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Spectroscopic and X-Ray Diffraction Analyses of Asbestos in the World Trade Center Dust

Asbestos Content of the Settled Dust

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On Sept. 17 and 18, 2001, samples of settled dust and airfall debris were collected from 34 sites within a 1-km radius of the WTC collapse site, including a sample from an indoor location unaffected by rainfall, and samples of insulation from two steel beams at Ground Zero. Spectral and XRD analyses of the field samples detected trace levels of serpentine minerals, including chrysotile asbestos in about two-thirds of the dust samples at concentrations at or below ~1 wt%. The chrysotile content of the dust is variable and may indicate that chrysotile asbestos was not distributed uniformly during the three collapse events.

Introduction

Spectroscopy is a useful tool for evaluating environmental contaminants at scales ranging from hand specimens to those available from airborne and orbital remote sensing platforms (1). Spectroscopic analysis frequently differs from x-ray diffraction analysis (XRD) in its sensitivity to materials, and often provides complimentary information. Reflectance spectroscopy over the visible to near-infrared (VIS-NIR) wavelength range (0.4 - 2.5 μm) is particularly sensitive to hydroxyl (OH) and water-bearing materials (2), organic C-H containing compounds, such as oil, paper, and wood, carbonate-bearing rocks such as marble

and limestone (3), water-bearing sulfates such as gypsum found in wallboard and concrete (4), and iron-containing compounds such as hematite – a pigment used to color bricks red (2). Spectral reflectance is defined here to be the ratio of reflected to incident light relative to a diffuse standard, with reflectance values varying between 0 and 100%. Laboratory spectroscopy differs from airborne imaging spectroscopy in three ways: 1) individual samples are analyzed under controlled conditions using artificial illumination; 2) there is little interfering atmosphere to block portions of the electromagnetic spectrum; and 3) spectral resolution and signal-to-noise ratio can be much higher. Consequently, laboratory spectral measurements can have much higher sensitivity to the individual materials in a complex sample compared to remote spectral measurements.

On September 16, 2001, five days following the collapse of the World Trade Center (WTC) Towers, hyperspectral data were collected over Ground Zero with the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS). These data were collected to rapidly assess the potential asbestos hazards of the dust that settled over lower Manhattan (5, 6). Within two days of the overflight, field samples of settled dust and airfall debris were collected from lower Manhattan, including samples from two indoor locations unaffected by rainfall, and samples of insulation from two steel beams at Ground Zero, to verify imaging spectrometer mineral maps. A U.S. Geological Survey (USGS) study then underway at Libby, Montana (7), indicated that laboratory spectral measurements could detect an absorption feature diagnostic of potentially asbestiform minerals that is at a wavelength often obscured by atmospheric absorptions in airborne remote sensing data. Laboratory reflectance measurements and XRD analyses of the WTC dust, beam-insulation, and concrete samples were made. Samples were also analyzed for a variety of mineralogical and chemical parameters using scanning electron microscopy and chemical analyses (8, 9).

Method

Sample Collection

A two-person U.S. Geological Survey team (authors Hoefen and Swayze) collected settled dust and coarser airfall debris samples from 35 localities within a 1 km radius centered on the WTC site on September 17 and 18, 2001 (Figure 1). Samples collected outdoors were exposed to wind and precipitation during a rain storm on the night of September 14 prior to collection. One sample (WTC01-20) was collected indoors near the gymnasium in the World Financial Center across from the WTC site on West Street. A sample of dust (WTC01-36) blown by the collapse into an open window of an apartment, located 30 floors up and 0.4 km southwest of the center of the WTC site, was also acquired a few days later. Two samples of insulation coatings (WTC01-8 and WTC01-9) were collected from steel beams that had been removed from the debris pile of the WTC. Samples of

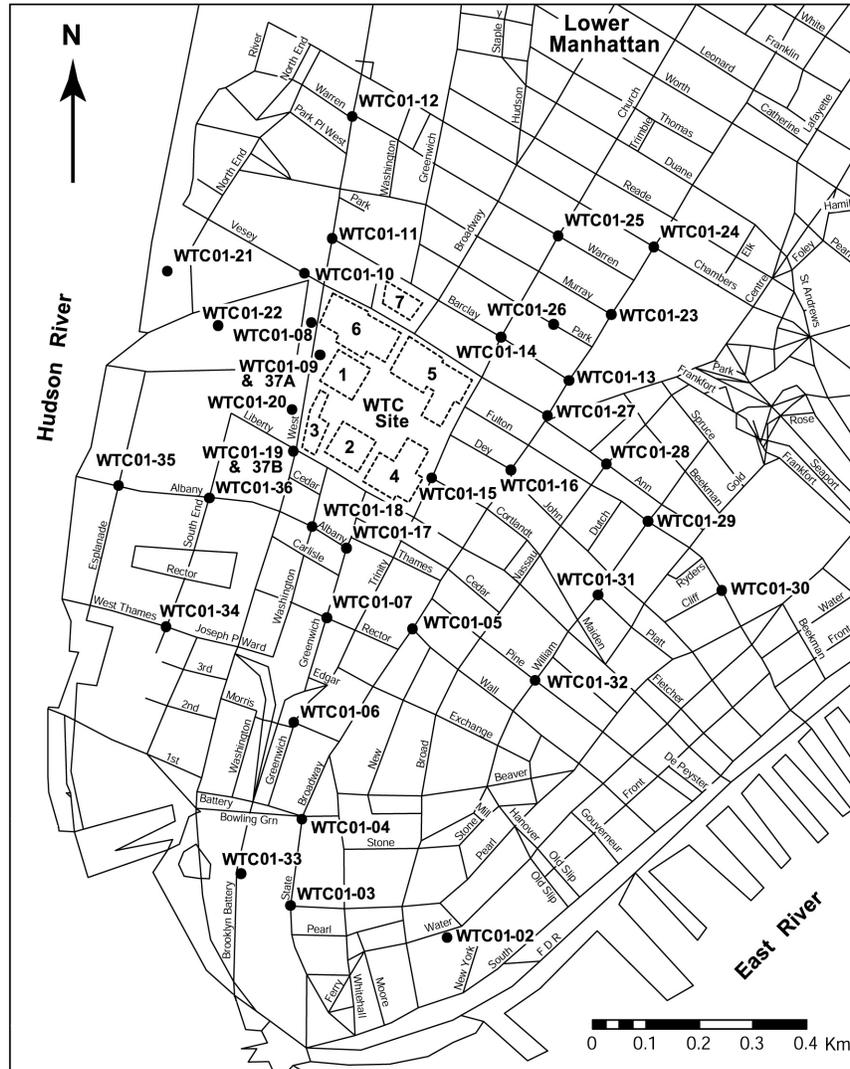


Figure 1. Location of settled dust and debris samples collected in lower Manhattan for this study and other studies (5, 6, 8, 9). The original locations of the World Trade Center towers and buildings are indicated by the dashed outlines.

concrete (WTC01-37A and WTC01-37B) were collected from the WTC debris at the same location as WTC01-8 and WTC01-9, respectively.

