

CHARACTERIZATION OF CHRYSOTILE SAMPLES FOR THE PRESENCE OF AMPHIBOLES: THE CAREY CANADIAN DEPOSIT, SOUTHEASTERN QUEBEC, CANADA

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ABSTRACT

Samples were collected from the former chrysotile-producing mine operated by Carey Canadian Mines, located approximately 30 km northeast of Thetford Mines, Quebec, in the Eastern Townships mining district, and analyzed to determine if they contained amphiboles. A total of ten samples, six of ore, two in-place rock samples, and two tailings samples, were first analyzed by routine PLM (polarized light microscopy) dispersion staining and powder X-ray diffraction (XRD) methods. One sample was found to contain trace amounts of an amphibole. Quantitative XRD methods were developed and showed this one sample contains between 500 to 1000 ppm amphibole; the detection limit of this new XRD method was between 100 to 500 ppm for tremolite mixed into a chrysotile ore. A chemical method was also developed to relate the calcium content of the samples and their possible maximum content of tremolite, assuming that all the Ca in the sample is in tremolite. This method showed that the single amphibole-containing sample could contain no more than 0.213% or 2130 ppm tremolite by weight. The same chemical predictor was applied to the other nine samples and showed ranges of maximum tremolite from 50 to 120 ppm; however, this method clearly overestimates the tremolite content. Scanning electron microscopy (SEM) and PLM analyses of amphiboles in the one amphibole-containing sample revealed nonasbestiform amphiboles with approximately 50% anthophyllite and the remainder actinolite, plotting close to the tremolite–actinolite boundary as determined by SEM–EDS (energy-dispersive spectroscopy).

Keywords: chrysotile, amphibole, amphibole asbestos, powder X-ray diffraction, Carey Canadian deposit, Quebec.

SOMMAIRE

Nous avons prélevé des échantillons à la mine de chrysotile autrefois la propriété de Carey Canadian Mines, située environ 30 km au nord-est de Thetford Mines, Québec, dans le district minier des Cantons de l'Est, et nous les avons analysés pour déterminer s'ils contiennent une amphibole quelconque. Un total de dix échantillons, parmi lesquels six représentent le minerai, deux sont des échantillons de roche pris sur place, et deux sont pris des rejets, ont d'abord été étudiés par microscopie optique en lumière polarisante avec témoins de la dispersion, et avec la diffraction X (méthodes des poudres). La présence d'une amphibole à l'état de traces est documentée dans un des échantillons. Des méthodes quantitatives utilisant la diffraction X ont été développées; elles montrent que cet échantillon contient entre 500 et 1000 ppm d'amphibole; le seuil de détection de cette méthode est établi entre 100 et 500 ppm pour la trémolite mélangée au minerai de chrysotile. Une méthode chimique a aussi été développée pour relier la teneur en Ca des échantillons à leur contenu maximal de trémolite, en supposant que le Ca de l'échantillon réside uniquement dans la trémolite. Avec cette méthode, nous montrons que l'unique échantillon porteur d'amphibole pourrait contenir un maximum de 0.213% ou 2130 ppm de trémolite (base pondérale). Le même indicateur chimique, appliqué aux neuf autres échantillons, montre des teneurs possibles de trémolite entre 50 et 120 ppm; toutefois, cette méthode surestime la teneur en trémolite. La microscopie électronique à balayage (avec dispersion d'énergie) et la microscopie optique appliquées à l'échantillon porteur d'une amphibole ont révélé la présence de particules non-asbestiformes contenant environ 50% d'anthophyllite, et le reste, de l'actinolite voisine de la limite entre trémolite et actinolite.

(Traduit par la Rédaction)

Most-clés: chrysotile, amphibole, amphibole asbestiforme, diffraction X (méthode des poudres), gisement Carey Canadian, Québec.

