayon by PLM. This would be 24-40 percent in the talc powder using the approximate conversion factors from the TEM column in Table 3. Similarly, the estimated amount of tremolite is 5-10 percent in the crayon (by PLM), converting to 40-80 percent in the original talc product. This is dramatically different than the reported TEM results for the crayon or talc material.

Alternatively, if the PLM results reported in Table 3 are actually for the residual after ashing, there is a different difficulty with the results. The total fiber content (anthophyllite, transitional, and talc fibers) estimated by PLM is in the range of 3-7 percent. The concentrations in the TEM analysis represent more than 21 percent of the sample. This represents a 3-7 fold difference in mass estimate.

RTI separately states that the “anthophyllite transitional fibers represent 5-7 percent of the talc product”, when analyzed by optical microscopy, again inconsistent with the TEM data.

These results also contradict the nominal XRD data which indicates that the anthophyllite is the smallest component based on the relative intensity of the peak, and that tremolite is a dominant component in the crayon residue. This is inconsistent with RTI’s TEM results.

RTI Drew an Erroneous and Non-Physical conclusion about the Low Refractive Index of The Transitional Particles

Taken at face value, RTI’s optical data do not differ dramatically from other studies. They indicate at most, extremely rare occurrences of fibrous anthophyllite (either two particles in twenty slides, or 4 particles in forty slides of talc residue, and powdered talc product). They indicate trace to two percent fibrous talc and 3-7 percent transitional fibers.

In contrast the TEM results suggest trace amounts of fibrous talc (0.5-0.8 percent), and significant quantities of transitional fibers and anthophyllite (16 and 4.4 percent). This on the basis of 19 “anthophyllite particles” and one indexed 100 zone axis diffraction pattern.

In attempting to clarify these conflicting results, RTI concluded that the optical properties of anthophyllite are not well understood due to the chemical nature of the observed minerals, and that, therefore, the optical data is unreliable. They speculate the problem occurs with the high magnesium content which they suggest reduces the refractive index into the range of talc.

Incorrect Analysis of the Optical Properties of Anthophyllite

RTI's conclusions are untenable, even absent the incorrectly indexed diffraction pattern on which their entire conclusion is based for the following reasons:

- 1) RTI found particles of anthophyllite with the optical properties consistent with those expected for anthophyllite. Anthophyllite is well recognized as a minor component of the deposit in question.
- 2) There is a distinct gap in the indices of refraction reported for anthophyllite and transitional fibers optically.
- 3) There are recognized variations in the amount of magnesium, iron, manganese, and calcium in the fibers in question. These are the primary factors affecting the indices of refraction.
- 4) In order for the low index material to be anthophyllite, there would have to be a continuum of indices observed. This is not the case.
- 5) Magnesio Anthophyllite, to the extent it exists, is the end member of a solid solution series. Nature abhors a vacuum, and does not permit a gap a significant property in a solid solution series.

For these reasons, one must conclude that the interpretation of the electron diffraction patterns is in error and that RTI's conclusion that the optical properties of anthophyllite are not understood is incorrect.

