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LETTER

Quantification of amphibole content in expanded vermiculite products from Libby, Montana U.S.A. using powder X-ray diffraction

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ABSTRACT

Five expanded vermiculite samples known to have originated from the former vermiculite mine near Libby, Montana were analyzed using powder XRD to quantify their amphibole content. An expanded vermiculite with no detectable amphibole based on our XRD methods discussed herein was spiked with 100, 500, 1000, 2500, 5000, 7500, and 10 000 ppm Libby amphiboles to determine the detection limit of XRD and to develop a calibration method. The 110 amphibole peaks were not detectable in the 100 and 500 ppm samples; thus, defining the detection limit. The 110 peak areas for the remaining samples were measured and used to form a calibration curve relating peak area to ppm amphibole. Of the five Libby samples, each had detectable levels of amphibole and their amphibole content ranged from 1171 to 9218 ppm. The XRD method provides a bulk measurement of the total amphibole content. To determine the amount of asbestiform amphiboles, morphological considerations obtained by microscopy techniques are required. From the results of a previous polarized light microscopy study, the five expanded vermiculites in this study would contain from 390 to 3073 ppm asbestiform amphiboles and not be subject to regulation on the basis of the 1% rule used by regulatory agencies in the U.S.A.

Keywords: Amphibole, asbestos, powder X-ray diffraction, vermiculite

INTRODUCTION

In late 1999, Libby, Montana, was brought to the national stage by a series of articles published in the Seattle Post-Intelligencer (Schneider 1999). The controversy surrounded the then closed vermiculite mine near the town. This mine was in operation from 1920 to 1990 and was the largest vermiculite mine in the world. Two separate health studies were conducted in the mid-1980s, one by McDonald et al. (1986a, 1986b, 1988) and a second by Amandus and Wheeler (1987) and Amandus et al. (1987a, 1987b). Both studies showed increased mortality rates due to asbestosis, mesothelioma, and lung cancer in those occupationally exposed to amphibole asbestos at the mine.

The Environmental Protection Agency (EPA) became involved within days after the Schneider newspaper articles made the national media. The concerns voiced by the media extends beyond the welfare of the occupationally exposed and their families in the Libby area and extends to the nation at large. The vermiculite from this mine was sold as house insulation, packing product, and garden additive. The EPA published estimates that up to 940 000 homes in the US could contain expanded vermiculite as insulation (U.S. EPA 1985). Since the EPA became involved in 1999, procedures were created to quantify the amount of asbestos in the vermiculite (U.S. EPA 2004). Other EPA studies expanded the search for amphibole asbestos in other commercial vermiculite products with non-Libby sources (U.S. EPA 2000).

The vermiculite deposit formed in an ultramafic igneous body dating from the Cretaceous. The deposit consists of a series of ring dikes followed by a syenite intrusion. This core of the intrusion is a biotitite surrounded by a biotite pyroxenite. The biotite in the biotite pyroxenite altered to vermiculite and hydrobiotite by low-temperature alteration, while the pyroxenes altered to amphiboles by high-temperature alterations (Boettcher 1966). These mineral phases coexist in the deposit and coexist in expanded vermiculite products (Gunter et al. 2005). After the vermiculite was mined and the ore enriched, it was shipped to expanding plants. These plants would heat the vermiculite at high temperatures, thus expanding it, and the resulting product was sold as the industrial useful expanded vermiculite.

Typically PLM and TEM are used to quantify the asbestos content of materials. This study explores the use of powder X-ray diffraction as a means to quantify the concentration of amphibole in bulk, expanded vermiculite attic insulation using samples originating from the Libby mine. The concentration of amphibole is important in that the regulated weight percent of amphibole asbestos is 1.0% or 10 000 ppm. If quantities of amphibole are undetectable or below the 1 wt% level using approved methodologies, then the material is not subject to regulation. However, if the amphibole content is 1% or greater, than some type of microscopic analyses is required to determine the proportion of the sample that is asbestiform. This study was inspired by previous work done on low-level detection of erionite by Bish and Chipera (1991). They also encountered similar problems of sample homogeneity and peak reproducibility when making their calibration standards as we discuss below.