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INTRODUCTION

The former Carey Canadian chrysotile mine is located at the northeastern end of the chrysotile mining district in the Thetford Mines region of Quebec (Fig. 1). This mining district is well known for the production of chrysotile over the past century, and some of the mines are still in operation today. Geologically, the mine is located in a northeast-trending series of Paleozoic ultramafic rocks that somewhat coincide with the Appalachian Mountains in both the United States and Canada (Lamarche & Riordon 1984, Riordon 1957, 1975). In general, these ultramafic rocks have been altered to serpentine-group minerals, and locally to chrysotile. Interestingly, the Carey mine is located in a different geological setting from the major deposit and produced chrysotile ore from the Pennington dyke (Fig. 1), which lacks granitic intrusions that occur in many of the other areas (Merrill 1957). For amphiboles to occur in these altered ultramafic deposits, these later felsic intrusions are a prerequisite in that they provide the extra silica required for the local formation of amphiboles (Williams-Jones *et al.* 2001). In fact, Williams-Jones *et al.* correlated the occurrence of the silica-rich intrusive bodies with amphiboles in the Jeffery mine located in Asbestos, Quebec and found that whereas the chrysotile ore is amphibole-free, an amphibole impurity can occur near the contact with the silica-rich intrusive bodies. Thus, if these veins are avoided during the mining

process, the chrysotile ores should be amphibole-free. The main goal of this project was to characterize samples from the Carey Canadian chrysotile mine and to ascertain if amphiboles are present.

BACKGROUND INFORMATION

McDonald & McDonald (1997) pointed out that workers at the mines located in the central portion of the Thetford Mines region have higher rates of mesothelioma, and their lungs commonly contain small amounts of amphiboles, whereas at the peripheral mines (of which the Carey mine would be an example), there is little risk of mesothelioma among the workers, and one-quarter lower levels of amphiboles. Although they cited references for the rates of incidence of mesothelioma, they did not cite references for the levels of amphibole. To our knowledge, no thorough, published, mineralogical characterization of the Carey mine has been performed. F. Pooley (pers. commun., November, 2005) characterized some samples collected from the mine and found no amphibole.

In our project, a suite of samples (Table 1) was collected from the mine in July 2004, and a series of analytical methods were developed to search for and characterize amphibole-group minerals in the samples. Two analytical methods were chosen for the initial screening of samples: polarized light microscopy (PLM) assisted by dispersion-staining techniques, and powder

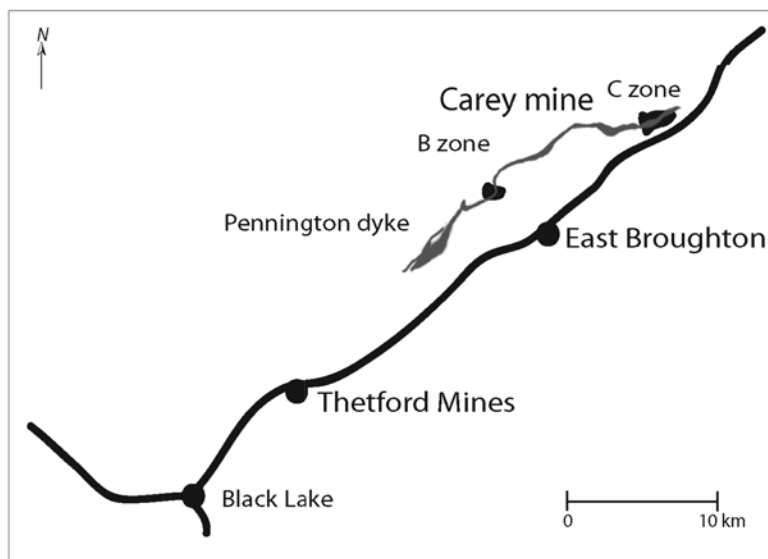


FIG. 1. A sketch map showing the location of the chrysotile mining district in southeastern Quebec, the Thetford Mines region, and the abandoned Carey Canadian deposit, including the location of the two major pits (B and C zones) of the Carey Canadian mine, as well as the location of the Pennington dyke.

