The Database Solution to Particle-by-Particle Analysis of Mixed Mineral Dusts

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Introduction

This work involves the development and application of a database for the morphological, crystallographic, and chemical characterization of amphibole particles that occur as accessory minerals in the former vermiculite mine in Libby, Montana. The data in the database were collected using transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) techniques for particle-by-particle characterization of mixed mineral dust samples.

In the fall of 1999, public attention was focused on the small town of Libby due to health concerns over potential amphibole asbestos exposure that occurred in the now closed vermiculite mine [1]. The vermiculite deposit, located in the Rainy Creek Igneous Complex, about seven miles northeast of Libby, was discovered in 1913 and commercial production of vermiculite began in 1923. W.R. Grace & Co. purchased the mining operations in 1963 and continued vermiculite production until 1990 when all mining and milling operations were closed. The mineralogy in the Libby area is quite complex. There is ongoing research and debate on the composition and morphology of the various types of asbestos and non-asbestos amphibole particles present in the mixed mineral dust and their relative quantities and potential health risks. Therefore, the distinction between asbestos and non-asbestos amphibole particles is important from both a scientific and regulatory standpoint. During the period of 1999-2003, the U.S. Environmental Protection Agency (EPA) collected thousands of ambient air, indoor dust, bulk soil, mine waste, vermiculite, and other related samples. As part of cost recovery litigation filed by the EPA against W.R. Grace & Co., splits of approximately two hundred ambient air and scenario samples were requested from the EPA by W.R. Grace & Co. These air samples were collected from outdoor, residential, and former vermiculite plant locations in the Libby area. Many of the indoor dust samples were collected during scenarios that may have disturbed vermiculite or asbestos minerals, such as dusting, vacuuming, and moving furniture. The EPA provided the sample splits, field and sampling data sheets, and results of the corresponding analyses to RJ Lee Group, Inc. as part of their litigation production.

Methods

In this study, the Yamate Level III [2] method for TEM analysis of air samples for asbestos was enhanced by the additional FESEM imaging of each particle. The ambient air samples obtained from the EPA were examined with either JEOL JEM 1200EX or 2000FX TEMs operating at an accelerating voltage of 120 kV. All particles in 40 grid openings having a 3:1 or higher aspect ratio and a length ≥ 5 μm were counted and multiple selected area electron diffraction (SAED) patterns and energy dispersive X-ray spectroscopy (EDS) spectra were collected. All particle mineral assignments were determined from the EDS/SAED results using the nomenclature developed by Leake *et al.* [3]. During the TEM analyses, a sketch was made showing the locations of the particles of interest on the TEM grid. Prior to FESEM analysis, the TEM grids were platinum coated and mounted in a JEOL EM-Q2 Quick Change Retainer, which was attached to a modified aluminum pin mount stub with aluminum screws. Secondary electron (SE) images were obtained with an FEI Sirion 400 FESEM operated in the "ultrahigh resolution" mode with a Through-the-Lens Detector and an accelerating voltage of 3 kV, a beam current of 200 pA, and a 4.0 mm working distance. The particles were relocated in the FESEM with the aid of TEM field images and TEM analyst sketches.

The enhanced Yamate Level III protocol developed by RJ Lee Group, Inc. required the collection of SE images of the full structure, both structure ends, and the particle surface. FESEM images provide information on the morphology and surface characteristics of fine dust particles that cannot be readily ob-