Many of the streets bordering the collection locations had been cleaned or were in the process of being cleaned at the time of sample collection. Given these limitations, collection of dust samples was restricted to undisturbed areas such as window ledges, car windshields, flower pots, building entrances, covered steps, or from sidewalks adjacent to walls where the dust was sheltered from the weather and cleanup process. In many cases, the samples formed compact masses suggestive of having been dampened by rain and subsequently dried during the intervening 3-4 days. Samples were gathered by scooping with a nitrile-glove covered hand, and then placed in doubled plastic ziplock freezer bags. When possible, several handfuls of material were collected from different locations within a few-square-meter area and combined into one sample. Collection locations were identified by street intersections.

Spectral Measurements

Reflectance spectra of the samples were measured in a laboratory High Efficiency Particulate Air filter (HEPA) fume hood with an Analytical Spectral Devices (ASD) Full Range Spectrometer® over the wavelength range from 0.35 - 2.5 μm using a halogen lamp for illumination and Spectralon® panel for reference (*1*). The ASD spectrometer has 5 nm spectral resolution from 0.35 - 1.0 μm and 11 nm spectral resolution from 1.0 - 2.5 μm . The entire sample was first poured from the plastic sample bag onto white paper, then the sample was mixed with a spatula leaving a relatively flat pile about a centimeter thick for spectral measurement. By mixing the sample, we hoped to avoid possible inadvertent effects of particle sorting that may have occurred during transport or pouring from the bag.

Given that VIS - NIR reflectance spectroscopy detects materials down to a few millimeters, in most cases, beneath the surface of the dust, ten spectra of the pile were measured, using a six second integration time for each spectrum, and then the pile was re-mixed before collecting an additional ten spectra, to expose previously unmeasured material at the surface. The spectrometer optical fiber was held a few centimeters above the pile and moved constantly in an elliptical manner to spatially average the surface of all but the edges of the pile. This method allowed about 40-60% of the entire sample volume to be spectrally characterized. Spectra of each dust sample were averaged and corrected to absolute reflectance (*10*). Low levels of noise observed in the averaged spectra indicate that we achieved a very high signal-to-noise ratio of 28,000:1 based on the standard deviation of reflectance values in a flat portion of the spectral average of a relatively dark (23% reflectance) dust sample (WTC01-31) near 1.38 μm . Sample splits for analyses were obtained by the cone and quartering method (*11*).

X-Ray Diffraction Measurements

Most crystalline materials have unique x-ray diffraction patterns that can be used to differentiate between materials. X-ray powder diffractometry was used to characterize the mineralogy of the WTC samples. Three gram aliquots of the research splits were dry pulverized with a mortar and pestle to an average particle size of about 50-150 μm . About one gram of each specimen was then packed in an aluminum sample holder and analyzed with a Scintag X-1 Automated Diffractometer® fitted with a spinning sample holder using copper (Cu) K-alpha radiation (12). Complete XRD analyses for all samples are listed in (5) and summarized in (8).

Results and Interpretation

Spectra of the dust samples, in general, look nearly identical with reflectance levels that vary between 20 - 45% and strong absorption edges between 0.35 - 0.8 μm (Figure 2A). There are only weak spectral absorptions, apart from the absorption edge, in the electronic absorption region (0.35 - 1.35 μm) of the spectra indicating that the dust contains only low abundances of materials with Fe or other transition elements. However, there are numerous spectral absorptions in the vibrational spectral region (1.35 - 2.5 μm) principally at 1.45, 1.75, 1.94, 1.97, and from 2.2 - 2.4 μm (Figure 2). The strongest spectral feature is at 1.94 μm and is due to structural and adsorbed water. A weaker feature at 1.45 μm is due to water and/or OH, and varies in depth from 2 - 13%. Spectral features at 1.75 μm are even weaker with depths of only a few percent. Spectral features in the 2- μm region are weakest and vary from a fraction of a percent up to 1% depth.

Absorption features can be diagnostic of some materials contained in the dust. Gypsum, from pulverized wallboard and concrete (13), has the strongest spectral features, accounting for most of the bands observed in the vibrational portion of the spectra. This mineral has three diagnostic absorption features that form a stair-step like triplet between 1.42 - 1.54 μm recognizable in nearly all dust samples (Figure 2B). It also has absorption features at 1.75, 1.95, 1.975, 2.17, 2.217, and 2.268 μm , which closely match the positions and geometry of the absorption features observed in the dust. Figure 3 shows spectral estimates of gypsum based on the relative band depths of its 1.75 μm absorption in the dust samples. Samples have strong bands near Ground Zero, grading to weak bands further away. This pattern suggests that gypsum is more abundant and/or coarser grained closer to Ground Zero. An absorption feature at 1.413 μm (Figure 2B) matches similar features in spectra of portlandite ($\text{Ca}(\text{OH})_2$) and muscovite/illite, both mineral components of the WTC concrete. Hydroxyl-related absorption features from other mineral components of the pulverized concrete could theoretically occur at or near this wavelength. Variable levels of muscovite/illite were found in two thirds of the dust samples,

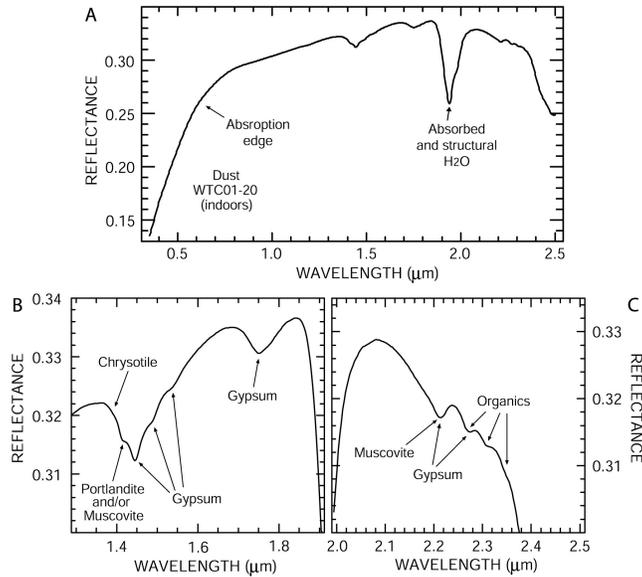


Figure 2. Plot A is a reflectance spectrum of a sample of World Trade Center dust collected indoors near the "gym" immediately adjacent to the WTC site. Plots B and C show details of absorptions in the vibrational region.

while portlandite was found in three samples (including the two indoor samples) using XRD analysis. Additional absorptions located at 2.307 and 2.343 μm are due to C-H stretches from organic materials (Figure 2C).

Electron microprobe analyses indicate fibrous glass with an elemental composition closely matched by slag wool, a type of mineral wool insulation, in all dust samples analyzed by this method (8). Slag wool has only weak spectral absorptions and is virtually transparent over the 0.35-2.5 μm wavelength range. Organic materials associated with slag wool may contribute to some of the spectral features observed in the dust (5). A non-asbestos coating (WTC01-9) taken from a steel beam removed from the debris pile west of WTC Tower 1 has relatively strong 2.307- and 2.34- μm absorptions that match the positions of similar, but weaker, bands in all of the dust samples. Although the positions of these bands are compatible with C-H absorptions in most organic materials (e.g., plastics, paper, fabrics), washing of sample 9 with methanol was sufficient to significantly reduce the strength of these absorptions, indicating they are caused by a soluble organic material, possibly oil used as a dust suppressant in insulation containing slag wool (5).