X-ray diffraction (XRD). All of the samples were screened with these two methods, and then ten samples were selected for more thorough characterization. Of these ten, a trace amount of an amphibole was found in one. The presence of the amphibole in one sample posed three questions: 1) how much amphibole is present? 2) Which amphibole species is it (*e.g.*, tremolite, actinolite, anthophyllite, *etc.*)? and 3) What are its morphological properties (*i.e.*, is it asbestiform)? To answer these questions, scanning electron microscopy with electron-dispersive spectrometry (SEM-EDS), XRD, and chemical analysis (for total Ca content) of the amphibole-containing sample and a series of tremolite-spiked samples were undertaken. Also, during this latter set of analyses, two separate methods of digestion were used to isolate the amphibole for SEM and PLM observations and to increase the sensitivity of amphibole detection by XRD, and a quantification method for species determination was developed for use with the SEM-EDS.

The questions posed in the above paragraph are important because greater amounts of amphibole lead to a greater risk to human health if these particles of amphibole are asbestiform. Asbestiform and nonasbestiform amphiboles have different health effects (*e.g.*, Davis *et al.* 1991, McDonald & McDonald 1997, Nolan *et al.* 1991). Based upon these and other studies, OSHA (1992) only regulated the asbestiform habits of the amphibole-group minerals tremolite, actinolite, and anthophyllite; however, OSHA (1992) did not give guidance on how to differentiate these two morphologies. Thus, several researchers have spent time developing means to distinguish between these differing morphologies (*e.g.*, Brown & Gunter 2003, Langer *et al.* 1991, Wylie 1979, 1988). The major distinction lies in their approach of observable characteristics, with either the PLM, the SEM, or the TEM.

SAMPLE COLLECTION

To accomplish the major goal of this project, it was necessary to obtain a representative suite of samples from the mine. Since to our knowledge no such suite existed, it was necessary to visit the mine site, which was done on July 27 and 28, 2004. As shown in Figure 1, ore from the mine was taken from more than one location in the Pennington dyke. We visited more than one former pit, but concentrated our collection efforts in zone C because it is the larger of the mined areas, and the geological context in the other locations appeared similar. Figures 2A and 2B are views of the mined-out pit, which is now partially water-filled. The orebody, contained in the Pennington dyke (Fig. 1), dips approximately 30° to the south. The north side of the pit is referred to as the footwall, and the orebody was mined down to the footwall contact with the country rock, as seen on the north side of the pit (*i.e.*, the rock unit that enters the water on left side of Fig. 2A and the right

side of Fig. 2B). Two types of chrysotile fibers formed at the mine site: slip fiber (Fig. 2C) and cross fiber (Fig. 2D). However, the predominant ore came from the slip fiber (Merrill 1957, Riordon 1975). Also, several other minerals at the mine occur in a fibrous habit [*e.g.*, brucite (Fig. 2B) and magnesite (Fig. 3D)].

The sampling plan was to obtain in-place, float, tailings, and, hopefully, some of the final ore produced from the mine. Such a collection of samples would represent the source of the chrysotile ore as well as any waste products, all of which might contain amphiboles. In Table 1, we list the ten locations around the mine site where samples were collected, and provide a description of each. All of the samples were collected in the C zone, with the exception of sample #5, which was located in another former pit mined to the southeast of the B zone and called the Montreal mine. Also, photographs of some of the samples are shown in Figures 2 and 3 and are also keyed to Table 1. Note that location #10 is the site of six separate samples. All are samples of processed ore, and all are prefixed with “#10” with differing letters to distinguish them. Not all the samples were analyzed in this study, as explained in the text.