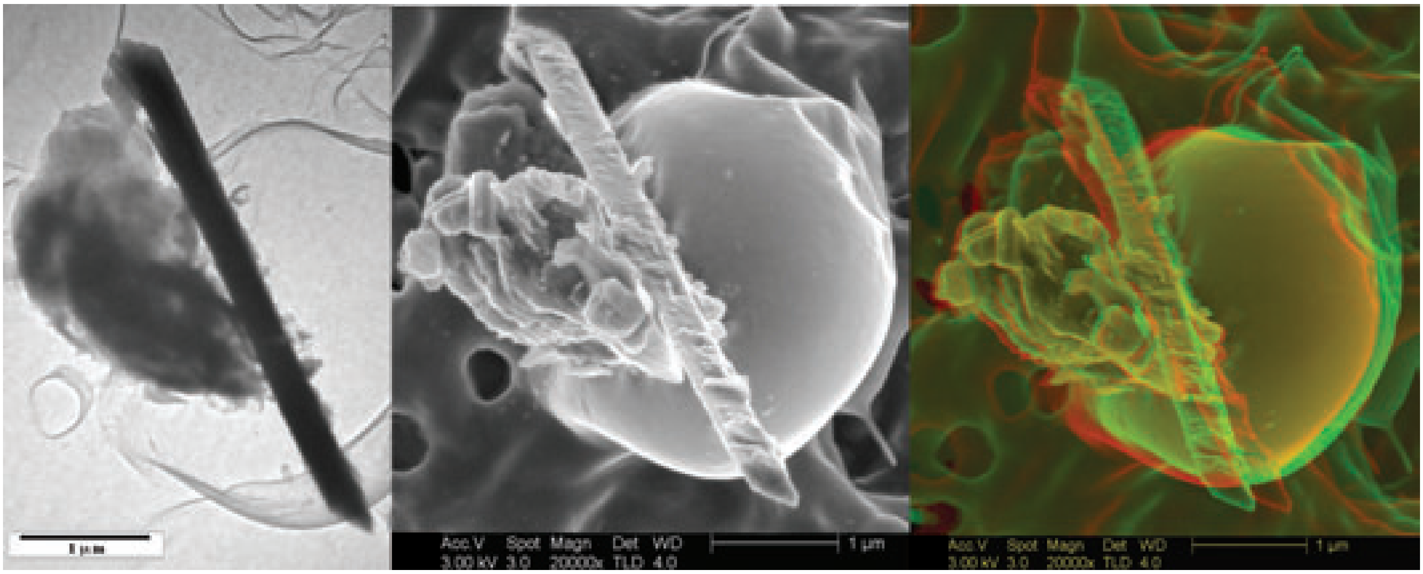

Fig. 1 (a-left) TEM image, (b-center) FESEM secondary electron image, and (c-right) stereo pair image of a prismatic richterite particle identified in a Libby air sample. The particle has a wedge-shaped cross-section as seen in the FESEM image.