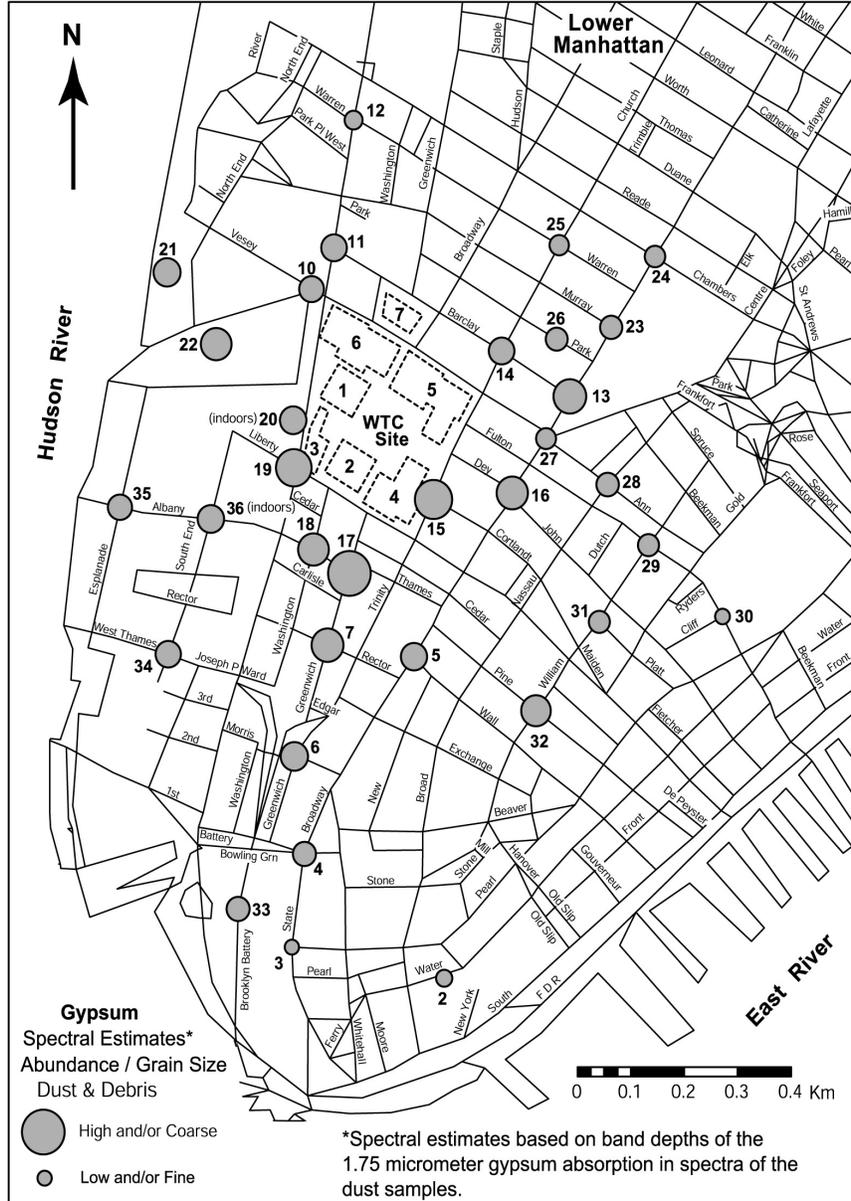


Figure 3. Spectral estimates of gypsum abundance/grain size in surface samples of the WTC dust and debris.

Spectra of both beam coatings (samples 8 and 9) have an absorption at 1.725 μm that closely matches the position of a C-H absorption found in oil. Use of slag wool was widespread in the WTC Towers (14) as part of fireproof coatings on steel beams and the undersides of floors, and possibly in ceiling tiles. The apparent widespread use of slag wool and its brittle nature may explain its presence in all of the dust samples as a volumetrically significant component. Figure 4 shows spectral estimates of organic materials in the dust based on the relative band depths of the C-H combination absorption at 2.31 μm . Samples have relatively weak bands near Ground Zero and stronger bands further away. Because grain size should decrease outward, this pattern suggests that the organic material responsible for the absorption is more abundant further from the source, perhaps because it coats pulverized slag wool or other materials which were widely distributed during the collapse.

Possible Sources of Asbestos in the WTC Dust

Asbestos refers to a fibrous crystal form that is characteristic of several different minerals (15). The two main types of asbestos used commercially are chrysotile, a fibrous member of the serpentine mineral group, and several amphibole minerals. Inhalation of asbestos has been associated with asbestosis, mesothelioma, and lung cancer (16).

There are several possible sources of asbestos in the collapsed buildings at the WTC: fireproof coatings sprayed onto steel beams, on the undersides of floors, and in the elevator shafts, having been used up to the 38th floor of Tower 1 (17, 18, 19). Sample 8 was taken from a coating on a steel beam removed from the debris pile west of WTC Tower 1. A spectrum of this sample shows absorption features at 1.385 and 2.323 μm , which match in position and overall shape to those of chrysotile asbestos (Figure 5). XRD analysis and the depth of these spectral absorptions is consistent with chrysotile forming up to 20 wt% of this coating material (5, 17). In sample 8, the position of the 2.32- μm absorption is consistent with that of chrysotile, but the band width is somewhat wider possibly indicating the presence of overlapping 2.307- and 2.343- μm absorptions from dust suppressant oil (14) or other organic compounds.

Other potential sources of asbestos in the dust include vinyl floor tiles (typically 10-15% chrysotile), insulation on pipes, and amosite asbestos insulation possibly from boilers (14, 19). Spectroscopy and XRD analyses of the two concrete samples did not detect any measurable chrysotile. Asbestos abatement and insulation repairs in WTC Towers 1 and 2 involved replacement of easily-accessible original fireproof coatings that may have contained vermiculite (17). Vermiculite has the potential to contain amphibole asbestos (20, 21), however, only minute amounts (<0.02 wt%) of fibrous amphibole were found in a dust sample collected by Chatfield and Kominsky (22) north of WTC Building 7. Vermiculite

