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Amphibole content of commercial vermiculites by powder X-ray diffraction

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Abstract. — Seven commercial expanded vermiculite products were obtained and a powder X-ray diffraction method used to determine if they contained amphibole, and if so, what quantity. Of the seven, two contained approximately 0.2 and 0.5% amphiboles, while two others had no detectable amphiboles; the lower detection limit is 0.05 to 0.10% for this method. The remaining three samples showed levels of amphiboles that are within our lower detection range. USEPA had conducted a similar test by TEM and our results are in agreement with theirs. The methods discussed herein should be used for unbiased detection of amphiboles in bulk samples, and supplemented, when significant amounts of amphiboles are found, by microscopic methods to determine the morphology of the amphibole particles.

Riassunto. — Sono stati preparati sette prodotti di vermiculite espansa commerciale al fine di verificare, tramite indagini diffrattometriche a raggi-X, l'eventuale contenuto di anfiboli e, in caso positivo, di valutare la loro quantità. Dei sette campioni investigati, due contenevano approssimativamente 0,2 e 0,5 % di anfiboli, mentre altri due non hanno dato valori rilevabili; per questo metodo, il limite di detenzione più basso è 0,05 e 0,10 %. I restanti tre campioni mostrarono contenuti di anfiboli che rientrano nel nostro più basso intervallo di rivelabilità. L'Agenzia per la Protezione dell'Ambiente degli Stati Uniti (USEPA) ha condotto un'indagine simile utilizzando il TEM e i risultati ottenuti sono in accordo con quelli qui presentati. I metodi qui discussi dovrebbero essere usati per la corretta rilevazione di anfiboli nei campioni tal quale. Ove le quantità di anfiboli fossero significative, le indagini dovrebbero essere integrate con metodi microscopici al fine di determinare la morfologia delle particelle.

Key words: *Vermiculite, amphibole, amphibole asbestos, powder X-ray diffraction.*

Introduction

In the fall of 1999 the former vermiculite mine near Libby, Montana USA gained media attention because of the increased rate of respiratory diseases in former miners believed to be related to the amphiboles that were associated with the vermiculite ore (see Gunter *et al.*, 2007a and Bandli and Gunter, 2006 and references therein). Concern widened to the possible health issues of the residents of Libby as well as the homes nation-

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wide in which the commercial product produced at Libby, named Zonolite, had been used as an insulation in the house attics and walls. However, as pointed out in the health based studies reviewed in Bandli and Gunter (2006) knowledge of elevated disease rates in the Libby miners were documented in the mid-1980s and the USEPA (1985) was also concerned about the number of houses in the USA that may contain vermiculite, with the major concern being that the vermiculite might contain amphibole asbestos. Based on USEPA (1985) and the discussion in Gunter *et al.* (2005), there appears to be approximately 1 million houses in the USA that may contain vermiculite; far below the 35 million number routinely used in the popular media.

The concerns generated based on the Zonolite product spread to the entire vermiculite industry and prompted the USEPA (2000) to conduct a screening of commercially available vermiculite. At the same time we acquired a set of commercially available vermiculite samples, and begun our own testing. The first set of results appeared in Gunter *et al.* (2005) where we showed how to use the composition of the vermiculite to determined its source (i.e., what mine produced the ore). Next we developed a powder X-ray diffraction (XRD) method to determine the amphibole content of vermiculite products with a known Libby source (Sanchez and Gunter, 2006). The work discussed herein is a continuation of our research whereby we determine the amphibole content of non-Libby source vermiculite with our XRD method, and compare our results to those of the USEPA (2000).

Methods

Sample selection: Seven commercial, expanded vermiculite samples were used in this project (Table 1 and Figs. 1 and 2); these same samples were used in Gunter *et al.* (2005) as discussed above. Six of the samples were purchased in the Moscow, Idaho USA area in 2000; the remaining sample came as packing material from a chemical supplier. The Black Gold sample was specifically chosen as the sample to be used for the calibration method (discussed below) because it contained no detectable amphibole based on an earlier study (Sanchez and Gunter, 2006). MEG collected the amphibole used to spike the Black Gold sample from the Libby mine in October of 1999; that sample is labeled as the "float" sample in Bandli *et al.* (2003), Brown and Gunter (2003), and Gunter *et al.* (2003).