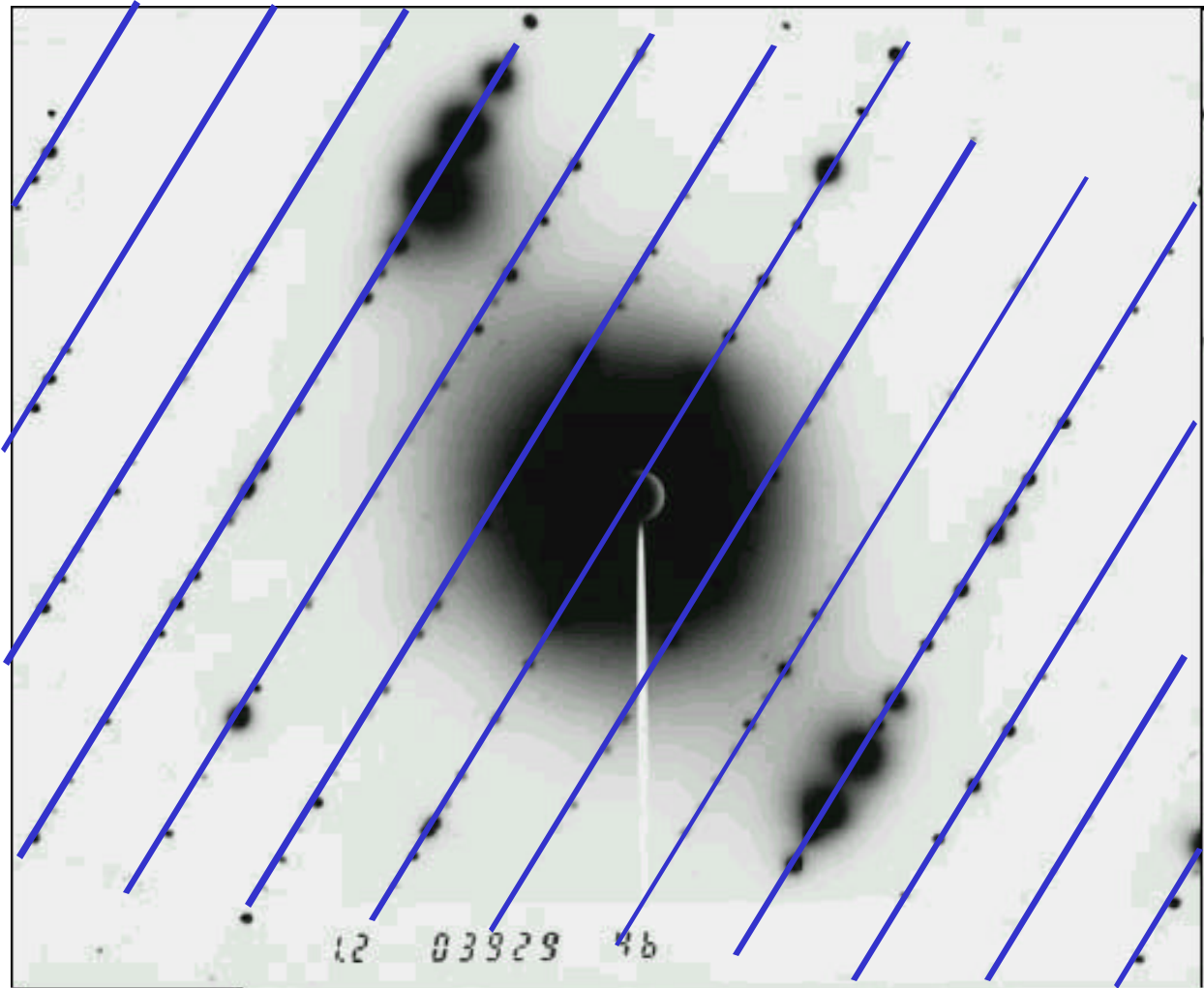


Illustration 1. Parallel lines have been drawn through the rows of the diffraction spots. Notice the curvature of the rows in the upper quadrant of the negative.