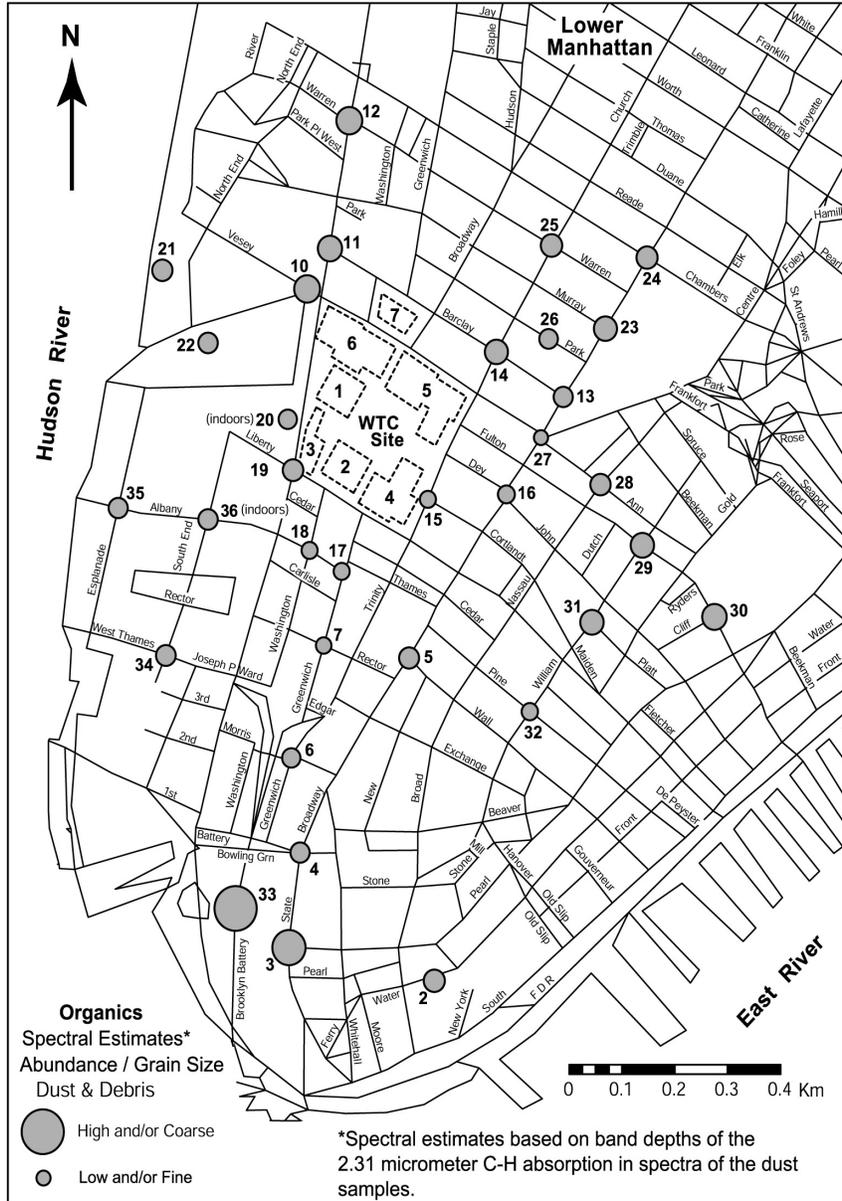


Figure 4. Spectral estimates of organic material abundance/grain size in surface samples of the WTC dust and debris.

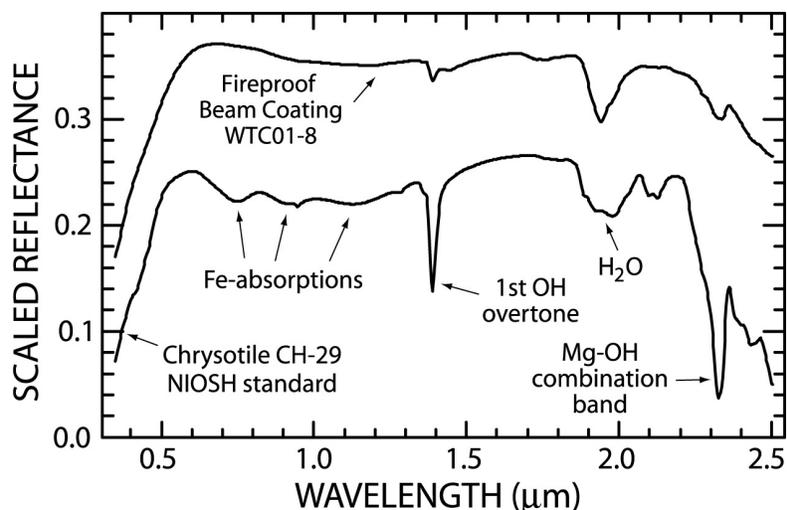


Figure 5. Reflectance spectrum of the fireproof coating collected from a steel beam at Ground Zero compared with a spectrum of pure chrysotile asbestos. The 1.3 - 2.5 μm region of the asbestos standard is dominated by strong 1.385- and 2.323- μm vibrational absorptions. The spectrum of the fireproof coating has similar but weaker absorptions. Bottom spectrum is offset downward 0.3 units for clarity.

was not detected in either sample of the beam coatings collected at Ground Zero by spectroscopy, XRD, or visual inspection. Vermiculite was detected in several dust samples during scanning electron microscope (SEM) and visual examinations (8). Trace levels of amphibole were found in samples 22 and 33 by XRD analysis, but it is unknown if these were fibrous. SEM observations detected chrysotile, but not fibrous amphiboles, in all dust samples examined (approximately one half of the samples collected (8)).

Spectral Detection of Chrysotile

To better constrain the abundance of chrysotile asbestos in the dust, mixtures of dust and chrysotile were prepared. Sample 6 was selected as a representative dust sample with a relatively low level of asbestos (~ 0.1 wt%) based on high spectral resolution measurements, which resolved the chrysotile spectral features in detail (Figure 6). This spectrometer was not used to measure the suite of WTC dust samples because of its small sample size and long measurement time requirements. Known amounts of a well characterized, very finely ground, National Institute of Occupational Safety and Health (NIOSH) Chrysotile standard

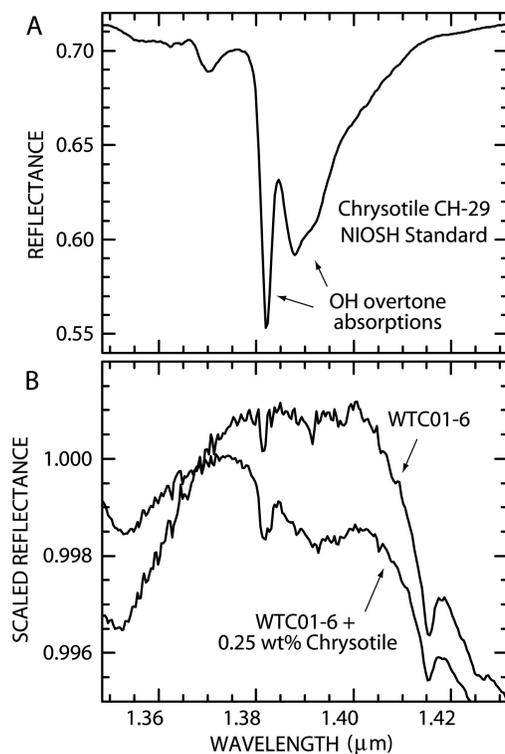


Figure 6. High spectral resolution reflectance spectra of A) pure chrysotile and B) the dust sample 6 alone and with 0.25 wt% added chrysotile. At this spectral resolution the chrysotile feature is resolved into multiple absorptions, which can be seen weakly at 1.38 and 1.388 μm in upper spectrum of plot B. Measurements of the relative depth of the 1.388- μm absorptions in both samples indicates the presence of ~ 0.1 wt% chrysotile in dust sample 6. Spectra were measured with a Nicolet 760 Magna Fourier Transform Infrared Spectrometer[®] at 4 cm^{-1} spectral resolution, and were scaled to allow comparison in Figure 6B.