TABLE 1. SAMPLE NUMBERS AND DESCRIPTIONS ALONG WITH UTM READINGS AND ELEVATION FROM A HAND-HELD GPS

Sample	Description	UTM
#1	predominantly fibrous brucite from boulders (Fig. 2B)	19 t 0343 262 E, 5124 241 N, 288 m
#2	predominantly fibrous brucite from boulders (Fig. 2B)	Same as #1
#3*	waste conveyor belt by former processing plant (Fig. 3A)	Not determined
#4	waste from the tailings pile near former processing plant	19 t 0343 516 E, 5124 026 N, 374 m
#5	float from Montreal mine, a slip-fiber “log” (same as #9 below)	19 t 0336 340 E, 5119 044 N, 421 m
#6*	tailings sample from (Fig. 3B) on south side of pit C	Not determined
#7*	in-place fish-scale morphology (Fig. 3C) from footwall on north side of pit C	19 t 0342 292 E, 5124 266 N, 362 m
#8	in-place chrysotile slip fiber (Fig. 2C) from footwall on north side of pit C	19 t 0342 292 E, 5124 289 N, 407 m
#9*	in-place, slip-fiber magnesite “log” (Fig. 3D), collected from western end of pit C	19 t 0342 212 E, 5124 194 N, 391 m
#10*	six samples of processed ore collected on-site (Fig. 3E): 10A, 10B, and 10C are splits from 500-gram sample bags; 10b1, 10b2, and 10b3 are the entire 500-gram bag (Fig. 3F)	Not determined

Samples with an asterisk were characterized by PLM, SEM, XRD and AA.



FIG. 2. A series of photographs (taken on July 28, 2004) giving an overview of the Carey Canadian mine. A) A view across the zone-C pit looking east; the mill can be seen in the background with a large tailings pile to its right. Note the footwall of the Pennington dyke dipping into the water filling the pit on the upper left side of the photograph. B) A view across the zone C pit looking west. The footwall of the dyke dips into the water, on the right side of the image. The rock pick in the foreground marks the location for the fibrous brucite samples #1 and #2 (Table 1). C) Slip-fiber exposed on the mined surface of the footwall of zone C. This is sample #8 (Table 1). D) Cross-fiber exposed on the surface of the footwall of zone C.

ANALYTICAL METHODS

All fifteen samples from the ten locations (Table 1) were first screened simultaneously by XRD and PLM to identify the different mineral phases in each and to determine if amphiboles are present in significant amounts (*i.e.*, 1–5% range). Then, ten samples (Table 1) were selected for more thorough examination. Next, it was necessary to determine the detection levels for amphibole in both the XRD and PLM experiments. Because amphibole was found in one of the ten samples, several more analytical methods were used to address the following three questions: 1) how much amphibole is present in the sample? 2) What is the species of the amphibole? 3) Is it asbestiform (*i.e.*, is the particle composed of longitudinally separable fibers)? To address #1, a series of tremolite-spiked samples was made and characterized by XRD. Concurrently, an acid-digestion method was utilized to remove other minerals phases, thus increasing the sensitivity of the XRD method for amphibole detection. Also, a chemical

test was developed whereby the total Ca content of the sample was used as a proxy for the amphibole content (there are several assumptions in this method; these are discussed later in the paper); results from this method can be compared to those of the XRD method. A more extreme method of digestion was employed with the one sample containing amphibole as a means to isolate the amphibole from the bulk sample. This amphibole-enriched sample was then subjected to SEM–EDS analysis to address #2 (to determine the species) and simultaneously to address #3 (to determine if the amphibole particles are asbestiform), supported by morphological observations made with the PLM.

RESULTS

XRD (powder X-ray diffraction)

Recent advances in powder XRD methods have led to the detection of low-level amounts of amphiboles (Sanchez & Gunter 2005, 2006) in vermiculite-based

attic insulation. Their work was inspired by that of Bish & Chipera (1991), who showed the value of XRD in low-level determination of erionite, a zeolite related to elevated rates of mesothelioma in Turkey. The XRD methods were applied to the samples herein as follows: for each of the ten samples, approximately four grams

were prepared for XRD by grinding in acetone using a mortar and pestle. (All of the samples except #7 and #9 were already in powder or fiber form.) As the acetone evaporated, the sample was molded into a paste and, when dry, placed into a back-mount holder for the XRD. Three separate 4-hour scans were performed on