SAMPLE SELECTION AND EXPERIMENTAL METHODS

Sample selection

Four of the five expanded vermiculite samples used in this study are known to originate from Libby using techniques of Gunter et al. (2005) in demonstrating a chemical method to determine the source of the vermiculite ore, the same sample

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labels are used in this study. The 5th sample was collected at a later date and is called at_5_UI, and is assumed to be from Libby because the owner of the house remembers putting Zonolite in his attic in the 1970s and we found amphiboles similar to those occurring in the other Libby samples. The sample chosen as a base for the calibration is a non-Libby expanded commercial vermiculite product named Black Gold (Gunter et al. 2005). Black Gold was specifically chosen because it contained no detectable amphibole based on our XRD. The amphibole used to spike the Black Gold sample was collected by MEG from the Libby mine in October of 1999 and labeled as the "float" sample in Bandli et al. (2003), Brown and Gunter (2003), and Gunter et al. (2003). As discussed below, we estimate that the bulk composition is >95% amphibole.

Sample preparation

Each of the five Libby samples were prepared for powder XRD by: (1) grinding the vermiculite in a coffee grinder; (2) sieving the sample to –120 mesh; (3) placing 4.0 g of each –120 mesh sample into a McCrone Micronizing mill with 25 mL of acetone and milling for 12 minutes to reduce and homogenize the grain size; (4) cation exchange in 100 mL of 1 *M* KCl for 24 hours (the effect of this step exchanges K in the inner layers of the sheet silicates, in essence collapsing the vermiculite and hydrobiotite inner layers into spacing similar to biotite); and (5) placing the sample into back-packed powder XRD mount.

Four gram standard samples were prepared as above except using the commercial vermiculite Black Gold, and adding the appropriate amounts of Libby amphiboles. By using an expanded vermiculite the matrix of the calibrated and unknown samples is similar. Before addition, the amphibole was washed in 12N HCl to remove calcite to purify the amphibole. The HCl wash dissolved (ca.) 19% by weight of the bulk amphibole. X-ray data of the bulk Libby amphibole also showed minor amounts of hydrobiotite, vermiculite, and biotite. Thus, it actually was not 100% amphibole, so our quantification method will overestimate the amphibole content in the unknown samples.

To homogenize the added amphiboles in the spiked samples, an ultrasonicator probe at 33% intensity for five minutes was used while the sample was still in the KCl solution. To minimize heterogeneous settling due to density differences of the mineral phases, the sample was filtered, placed in acetone, and continually agitated by use of a magnetic stir plate until the solution evaporated.

Powder X-ray diffraction

Powder X-ray diffraction was chosen as the analytical tool to use in this study for two reasons: (1) both the PLM and TEM are routinely used to determine the amount of amphibole asbestos in commercial vermiculite products (see for example U.S. EPA 2000); however, these methods use only small portions of the materials (often counting only a few fibers) and then extrapolate to the entire sample. We believe using XRD to quantify amphibole content is less subjective and can be used on bulk samples when available, which is consistent with the 1% rule; and (2) to our knowledge no one has successfully used XRD to quantify the amphibole content in bulk expanded vermiculite products. Addinson and Daveis (1990) performed XRD work on samples of various amphibole-containing materials, but prior to X-ray diffraction they digested the non-amphibole material (i.e., the matrix, which in our case would be vermiculite) by first boiling the samples for one hour in full strength H_2SO_4, followed by boiling in full strength NaOH. Thus, their method is somewhat difficult to perform and did not deal with the samples in their bulk state.

The X-ray diffractometer used for this project is a Siemens D5000 located at the University of Idaho. Cu$K\alpha$ radiation was used at 40 kV and 30 mA. Two separate scans were made for each sample. The first scan is over the 2θ range 2° to 45° with 9 s/step, and 0.02° steps. This scan is referenced as the long 2θ scan. The second scan, referenced as the short 2θ scan, is over the 2θ range 9.5° to 11.5°, with 180 s/step and again 0.02° steps. This short scan is specifically over the 2θ region that overlaps the 110 amphibole diffraction peak and takes 4 hours to run. To quantify the amount of amphibole present in each sample, the area of the 110 amphibole peak was measured using the D5000 system software.