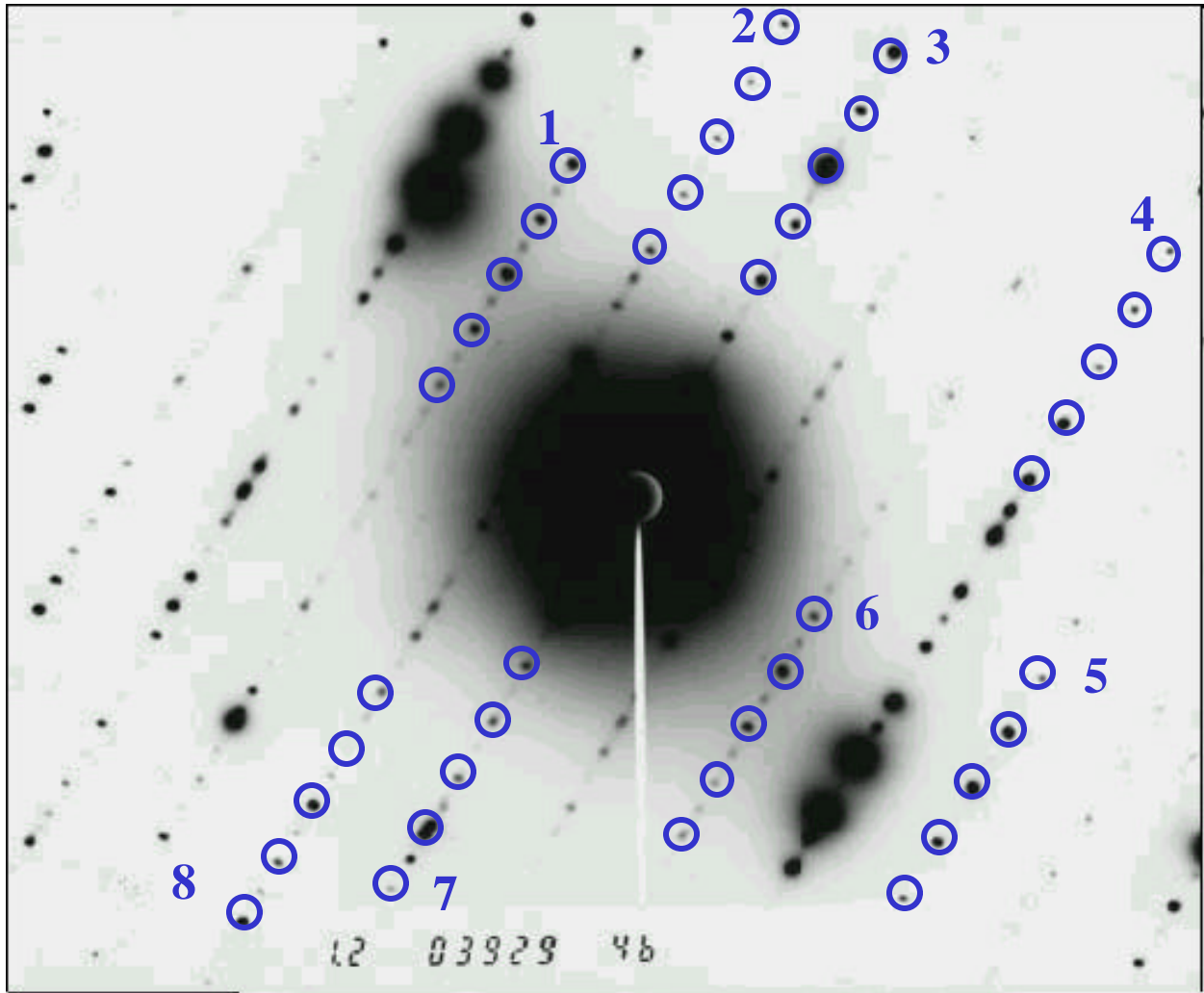


Illustration 2. Representative sets of spots have been selected and measured to determine if the distance and angles are consistent across the image. The following summarizes the data for the pattern:

Line	Measured Distance, mm	d-space	Angle
1	7.328	9.175	59.033
2	7.566	8.886	58.950
3	7.556	8.898	60.067
4	7.657	8.781	58.767
5	7.488	8.979	57.983
6	7.328	9.175	59.033
7	7.453	9.021	58.417
8	7.692	8.741	58.350