FIG. 3. Photographs of some of the locations of the collected samples. A) Sample #3 was collected from this conveyor belt next to the rock pick. The belt was located next to the old mill and is assumed to be carrying this material to the tailings piles. B) Sample #6 was collected from the top of this tailings pile (in front of the rock pick), which is located on the south side of pit C. C) Sample #7, an in-place sample showing “fish-scale” morphology, was taken from the footwall on the north side of pit C. D) This photo shows sample #9, which was dug out of the western end of the Pennington dyke from pit C. Also shown is an in-place sample (to the right of the rock pick). E) All six samples labeled #10 came from this storage area in the basement of the laboratory building. F) This photo shows a close-up of one of the plastic bags containing processed chrysotile, stored in paper bags seen in Figure 3E. This is sample #10b3, collected at the mine on December 20, 1979.

each sample with a Siemens D5000 θ - θ diffractometer using $\text{CuK}\alpha$ radiation operating at 40 kV and 30 mA and equipped with a solid-state detector over different 2θ ranges and count times with a step size of 0.02° 2θ : 1) 5 – 40° 2θ with count times of 9 seconds per step (Fig. 4A), 2) 9.5 – 11.5° 2θ with count times of 180 seconds per step (Fig. 4B), and 3) 27.5 – 29.5° 2θ with count times of 180 seconds per step (Fig. 4C). The 5 – 40° 2θ scan was mainly used to identify all the mineral phases present, whereas the 9.5 – 11.5° 2θ and 27.5 – 29.5° 2θ scans were used to test for amphibole because these are regions that contain the most sensitive diffraction peaks of the amphiboles [*i.e.*, the (110) and (310), respectively].

In Figure 4A, XRD patterns for all ten samples are shown stacked on top of each other. The intensity of each scan was standardized to 100%, and the 2θ positions were standardized to that of the brucite peak at 18.47° 2θ to aid in comparing the patterns. As can be seen, all of the samples except #9 contain chrysotile (or serpentine), ideally $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. Also, all of the samples except #7 and #9 contain brucite, $\text{Mg}(\text{OH})_2$, and hydroxalcite, $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$. Sample #7 exhibits a massive fish-scale morphology (Fig. 3C) and contains only serpentine, whereas sample #9 (Fig. 3D) is the slip-fiber “log,” composed predominantly of magnesite, MgCO_3 , with some calcite, CaCO_3 . (The term log was used in the preceding sentence to describe the shape of the sample.) Minor talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, appears in #3, #6, and #10b2. Magnetite, Fe_3O_4 , occurs sufficiently in #6, #10A, and #10b3 to produce diffraction peaks; magnetite can be seen visually in most of the light-colored samples because of color contrast.