Results and discussion

The result of the XRD scan without the K exchange is shown for the li_2_UI Libby sample in Figure 1a; this product was obtained from an unopened bag of Zonolite found on the University of Idaho campus (Gunter et al. 2005). There are 3 major phases of sheet silicates in expanded vermiculite products: hydrobiotite, vermiculite, and biotite. The corresponding peaks are labeled hy, ve, and bi respectively in Figure 1a and indexed. The higher intensity scan over the short 2θ range is the 180 second count time. The 003 hydrobiotite peak appears prominent in this scan and is problematic because it occurs in the same 2θ region as the 110 amphibole peak. The added step of K exchange during sample preparation removes this problematic 003 hydrobiotite peak. The lower scans in Figure 1b are the non-exchanged Black Gold samples with no added amphibole. Again notice the multiple sheet silicates in the long scan and the wide peak on the short scan. The upper scans in Figure 1b are the results after K exchange of the same Black Gold sample. The long 2θ scan shows the removal of the 001 and 002 hydrobiotite peaks and the 002 vermiculite peak. More importantly, the short 2θ scan no longer shows any peaks; thus, the 003 hydrobiotite peak is now absent and no detectable 110 amphibole peak occurs. Figure 1c is the scan of at_1_UI after the K exchange, and the shorter range scan shows the 110 amphibole peak, meaning there are detectable amounts of amphibole in this sample.

A series of seven spiked Black Gold samples (100, 500, 1000, 2500, 5000, 7500, and 10 000 ppm) were made as discussed above. Each calibration sample was mounted and analyzed 3 times. For each of the samples, short 2θ scans were used to measure the 110 amphibole peak area. Each time the reproducibility of the peak area was within 10%. No detection of amphibole was possible using this method below 1000 ppm; thus, our detection limit is at least 1000 ppm. Figure 2a shows the averaged peak areas for the bg_0, bg_1000, bg_5000, and bg_10000 ppm short scans, with a long scan of the bg_0 sample. Increasing amphibole content correlates to greater 110 peak areas. Figure 2b shows a plot of all the Libby samples and the bg_10000 sample. By visual inspection of this figure, it appears that all of the Libby samples, with the possible exception of at_5_UI, would contain below the regulatory limit of 1% amphibole, and in turn amphibole asbestos.

The XRD method determines the bulk wt% of amphibole in a sample, which is consistent with the 1% rule. It is important to determine the total amount of asbestiform amphibole, which is regulated, while nonasbestiform amphiboles are not. In 1992, OSHA (OSHA 1992) deregulated the nonasbestiform amphiboles because they found the health risk greater for the asbestiform morphologies. Also, recall that 1% is set as the level of concern for asbestos contamination. So, if our XRD method shows an amount below the 1% total amphibole, than clearly the amount