(23) were added to splits of sample 6 to create mixtures with 0.25, 0.5, 1.0, 2.5 and 5.0 wt% chrysotile. These mixtures were then measured to provide a series of spectra that could be directly compared to those of the dust samples.

At the coarser spectral resolution of the ASD spectrometer, chrysotile has two strong absorptions at 1.385 and 2.323 μm due to the first OH stretch overtone and a Mg-OH combination band, respectively (Figure 5) (1). Even though the 2.323- μm chrysotile absorption is the stronger of the two bands, its wavelength position is wedged between stronger C-H absorptions at 2.307 and 2.343 μm and overlaps

with a 2.317- μm absorption from pulverized concrete, all of which tend to mask the presence of chrysotile in the dust samples at levels below ~ 1 wt% in laboratory spectra. The weaker 1.385- μm chrysotile absorption occurs in a relatively less cluttered spectral region, providing a means of estimating chrysotile content. However, at concentrations less than 0.5 wt% the 1.385- μm absorption feature of chrysotile cannot be differentiated from a similar absorption feature of lizardite (a non-asbestiform variety of serpentine) at the spectral resolution of the ASD spectrometer.

Figure 7A shows spectra of constructed dust plus chrysotile mixtures with straight-line continua removed from the 1.4- μm region. Continuum removal consists of dividing the dust spectrum by a line (or curve) fit to the top shoulders of an absorption. In this way the depth of the absorption is normalized relative to 100% reflectance and interference from broader, nearby absorptions is minimized (24). This process helps make the absorptions of interest more comparable for samples of variable composition. Note the growth of the 1.385- μm chrysotile absorption from a mere inflection at 0.25 wt% to a full fledged band at 5 wt%, with increasing chrysotile content. Because the chrysotile absorptions are relatively weak, even for the 5 wt% mixture (about 0.5 % band depth), diagnostic spectral measurements must be done with a high signal-to-noise ratio.

Figure 7B shows curved-continuum-removed spectra of the mixture series centered on the spectral region of the chrysotile 1.385- μm absorption. Continuum removal of the mixture spectra produces distinct absorption bands even at the 0.25-wt% level. Continuum removal over the wavelength region corresponding to this absorption provided a means of estimating the amount of serpentine/amphibole/talc present in each dust sample based on the depth of the 1.385- μm absorption when compared to the mixture series spectra (Figure 8). Band depths used in this correlation were normalized for each mixture by dividing the 1.385- μm absorption band depth by the original reflectance value of the spectrum, in this spectral region, as described by Clark (25). A standard error of ± 0.2 wt% is an estimate of the uncertainty in a single value of the weight percent chrysotile calculated using the best-fit equation shown in Figure 8 for dust sample 6.

Some amphiboles (e.g., fibrous or non-fibrous varieties of tremolite, richterite, hornblende) and talc have spectral absorptions in the 1.39- μm region and their presence at levels < 0.5 wt% could potentially produce weak absorptions similar to those of chrysotile at the spectral resolution of the ASD spectrometer and, thus, add to the estimate of chrysotile. Alternatively, XRD analysis can detect amphiboles and talc without interference from chrysotile and the presence of amphibole was detected in dust samples 22 and 33 at trace levels. The potential presence of amphiboles and talc at concentrations below 0.5 wt% in the other dust samples means that our spectral estimates are upper limits for the abundance of chrysotile.

Other potential sources of error in the estimates of chrysotile in the WTC dusts depend on the grain size, albedo (brightness), and composition of the other dust

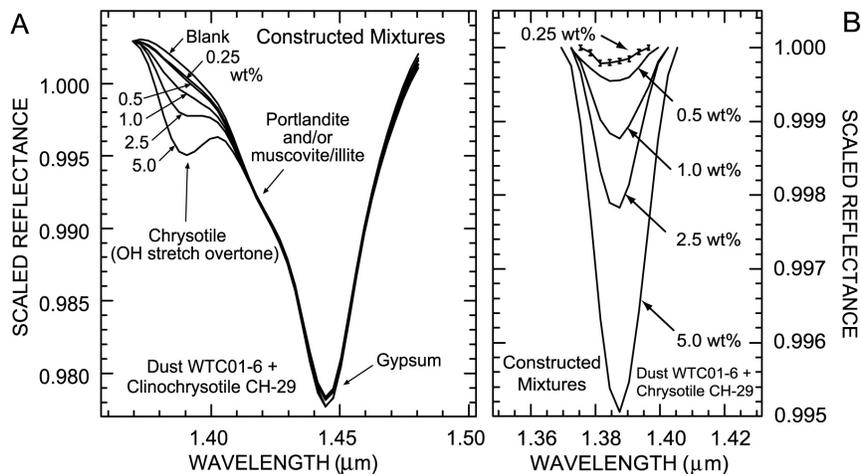


Figure 7. A) Continuum-removed spectra of the OH stretch-overtone region of dust + chrysotile synthetic mixtures constructed from WTC dust sample 6 and a NIOSH chrysotile asbestos standard. The spectrum labeled “blank” is of unmodified sample 6, which may contain ~0.1 wt% chrysotile as determined by high resolution spectroscopy (Figure 6). Each spectrum is labeled with the weight percent of added chrysotile. B) Same mixture spectra as in A, centered on the spectral region of the chrysotile 1.385- μm absorption, divided by a curved continuum. Error bars shown for the 0.25 wt% sample are ± 1 standard deviation of the spectral noise derived by averaging 20 spectral measurements, and are representative of the measurement precision for the other spectra in this wavelength region.

particles. Because diffuse reflectance is a non-linear process, decreasing the grain size of the dust particles results in more scattering causing a decrease in the strength of all the absorptions (24), including the chrysotile absorption, thus, decreasing the spectral sensitivity to chrysotile content. Because most of the dust samples have an albedo similar to that of the samples used to create the mixtures, errors in estimating chrysotile content will probably be smaller than those due to grain-size variations. Considering these potential sources of error, we estimate that application of this spectral calibration (Figure 8) to the other dust samples, apart from sample 6, to have an abundance error of approximately ± 0.3 wt%.