Sample preparation: The method developed in Sanchez and Gunter (2006) was used to prepare each expanded vermiculite sample for powder XRD, briefly: 1) use a coffee grinder to reduce

Table 1

Concentrations of amphibole in commercial vermiculite samples; the upper portion of the Table are samples studied by USEPA (2000) and our group, while the lower portion of the Table are results from Sanchez and Gunter (2006). Results are given in three columns with the first two taken from USEPA (2000), and the last column representing our XRD results

Sample	PLM EPA	TEM EPA (%)	XRD (%)
Black Gold	ND	ND	0.00
Coles	ND	0.45	0.46
Lepricon	-	-	0.10
Packing material	-	-	0.04
Schultz	ND	ND	0.00
Thermorock	trace	ND / 0.33 / 0.30	0.18
Whitney	trace	ND / ND /ND	0.07
Zonolite #1	trace	0.56 / 1.88 / 0.10	-
Zonolite #2	ND	ND	-
Samples from Sanchez & Gunter (2005)			-
Zonolite bag	-	-	0.11
Attic #1	-	-	0.75
Attic #2	-	-	0.21
Attic #3	-	-	0.56
Attic #5	-	-	0.92

- = not measured
ND = non-detect

Fig. 1 – A photograph showing vermiculite (left) and expanded vermiculite (right). In the middle of the photograph a flake of vermiculite is shown, expanded on its right side, by applying heat from the lighter.

particle size; 2) sieve the sample to -120 mesh; 3) place 4 grams of each -120 mesh sample into a McCrone Micronizing mill with 25 ml of acetone and mill it for 12 minutes to further reduce and homogenize the grain size; 4) cation exchange each sample in 100 ml of 1 Molar KCl for 24 hours; and 5) place the sample into back-packed powder XRD mount.

As discussed in detail in Sanchez and Gunter (2006) the two most difficult aspects of sample preparation were: 1) the need to first K-exchange the samples and 2) to produce homogenized amphibole-spiked standards to obtain a calibration curve. The former was required because the commercial vermiculite products are typically a mixture of several sheet silicates, predominantly vermiculite, hydrobiotite, and biotite. One of hydrobiotite peaks occurs in the same region of the XRD pattern as the 110 amphibole peak. The K-exchange process "collapses" the vermiculite and hydrobiotite structure to that of biotite, thus removing this interference. It proved very difficult to obtain reproducible XRD scans (i.e., to obtain the same area of the 110 amphibole peak as a function of amphibole content) on our amphibole-spiked standards. Several preparation methods

Fig. 2 – Photographs of the commercial vermiculite products used in this study (except for Thermorock). (left) These samples were purchased in local stores in the Moscow, Idaho USA area, and (right) a bag of unopened Zonolite obtained from the attic of building on the University of Idaho campus in Moscow, Idaho USA.

were tested, and finally a unique mixing method was developed as discussed in Sanchez and Gunter (2006).

Powder X-ray diffraction: A Siemens D5000 powder X-ray diffractometer, operating at 40kV and 30 mA using CuKα radiation, was used to collect the diffraction data on the K-exchanged vermiculite samples. Two separate scans were made for each sample. The first scan is over the 2θ range 2˚ to 45˚ with 9 second count time per step, and 0.02˚ step size. The main use of this scan was to determine if K-exchange was complete. The second scan was over the 2θ range 9.5˚ to 11.5˚, with 180 seconds per step, and 0.02˚ step size. This scan is the 2θ region that overlaps the 110 amphibole peak. The longer counting times were used to increase the detection limit for amphibole.

Results and Discussion

Fig. 3 shows XRD patterns of the Black Gold sample for the 9 and 180 second count times, and a 180 second count time scan for the same sample with 1% amphibole added. Notice the presence of the 110 amphibole peak in the latter and its absence in the former. Based solely on these scans, it is clear amphibole can easily be detected in expanded vermiculite at the 1%