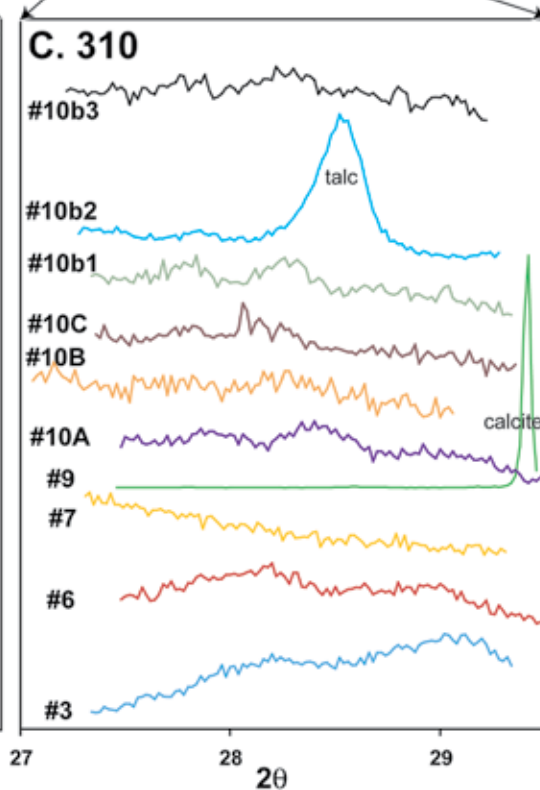
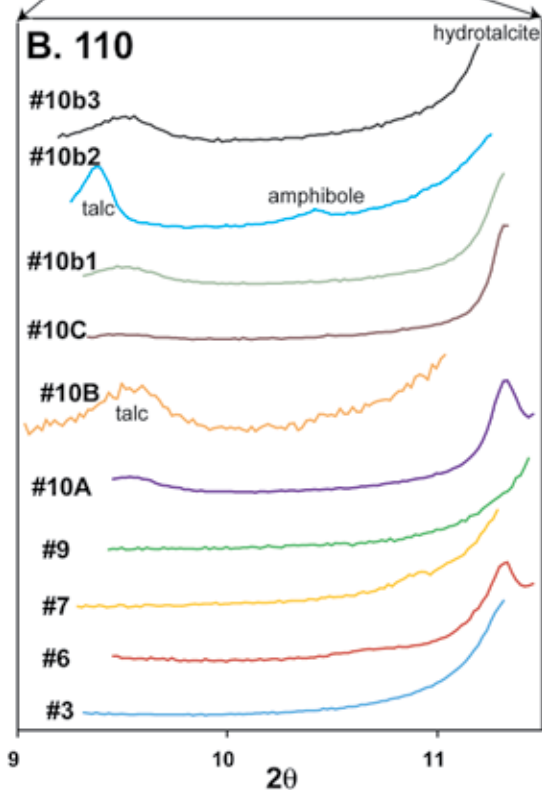
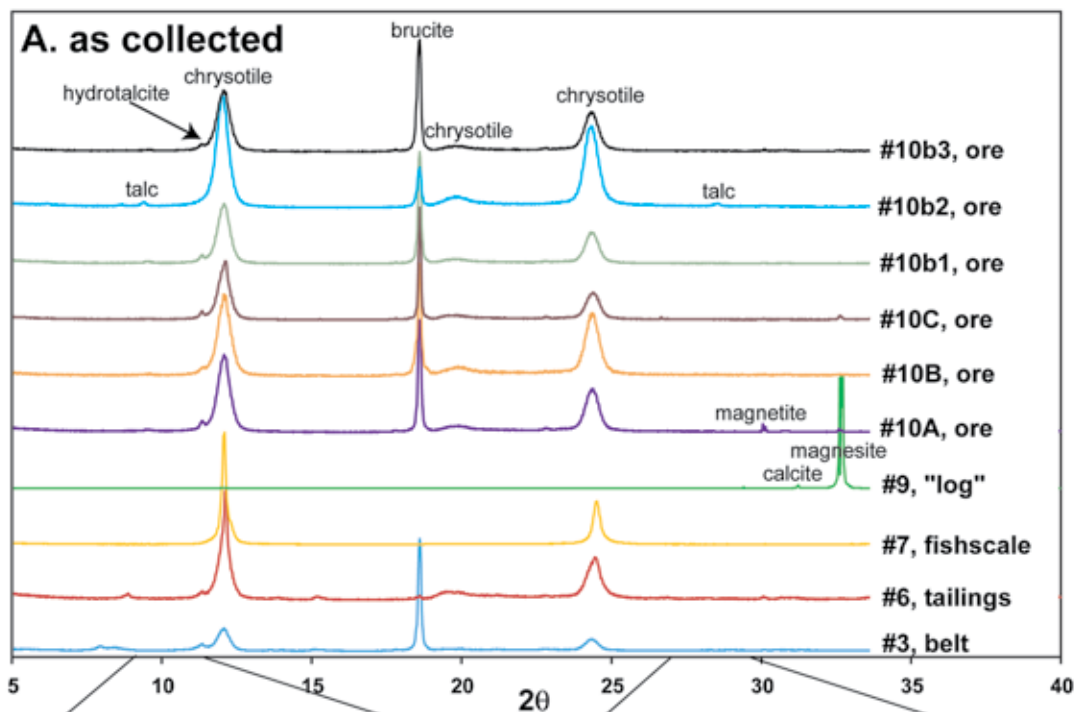
The patterns in Figures 4B and 4C were obtained at longer count-times over the regions for the (110) and (310) peaks for amphiboles, respectively. Of the ten samples in Figure 4B, only sample #10b2 shows the (110) diffraction peak for amphibole. Also, note that #10b2 has the most talc of any of the ten samples. In the (310) 2θ region, the amphibole peak should occur near 28.5° 2θ ; however, the talc (003) diffraction peak also occurs in the same region. Thus, the peak in #10b2 is labeled as talc but may also have a component of the (310) amphibole peak. On the basis of these scans, and the ones in Figures 5 and 6, we can see that the (110) peak is more sensitive for determining the presence of amphibole than the (310) peak, as no other phase in the samples interferes with it.