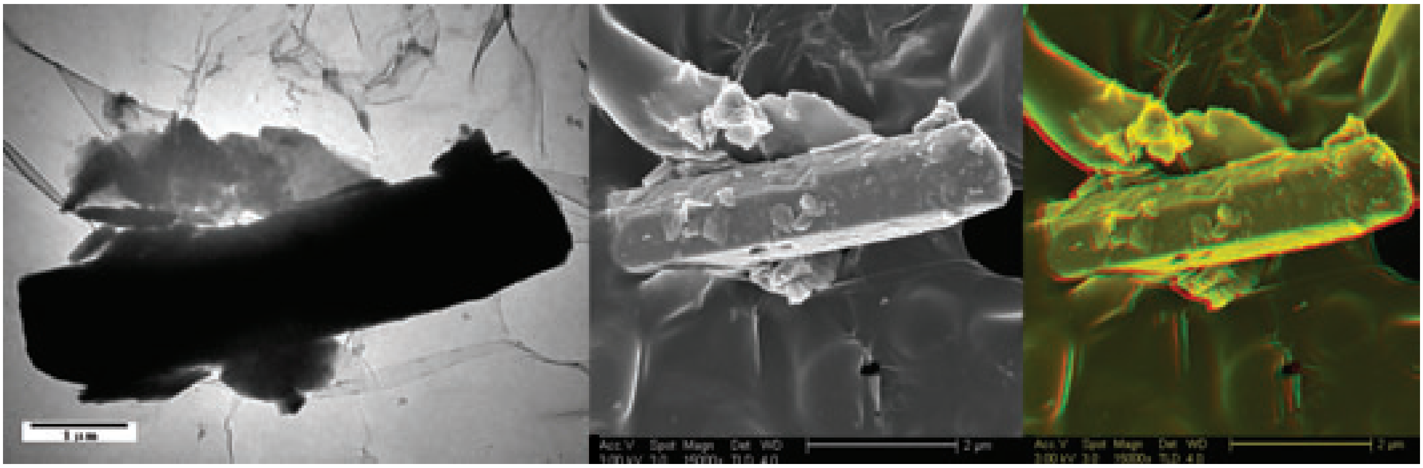

Fig. 2 (a-left) TEM image, (b-center) FESEM secondary electron image, and (c-right) stereo pair image of an aluminum silicate mineral particle identified in a Libby air sample. The particle has several distinct crystal faces as seen in the FESEM image.

served by optical microscopy or TEM (Figures 1-4). The full particle structure and the particle surface were imaged with the sample tilted at 0 degrees and 5 degrees. Stereo pair images were built by superimposing the 0 degree (tinted red) image and 5 degree (tinted green) image. When viewed with red-blue stereo glasses, stereo pair images provide depth perception information not obtainable from a single SE image (Figures 1-4). Please contact RJ Lee Group, Inc. to request a free pair of stereo glasses (e-mail: info@rjlg.com). Examples of FESEM stereo images of additional mineral particles from this and other similar studies can be found online at: http://www.rjlg.com/.

Discussion

In this study, more than 3,700 individual amphibole particles were examined by TEM followed by the complementary FESEM relocation analysis. The particle-by-particle TEM and FESEM examination of multiple samples generates large volumes of images, spectra, and SAED patterns. For each structure counted by TEM, a minimum of 1 TEM image, 1 SAED pattern, 1 EDS spectrum and 8 SE FESEM images were collected. To facilitate data review, more than 67,000 TEM and FESEM images, spectra, and diffraction patterns were imported into a FileMaker™ Pro 8 database. Each particle in the database is identified by: 1) Sample Number, 2) Field Number, and 3) Fiber Number. The database is organized by Sample Number, with the data for all particles associated with that sample being available for sequential viewing by selecting the proper Field and Fiber numbers for the particle of interest. The database was designed with eight data pages for each particle that allow simultaneous viewing of single or multiple TEM/FESEM images, EDS spectra and SAED patterns (Figure 5). Once an analyst opens the digital database program and selects a given particle for viewing, any one of the eight data pages can be accessed from any of the other pages.

Within the database, the structures were classified into categories, including particle shape, end and side geometries, and surface texture (Figure 5). The overall morphologic shape of the mineral particles relocated by FESEM could be described using the following seven primary classifications: fiber, acicular, prismatic, bladed, bundle, columnar, and irregular [4]. These classification terms were originally developed in 1977 by the U.S. Bureau of Mines to differentiate between common mineral rock fragments and their asbestiform varieties using optical microscopy [5]. The Bureau of Mines report has been widely used and recognized in the characterization of minerals and mineral dusts using optical microscopy. FESEM, however, provides an