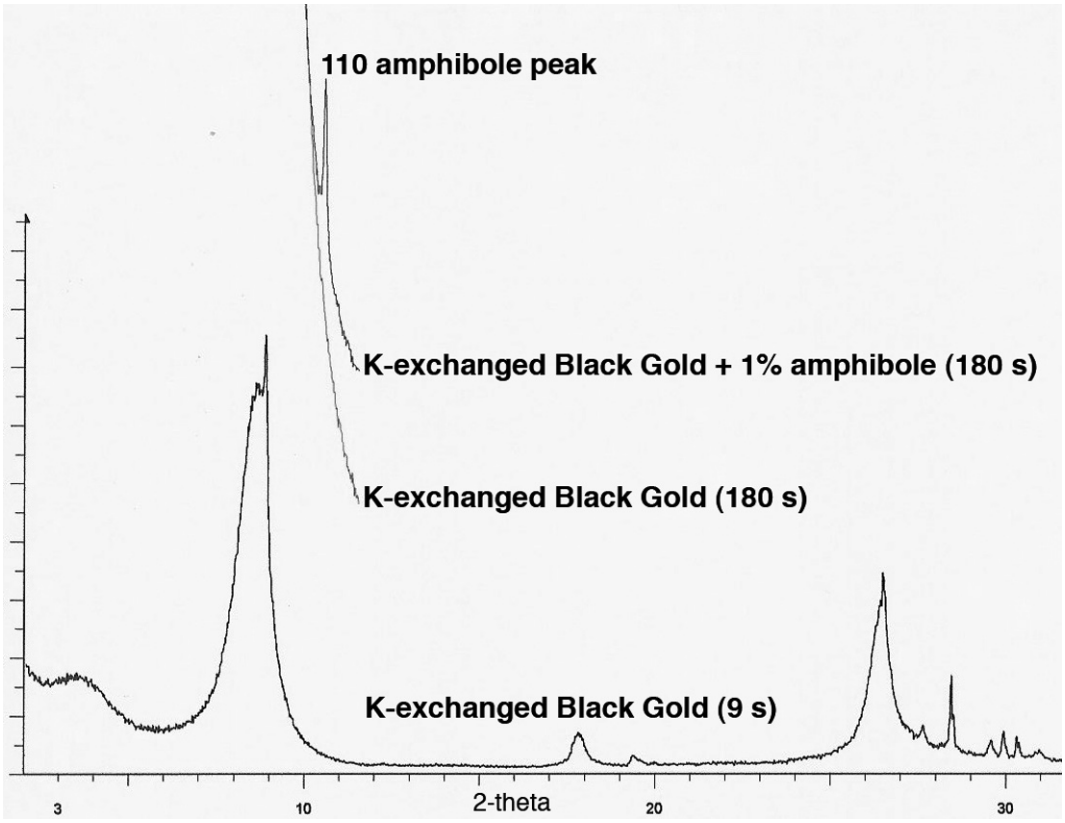

Fig. 3 – Powder X-ray diffraction scans of K-exchanged Black Gold. The long lower scan was collected at a count time of 9 seconds per step, while the two upper scans were collected at a count time of 180 seconds per step to better show location of the 110 peak for amphibole, if present. The lower of these two scans is on the same Black Gold sample, while the upper scan was Black Gold with 1% amphibole added.

level, while the lower detection was shown to be in the range of 0.05 to 0.10% (Sanchez and Gunter, 2006) Fig. 4 shows XRD scans for the six remaining expanded vermiculite products, along with the 1% amphibole-spiked Black Gold sample for comparison. This figure shows all of the commercial vermiculites contain significantly less than 1% amphibole. Further examination of the scans show a clearly observable 110 amphibole peak for Coles, Lepricon, and Thermorock, a possible peak for the Whitney sample, questionable peaks for the packing material, and no peak for the Schultz sample. Thus, by observation of the scans it appears the Black Gold and Schultz samples are amphibole-free.

To quantify the results, the 110 amphibole peak area can be measured for each sample and the calibration method developed in Sanchez and Gunter (2006) used. Table 1 lists these results and shows that the Coles and Thermorock samples contain 0.46 and 0.18% amphibole, respectively. Three samples (Lepricon, the packing material, and Whitney) contain amphibole amounts in the lower detection limit of this method, so their quantification is less certain. And, as previously noted, the Black Gold and Schultz samples appear amphibole-free.