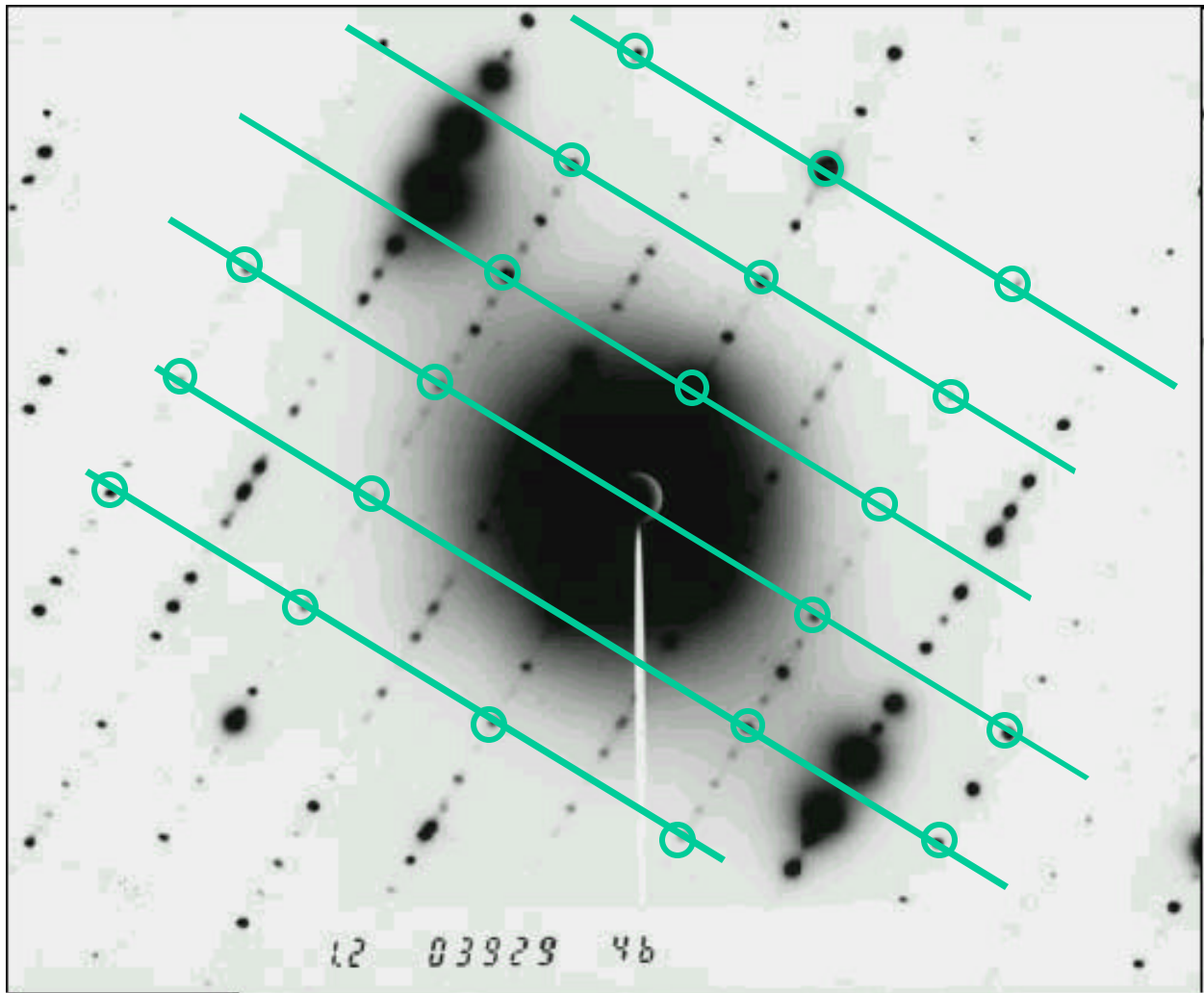


Illustration 3. The circles and lines illustrate the portions of the pattern consistent with anthophyllite. Note the missing spots in the second row.