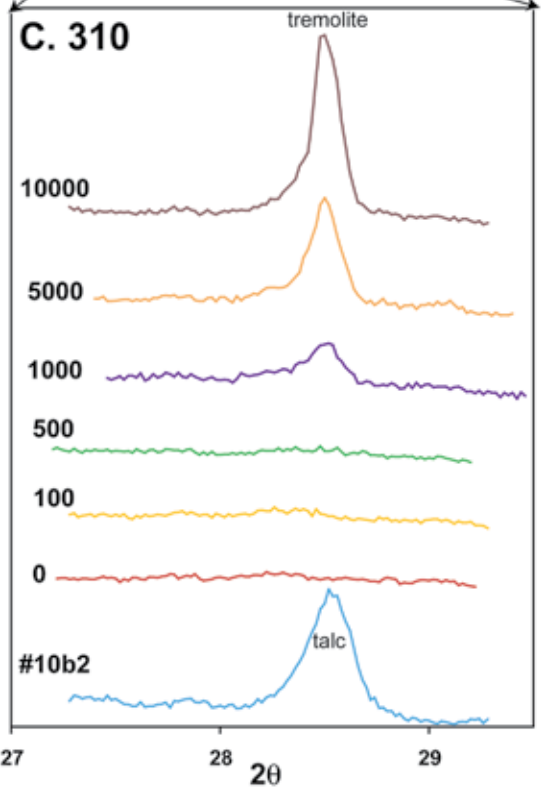
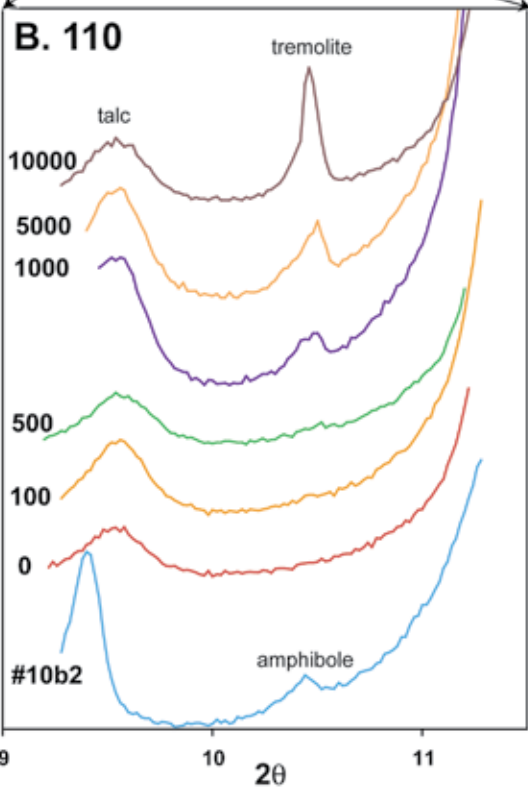
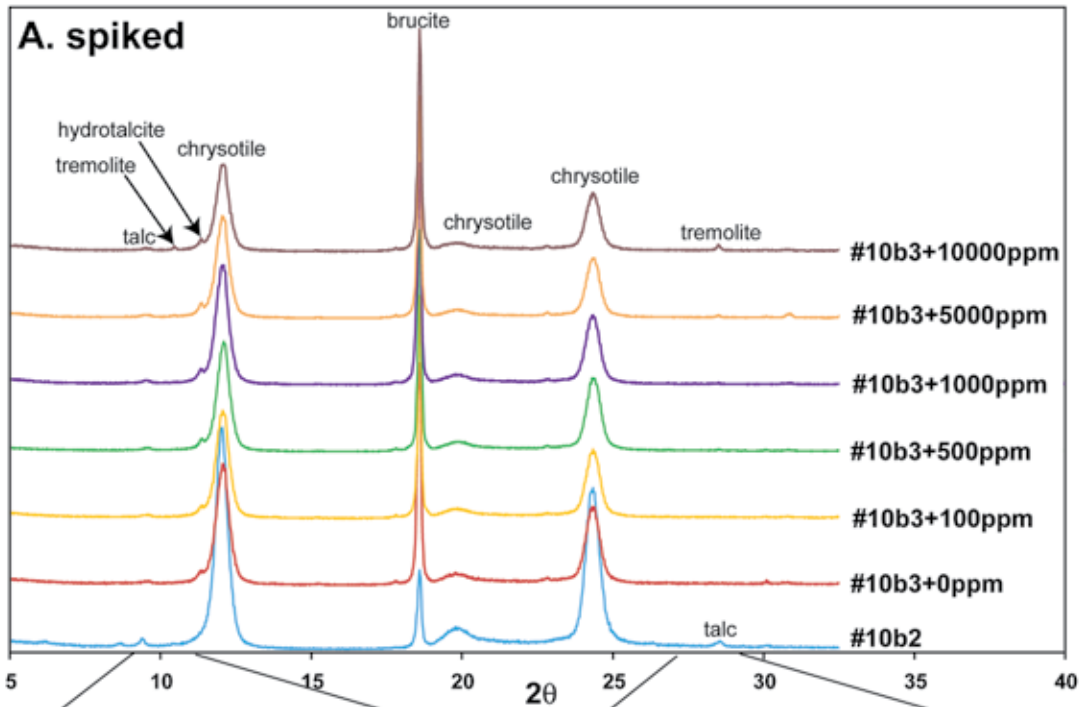
Tremolite-spiked samples: To ascertain the amount of amphibole represented by the (110) peak for #10b2 in Figure 4B and to determine the detection limit for amphiboles with the XRD method, a series of spiked samples were prepared and scanned with the same conditions as those for the natural samples described above. The intensity of the scans was not standardized to 100% because their bulk compositions are similar. Sample #10b3 was chosen to spike with differing amounts of a tremolite of known composition (Table 2)