Spectra of dust samples that contain spectrally significant concentrations of portlandite (from pulverized concrete) and muscovite/illite have wide 1.42- μm absorptions that can conceal chrysotile absorptions that may be present at 1.385 μm (5). Figure 9 shows a spectrum of a 1wt% chrysotile + dust mixture compared with

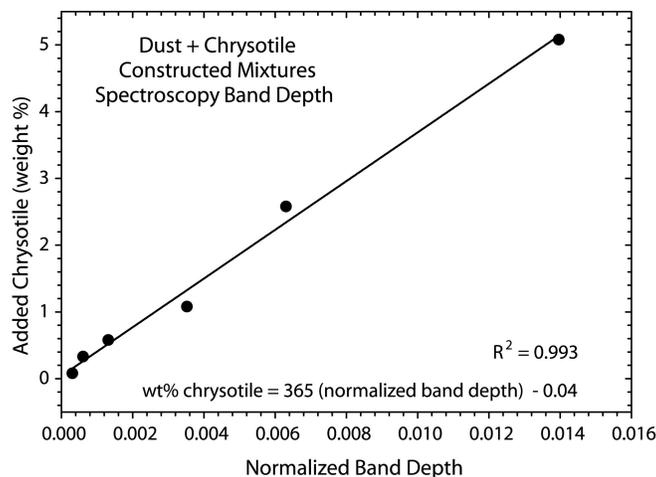


Figure 8. Correlation between normalized band depth of the 1.385- μm absorption and chrysotile content of mixtures constructed using dust sample 6 and variable amounts of the chrysotile NIOSH standard. To more accurately represent actual chrysotile contents in the correlation, the 0.25, 0.5, 1.0, 2.5, and 5.0 wt% chrysotile values of the mixture series were numerically adjusted to reflect an additional ~ 0.1 wt% chrysotile originally present in sample 6 (leftmost point on graph; see Figure 6 for details). R^2 is the correlation coefficient for the best fit line.

a spectrum of dust sample 2, which contains a relatively high concentration of portlandite and/or muscovite/illite and no spectrally detectable chrysotile. Spectroscopy could not be used to estimate chrysotile content of five dust samples because of interference from nearby spectral absorptions of portlandite and/or muscovite/illite. However, in many of the outdoor dust samples portlandite reacted with carbonic acid in rain water from thunderstorms on September 14 to form calcite (9), thus reducing portlandite's spectral interference with the nearby chrysotile absorption feature.

X-Ray Diffraction Detection of Chrysotile

The same mixture series was also characterized using XRD to provide a series of diffractograms that could be directly compared to those of the dust samples. Figure 10A shows x-ray diffractograms of mixtures of sample 6 and a NIOSH chrysotile standard, while Figure 10B shows x-ray diffractograms of sample 8 with up to 20 wt% chrysotile (8) from the steel beam fireproof coating, of sample 28 with a trace of serpentine, and of sample 6 in which no serpentine was detected with

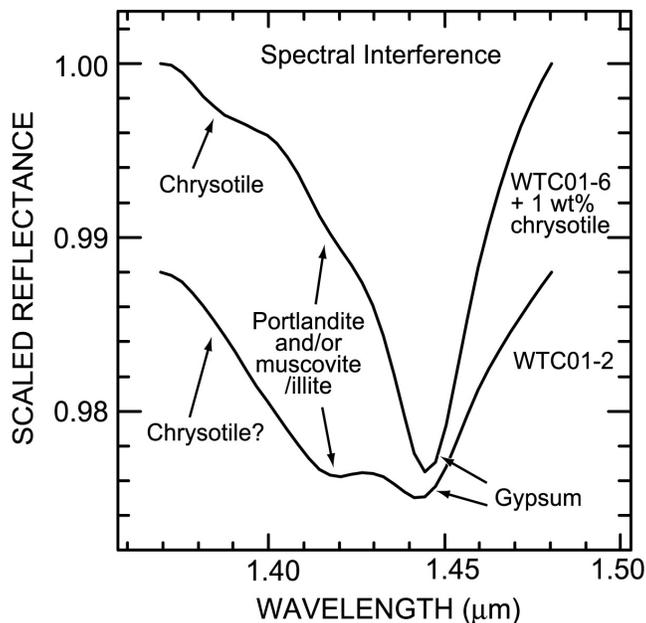


Figure 9. Spectra of dust samples that contain trace (top) and higher (bottom) concentrations of portlandite and/or muscovite/illite, which can interfere with spectral determination of asbestos content. The top spectrum is of a constructed mixture with 1wt% added chrysotile. The band depth of the 1.385- μm chrysotile absorption is 24 times greater than the standard deviation of the noise in this spectrum (see Figure 7B). Spectra continuum removed and offset vertically for clarity.

XRD analysis. A diffraction peak diagnostic of chrysotile occurs near 12 degrees two theta on the slope of a much larger gypsum peak at 11.7 two theta in the mixture series (Figure 10A). At concentrations below a few weight percent, XRD analysis cannot be used to differentiate chrysotile from the other serpentine minerals in the WTC dust samples. The mixture series diffractograms show possible detection levels of chrysotile down to the 0.25-wt% level. Because of the limited time available for analysis of the dust samples during the weeks following the WTC disaster, these mixtures were made using a hand-ground split from sample 6 so homogeneity, grain size, and mixing procedures did not meet the accepted criteria for quantitative XRD analysis. However, these diffractograms can be used as guides to determine possible quantities and detection limits for low concentration levels of chrysotile.

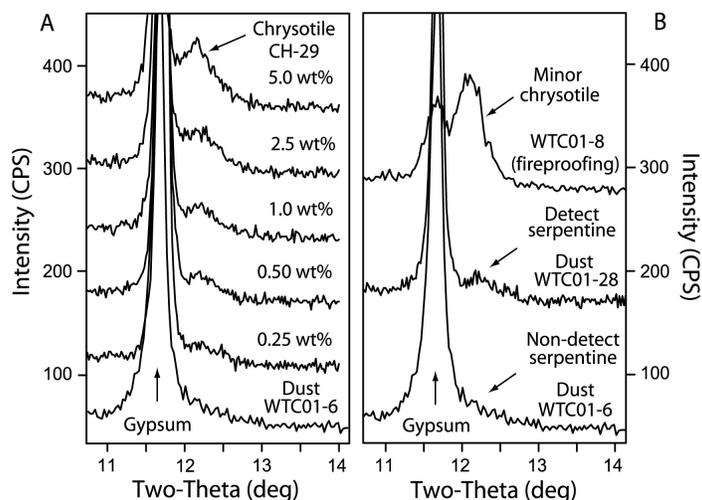


Figure 10. A) X-ray diffractograms of mixtures constructed using dust sample 6 and the NIOSH chrysotile standard. The weight percent of added chrysotile is shown to right of the diffractograms. B) X-ray diffractograms of a chrysotile-bearing beam coating and two dust samples. For clarity diffractograms are offset vertically. CPS = counts per second; deg = degrees.