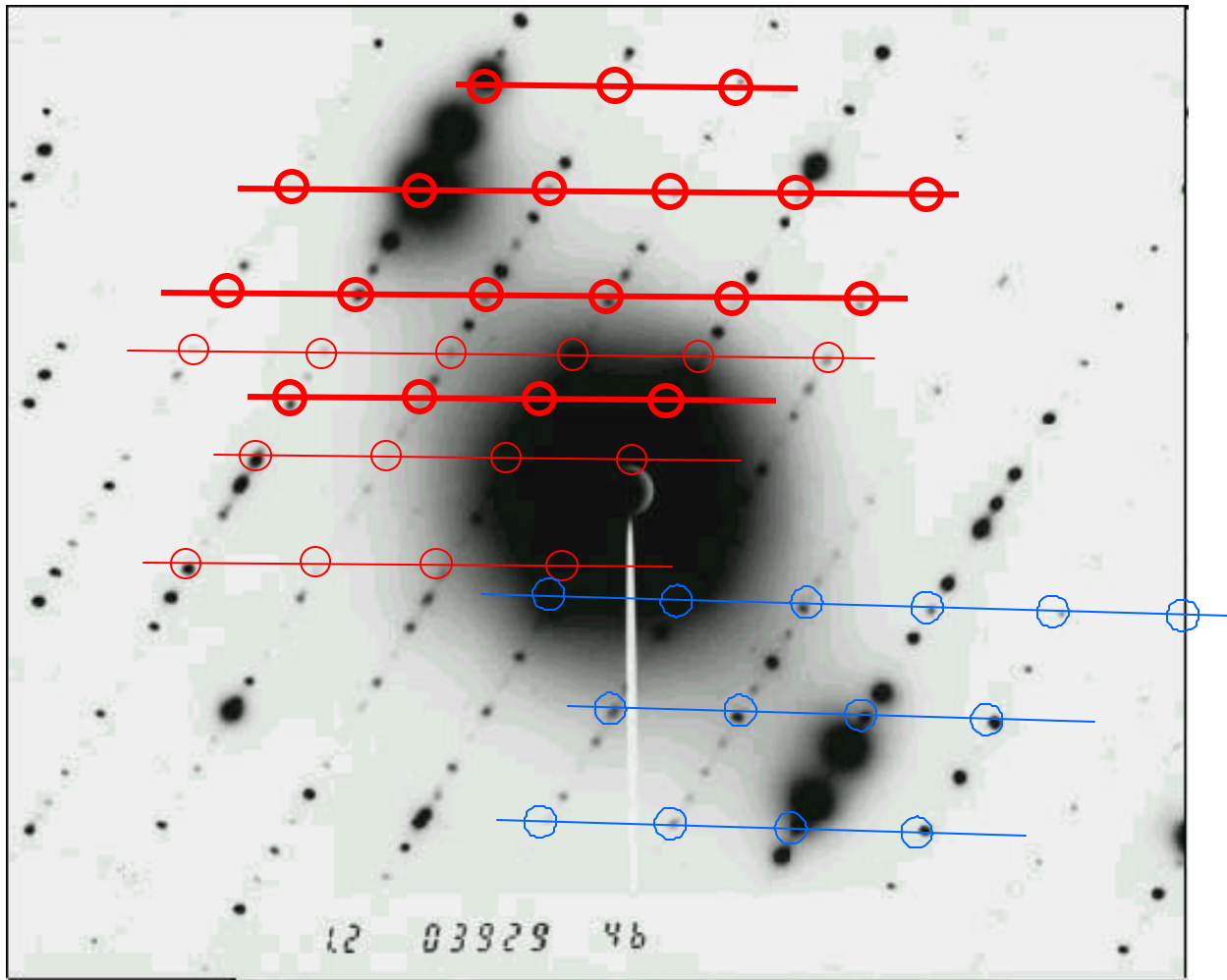


Illustration 4. The lines and circles show the portions of the pattern consistent with a talc diffraction. Note the differing angles in the lines between the upper and lower portions of the pattern.