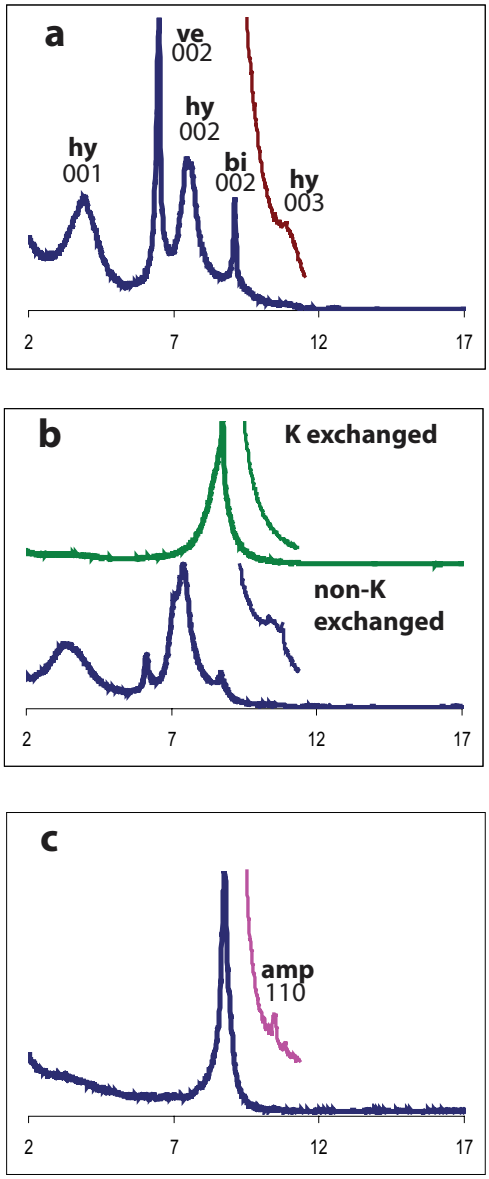

FIGURE 1. Powder XRD scans showing the mineral phases in expanded vermiculites. (**a**) Two scans of differing count times of Zonolite; the 2–17° scan (with count time of 8 s) shows the three mineral phases routinely found in an expanded vermiculite product with each of the peaks labeled and keyed to hydrobiotite (hy), vermiculite (ve), and biotite (bi), and an 8.5–11.5° scan with a 180 s count over the location of the 110 amphibole peak as well as the 003 hydrobiotite peak. (**b**) Two stacked XRD scans of the unspiked Black Gold sample with range and count times as in Figure 1a. Notice the three mineral phases in the lower scans and that K-exchanging the sample "collapses" them into the single biotite peak, thus removing the interference of the 003 hydrobiotite peak with the 110 amphibole peak. (**c**) This scan is a K-exchanged sample from Libby clearly showing presence of the 110 amphibole peak.

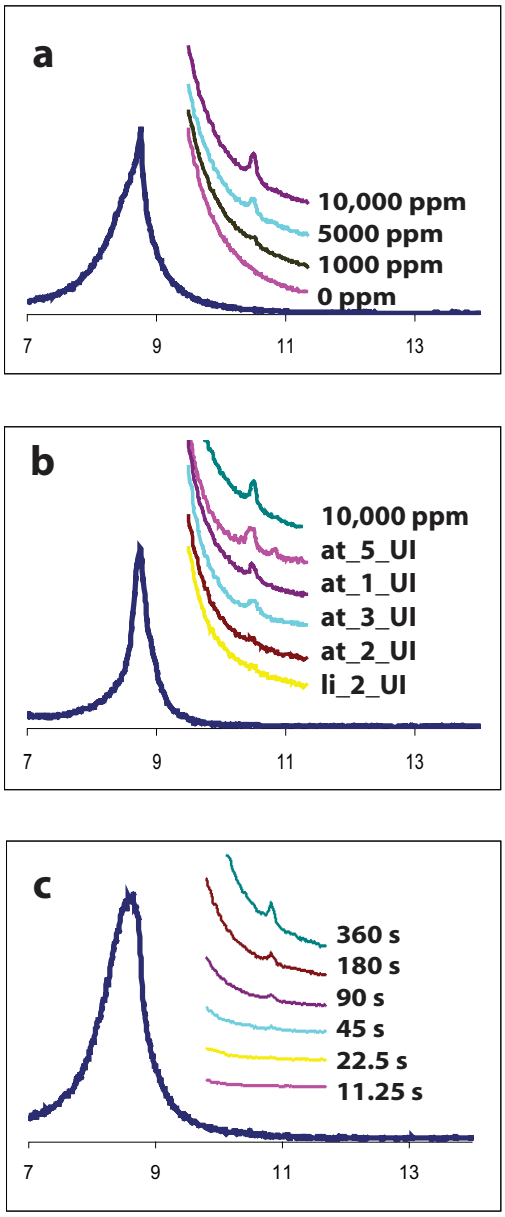

FIGURE 2. XRD scans for some of the K-exchanged amphibole-spiked Black Gold samples and the K-exchanged Libby sample, for each the longer 2θ scan is a count time of 8 s and the shorter 180 s. (**a**) A subset of the spiked samples showing the 1000 ppm sample's 110 peak that is our detection limit, and the relationship between the 110 peak area and added amphibole. (**b**) The top most scan is the bg_10000 ppm spiked sample with the unknown attic samples plotted in decreasing order of % amphibole. (**c**) A series of scans with differing count times for the bg_10000 ppm spiked sample, showing that at the 1% level, amphibole is detected by XRD at count times much less than the 180 s we used for our calibration method.

of asbestiform amphibole would also be below 1%. If, however, the amount of amphibole exceeded 1%, than the morphology of the amphibole could be determined by microscopy methods to find the proportion of asbestiform amphiboles. For example, Brown and Gunter (2003) showed the Libby amphiboles are approximately 1/3 asbestiform. So if the XRD method found 1% concentration of Libby amphiboles in a sample, than it would contain only 0.33% of asbestiform amphiboles.