Intra-Sample Variation of Chrysotile Content

One method of estimating the variability of chrysotile within a dust sample is to make replicate measurements on different portions of the sample. Because of the limited time available for analysis of the dust samples during the weeks following the WTC disaster, only one set of XRD measurements was made on all but two of the dust samples. However, twenty spectral measurements were made on separate portions of each dust sample. Figure 11A shows variations in the normalized band depth of the 1.385 μm absorption for each spectral measurement of dust sample 28. These measurements may indicate that serpentine/amphibole/talc is not distributed homogeneously within this sample. This observation is also supported by two replicate XRD measurements of dust sample 28, in which serpentine was detected in one run but not the other. X-ray diffraction measurements were made on hand-ground 3 gram splits of each dust sample, whereas spectroscopic measurements were made on approximately half of the entire sample volume (or between 35 - 200 grams of material). Figure 11B shows that the spectrally derived cumulative average for serpentine/amphibole/talc content of sample 28 becomes relatively stable after the first five measurements. If it is assumed that chrysotile accounts for most of the 1.385- μm absorption seen in sample 28, then the spectral estimates may

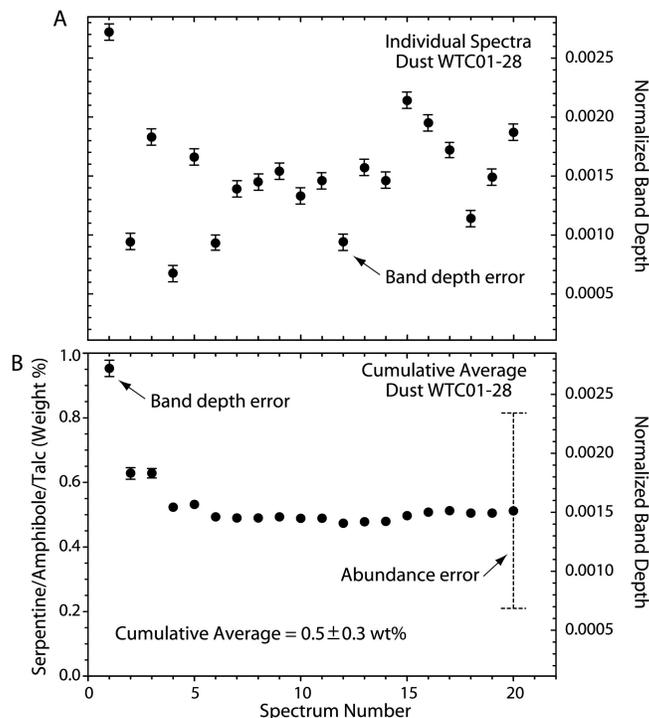


Figure 11. A) Estimates of normalized band depth of the 1.385- μm absorption feature in dust sample 28 for each of the 20 spectra measured. The band depth error bar represents ± 1 standard deviation of the channel-to-channel noise integrated over the wavelength interval of the 1.385- μm absorption. B) Cumulative average for estimates of serpentine/amphibole/talc contents of dust sample 28 based on band depths shown in A and the spectral regression shown in Figure 8. Note how the cumulative average becomes relatively stable, with a variation of only about 0.1 wt% units, after the first 5 measurements. The abundance error bar (± 0.3 wt%) represents the uncertainty in estimates of serpentine/amphibole/talc contents of the dust when using the calibration shown in Figure 8.

be more representative of the bulk chrysotile contents of the dust than are those derived from the more limited number of XRD measurements.

Chrysotile Asbestos Contents of WTC Dust Samples

Other studies have shown that chrysotile is a constituent of the WTC dust (8, 22, 26, 27, 28). Nevertheless, the spectral and XRD techniques describe above

cannot be used to evaluate chrysotile content, at low levels, without the potential for overestimation when other serpentine minerals, amphiboles, or talc are present. Therefore estimates provided by these methods should be considered to be upper limits for the chrysotile content of the WTC dust.

Except for the five samples with significant spectral interference, spectroscopy was used to estimate the serpentine/amphibole/talc content in all of the dust samples (Figure 12). At concentrations below ~0.5 wt%, spectroscopy cannot distinguish between the 1.385- μm absorption features caused by chrysotile, lizardite, antigorite, amphiboles, or talc at the spectral resolution used for these measurements. Levels of these minerals were above 0.3 wt% in 14 of these dust samples. Dust samples 13 and 14 had the highest spectrally derived concentration of serpentine/amphibole/talc at ~1 wt%. Samples with spectral interference were collected on the periphery of our collection area where the dust deposits were thin. This distribution may be evidence of compositional segregation of portlandite and/or muscovite/illite as the dust clouds settled. X-ray diffraction analysis detected serpentine in 16 of the dust samples (Figure 13), including 3 of the 5 dust samples determined to have significant spectral interference. There is only moderate agreement between the spectral and XRD estimates when they are considered on an individual sample basis. For instance, there were 6 samples, apart from those with spectral interference, where XRD detected serpentine but spectroscopy did not. This apparent discrepancy may be a consequence of the heterogeneous nature of the dust, different levels of sensitivity of each analytical method to materials in the dust, and different quantities of dust measured by each method. The problem of detecting unevenly distributed chrysotile in the WTC dust is likely to plague any comparison of analytical methods.

When the results of the two methods are combined, variable levels of serpentine, amphibole, and/or talc were detected in over two-thirds of the dust samples. Neither spectroscopy or XRD detected potential chrysotile concentrations higher than ~1 wt% in any of the 33 dust samples. Examination of these samples with other analytical techniques is needed to further substantiate the quantification levels shown on these maps. It is important to note that the dust and debris samples were collected within a few-square-meter area at sites shown on Figure 1, and that the circles shown in Figures 12 and 13 were made larger than the areas sampled for illustrative purposes only.

The combined results from the two analytical techniques used in this study suggest that potential chrysotile concentrations in the dust are higher to the west and east of Ground Zero and lower south of Ground Zero. If true, certain aspects of this pattern may be explained by noting that the WTC dust blanket was formed by three chronologically and spatially separate dust dispersal events, caused by initial collapse of Tower 2, then Tower 1, and finally Building 7 (29). At some locations, the dust blanket may have been composed of three dust layers. These layers may not have completely overlapped each other, leaving areas where dust from the collapse of one building compositionally dominated the dust blanket.