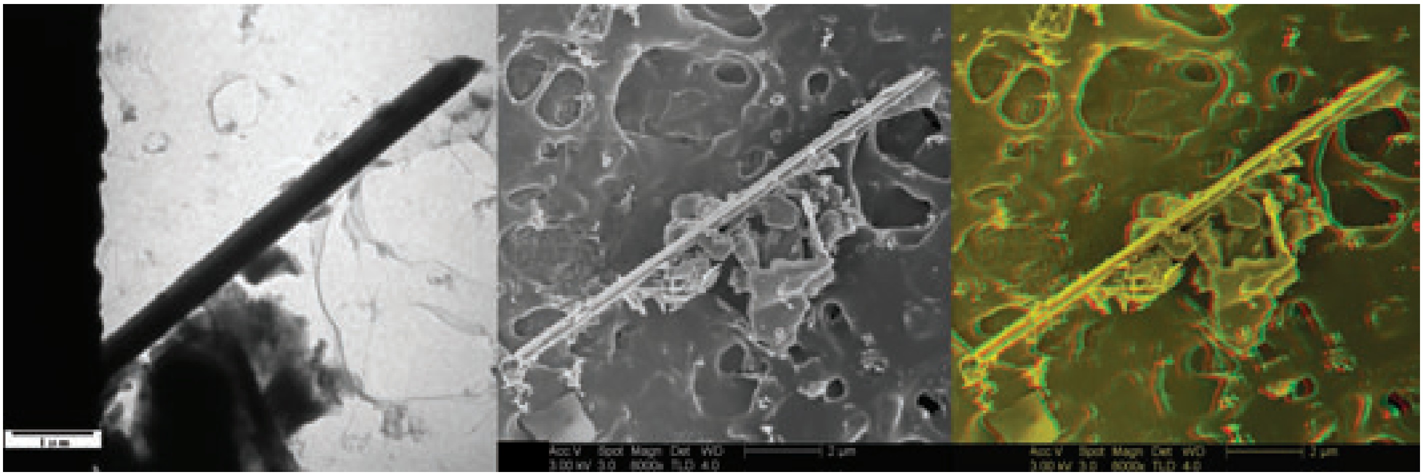

Fig. 3 (a-left) TEM image, (b-center) FESEM secondary electron image, and (c-right) stereo pair image of a bladed richterite particle identified in a Libby air sample. There is a significant difference between the height and width of the particle that is distinguishable in the FESEM image. One end of the particle is hidden on the grid bar in the TEM image; however, the entire particle is visible in the corresponding FESEM image.

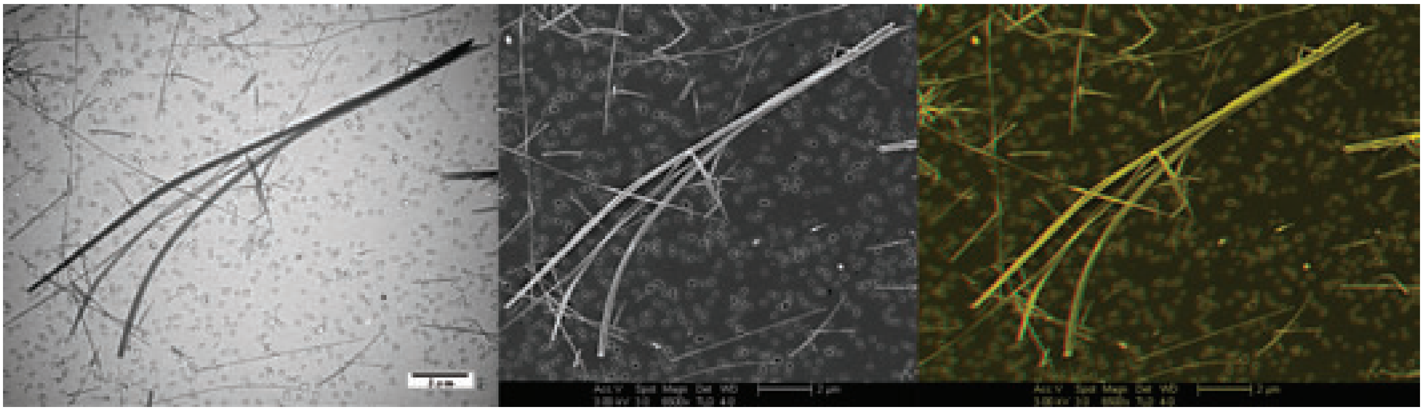

Fig. 4 (a-left) TEM image, (b-center) FESEM secondary electron image, and (c-right) stereo pair image of a bundle of chrysotile asbestos from a Canadian chrysotile mine. In the TEM and FESEM images, multiple asbestos fibers can be seen in the chrysotile bundle and individual asbestos fibers can be seen in the surrounding field of view.