Figure 2c shows six different count times used over the short 2θ range for the bg_10000 sample. Transitioning from the scan time used in this study of 180 seconds and decreasing by halving the count times, as expected, there is a gradual decrease in the size of the 110 amphibole peak and therefore a decrease in detection limit for samples containing less than 1% amphibole. However, the scans show that at ¼ the times used herein (i.e., 45 seconds) a sample with 1% amphibole can still be detected with this method. Thus this method should find use by commercial testing laboratories working toward the 1% regulatory limits. We also experimented with higher count times of up to 720 seconds with the 100 and 500 ppm samples to see if we could lower our detection limit. Unfortunately, these longer count times did not detect the 110 peaks for the 100 and 500 ppm samples.

To quantify the concentration of amphiboles in the Libby samples, the net peak areas of the five detectable spiked samples, bg_1000, bg_2500, bg_5000, bg_7500, and bg_10000 ppm scans were measured. Figure 3 is a plot of these data and show a clear linear trend. These data were fit to a linear regression and also shown in Figure 3. The regression was calculated assuming 0 ppm amphibole would yield a 0 net peak area. The resulting linear equation is: amphibole ppm = 14632(702) × 110 peak area. Using this equation, we calculated the concentration of the five Libby samples and the results are given in Table 1 and plotted in Figure 3. All five of the Libby samples contained calculated concentrations less than 10 000 ppm or 1.0% amphibole, and as stated above, based on the work of Brown and Gunter (2003) this would yield asbestiform amphibole contents 1/3 that of the total amphibole content or 390 to 3073 ppm.

The application of this method is intended to be used on expanded vermiculite insulation. Matrix differences in soils or in other waste products from the expansion process will probably require new calibrated samples of similar matrix.

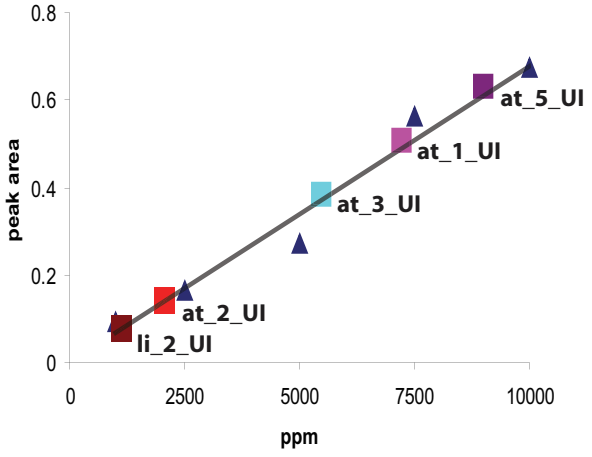

FIGURE 3. Plotted net peak area vs. concentration of the spiked and unknown expanded vermiculite samples. The triangles are the spiked calibration samples used to create the regression equation: amphibole ppm = 14632(702) × 110 peak area. The squares are the Libby samples fit to the regression line based upon their measured 110 amphibole net peak areas. All the Libby samples contain less than 10 000 ppm (or 1%) amphibole.

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TABLE 1. Sample names, measured net peak areas, and calculated concentrations, based on the calibration equation: amphibole ppm = 14632(702) × 110 peak area derived the amphibole-spiked Black Gold samples

Sample name	110 peak area	Calculated ppm
bg_1000	0.09	1317
bg_2500	0.17	2487
bg_5000	0.27	3951
bg_7500	0.56	8194
bg_10000	0.67	9803
li_2_UI	0.08	1171
at_1_UI	0.51	7462
at_2_UI	0.14	2048
at_3_UI	0.38	5560
at_5_UI	0.63	9218

Notes: bg = Black Gold with the following number the ppm of added amphibole, the nomenclature for the expanded vermiculite products are the same as used in Gunter et al. (2005).

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