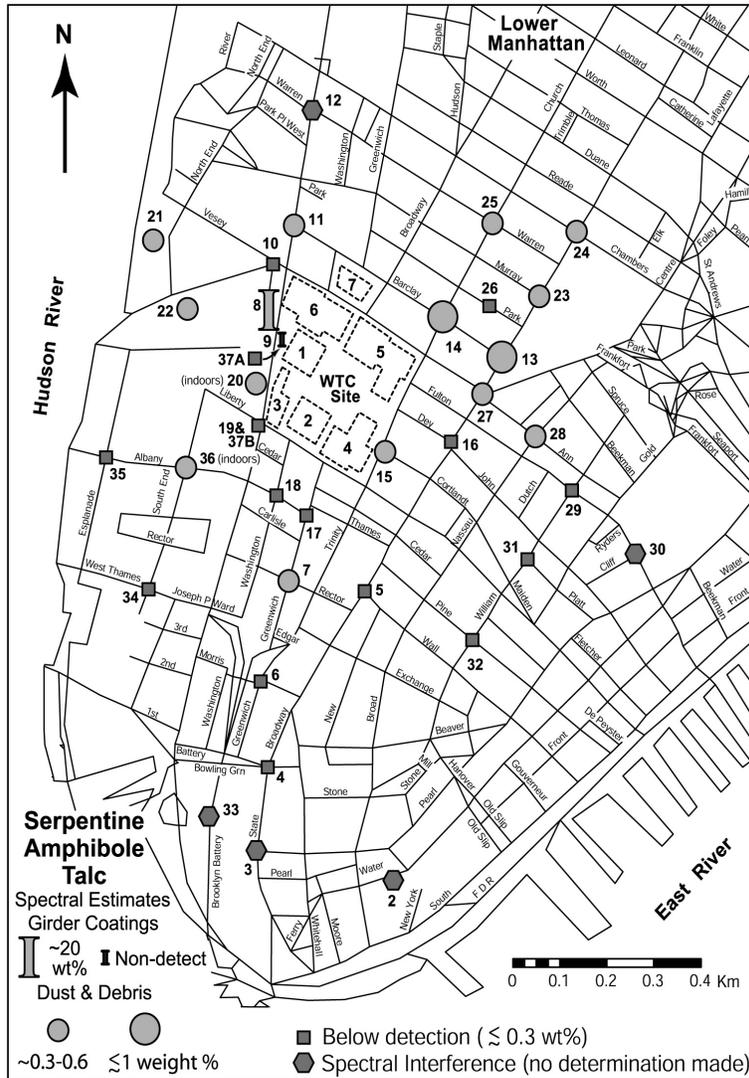


Figure 12. Spectral estimates of serpentine/amphibole/talc concentrations in settled dust samples in Lower Manhattan. Largest circle corresponds to ~ 1 wt% serpentine/amphibole/talc assuming the correlation shown in Figure 8 can be applied to dust sample 14. Scanning electron microscopy indicates that chrysotile is present, at unspecified levels, in “below detection” samples examined (8). Information shown on this map should not be viewed as a replacement for detailed, standardized sampling and test measurements for asbestos.

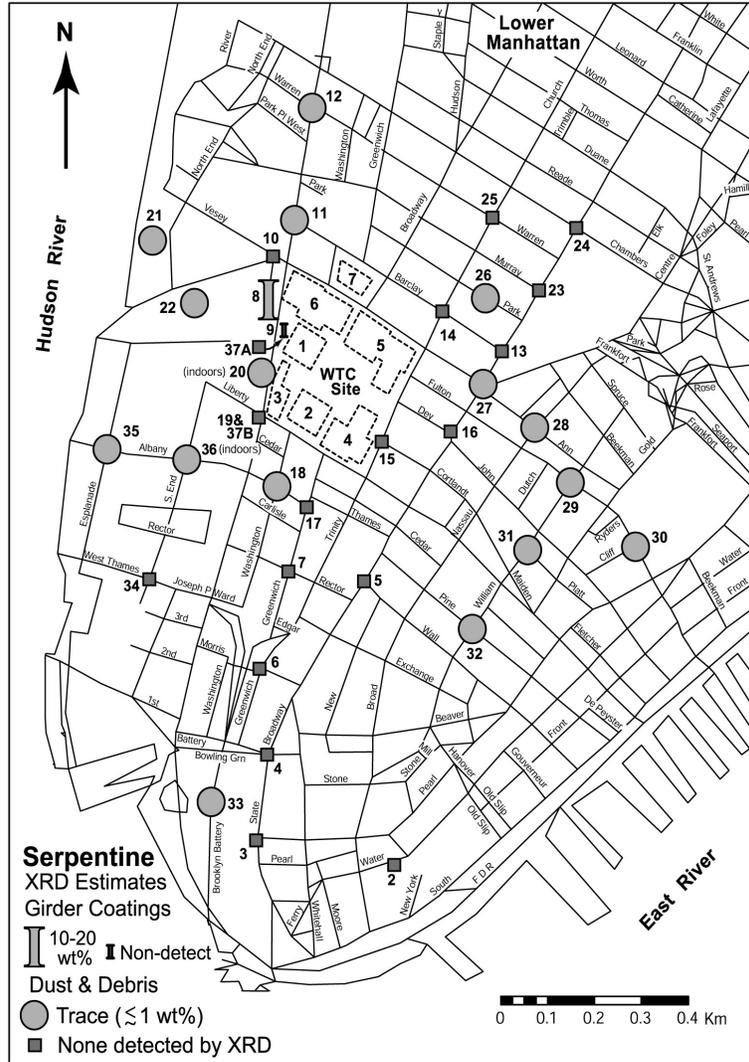


Figure 13. X-ray diffraction estimates of serpentine concentrations in settled dust samples in Lower Manhattan. Largest circle corresponds to ~ 1 wt% serpentine using the mixture series shown in Figure 10A as guides. Scanning electron microscopy indicates that chrysotile is present, at unspecified levels, in the XRD non-detect samples examined (8). Information shown on this map should not be viewed as a replacement for detailed, standardized sampling and test measurements of asbestos.

Because use of chrysotile-bearing fireproof insulation at the WTC was discontinued in 1969, prior to major construction of Tower 2 (17, 29), the dust produced by its collapse may have been relatively lower in chrysotile compared to dust produced from the collapse of Tower 1. It may be possible that the relatively lower chrysotile content of the dust south of Ground Zero may reflect this area's proximity to Tower 2, which did not use chrysotile-bearing fireproof insulation.

Conclusions

Laboratory spectral and x-ray diffraction analyses of WTC settled dust samples detected potential trace levels of chrysotile asbestos in about two-thirds of the dust samples (23 out of 33 samples), but at concentrations at or lower than ~1wt%, well below the detection level (~5 wt%) of the AVIRIS imaging spectrometer (6). Scanning electron microscopy indicates that chrysotile is present, at unspecified levels, in all of the non-detect samples examined (8). Information shown in Figures 12 and 13 should not be viewed as a replacement for detailed standardized sampling and test measurements for asbestos. One sample of a beam coating material contained up to 20 wt% chrysotile asbestos. Carbonic acid in rain water may have reacted with some of the portlandite, making spectral detection of chrysotile easier with the portable spectrometer. Increasing the spectral resolution to 4 nm in the 1.38- μm wavelength region would increase the portable spectrometer's sensitivity to chrysotile content while minimizing interference from other minerals. Spectra with a very high signal-to-noise ratio (28,000:1) were needed to estimate potential chrysotile content in the dust down to the ~0.3 wt% detection level. The need for this and, perhaps, even finer levels of detection present an extraordinary challenge for imaging spectrometers designed for emergency response. In addition to airborne imaging spectroscopy, laboratory spectroscopy was a necessary component of the spectral analysis of the dust because its sensitivity level extends well below that of AVIRIS (6) and it allowed measurements in spectral regions where atmospheric gases obscure the surface. Analyses indicate that trace levels of chrysotile were distributed with the dust radially to distances greater than 0.75 km from Ground Zero. These data also suggest that the distribution of chrysotile may not have been equal in all directions due to differences in sources of the dust.

In the years since our original study of the WTC dust (5), higher-spectral-resolution full-range portable spectrometers with battery operated contact light probes have been developed. These spectrometers could be used to screen thousands of spots for asbestos contamination over large, potentially-hazardous areas in a matter of days, producing data that could be spot checked with traditional evaluation methods. Automated identification software (1) could be used to search the spectra for signs of contamination real-time, producing results immediately after each spectral measurement.

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