opportunity to observe the morphological, surface, and other definitive characteristics of fine dust particles that cannot be readily observed by optical microscopy or TEM. Classifications were assigned to the particles identified in the air samples as well as to reference minerals. This allowed for comparison of minerals suspected of being asbestos against reference asbestos minerals. The database format allowed querying and summarizing classifications from a single sample or group of samples. The organization and viewing capacity of the database have also been useful for sharing technical results with other experts, communicating with the legal team, and training new analysts. RJ Lee Group, Inc. has since implemented similar databases in other projects where large volumes of data were generated by multiple microscopy techniques.

Conclusions

The FESEM is a valuable tool for characterizing the morphology and surface characteristics of particles suspected to be asbestos. The data obtained from the FESEM has helped the geological and microscopy communities better understand the morphology of the minerals found in the area of Libby, Montana. Advances in SEM technology and digital imaging have made FESEM a common and reliable tool in analytical laboratories and have allowed significant advances in the characterization of mineral particles. This study has shown that FESEM analysis, digital imaging, and database management are essential elements for accurate particle-by-particle examination of mixed mineral dusts. ■

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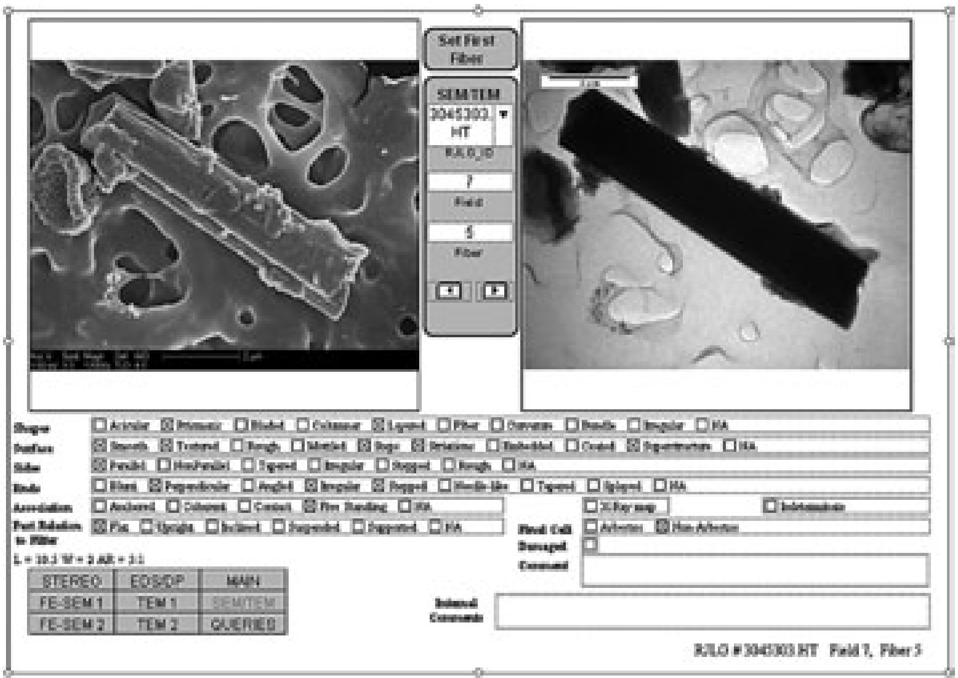

Fig. 5 Screen image of one page of the Filemaker^{TM} Pro 8 database for a single prismatic richterite particle showing the FESEM secondary electron image (left) and TEM image (right) side by side. The screen image shows the overall structure of the database including the classification system.