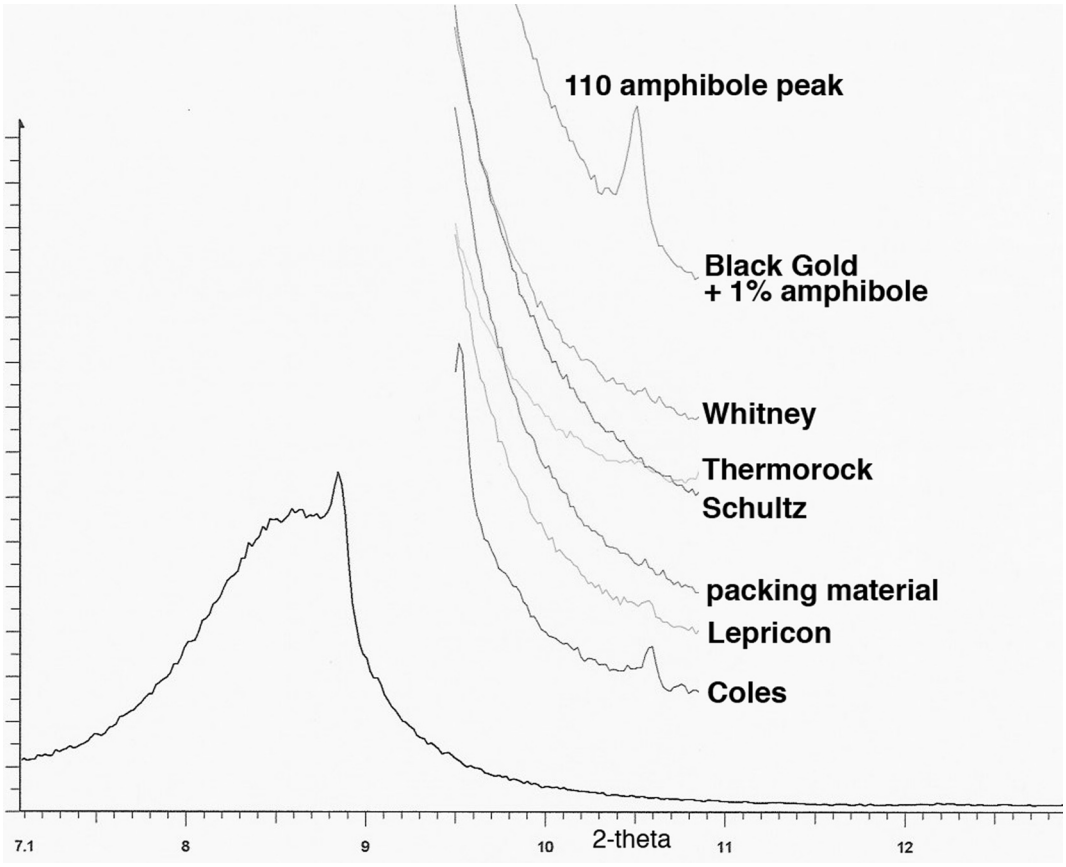

Fig. 4 – Powder X-ray diffraction scans of the remaining samples (Table 1) used in this study with the 1% amphibole Black Gold sample for comparison. Notice that addition of 1% amphibole results in a strong peak, while some of the samples exhibit a 110 amphibole diffraction peak (e.g., Coles), others are somewhat difficult to distinguish (e.g., the packing material), and others show no peak (e.g., Schultz).

The USEPA (2000) conducted a study on commercial vermiculite to determine if the products contained amphibole asbestos. Like us, they purchased their samples in local retail stores; they also had samples of vermiculite with a known source of Libby, Montana. For the non-Libby samples, our two studies shared five of the commercial products. In the USEPA study they used PLM and TEM methods to determine the amphibole asbestos content. Their results are shown in Table 1 and can be directly compared to our work for the five in-common samples. Notice the USEPA found the Coles sample to contain the largest amount of amphibole asbestos, 0.45%, which is similar to our findings. Also, note they found that Thermorock to contain the next highest level at around 0.3%, again a similar result to our findings. Like us, they found inconclusive results for the Whitney sample (i.e., trace in PLM and ND in TEM). And finally they did not detect any amphibole asbestos in their Schultz and Black Gold samples. The USEPA (2000) also tested the Coles and Thermorock products and found they did not release asbestos while simulating working conditions where the products might be used.

The last two entries in the upper portion of Table 1 are Zonolite. USEPA found variable amounts of amphibole asbestos in one sample (Zonolite #1) ranging from 0.10 % to 1.88%, and no amphibole asbestos in the other sample (Zonolite #2). At the bottom of Table 1 we list the five Zonolite samples we analyzed in Sanchez and Gunter (2006). Note, in those we found amphibole content from 0.11 to 0.92%.

Notice in our XRD method we have referred to the amount of amphiboles with no mention of asbestos content, while the USEPA referred to amphibole asbestos. There is an ongoing debate over how to distinguish the morphology of amphiboles (see for example Gunter *et al.*, 2007a and Brown and Gunter, 2003 and references therein). One of the advantages of the XRD method discussed here, and also in Gunter *et al.* (2007b) and Sanchez and Gunter (2006), is that it is an unbiased and efficient method to screen bulk samples for amphiboles. If amphiboles are found in significant amounts to cause concern, then microscopic methods should be used to ascertain the morphology of the amphibole particles. For instance, Brown and Gunter (2003) showed that about 1/3 of the amphiboles from the former vermiculite mine near Libby, Montana would be mineralogically considered "asbestos;" a more recent study (Bellamy and Gunter, 2008), yielded similar results. Thus it MUST be stated that detection of amphiboles in any sample by XRD must be followed with microscopic methods to determine if the amphiboles are truly asbestos. The main reason for this is there appears to be different risks of amphibole exposure based on its morphology (Gunter *et al.* 2007a and references therein), regardless regulatory agencies do not regulate the nonasbestiform amphiboles (OSHA, 1992). Thus we would encourage integrated use of XRD and microscopic methods in the characterization of bulk materials.

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