because it seemed amphibole-free and similar to #10b2. The composition of the tremolite is given in Table 3. Notice that this tremolite is near the boundary between tremolite and actinolite. Because it formed in a similar geological setting as ore from the Carey mine, it is an ideal phase to use for spiking the samples and for SEM-EDS chemical analysis to be discussed later. Four-gram mixtures of #10b3 were made by adding the appropriate amount of tremolite to make five spiked samples: 100, 500, 1000, 5000, and 10,000 ppm, which would correspond to 0.01, 0.05, 0.1, 0.5, and 1.0% tremolite by weight. The samples were mixed in acetone with a mortar and pestle, and XRD mounts were prepared in the same manner as the natural samples. For the 5 – 40° 2θ scans, the tremolite (110) and (310) peaks can only be seen in the 5000 and 10,000 ppm spiked samples (Fig. 5A). However, for the 9.5 – 11.5° 2θ scans, the (110) peak can easily be seen in samples spiked with 500 ppm or more, and possibly in the 100 ppm sample (Fig. 5B). For 27.5 – 29.5° 2θ scans, samples with 500 ppm and above show the (310) diffraction peak (Fig. 5C). Lastly, note that the (110) and (310) peak heights for the 1000, 5000, and 10,000 ppm samples correlate with the amount of tremolite added (Figs. 5B, C).

Digested spiked samples: To lower the level of detection of amphiboles, 1.5 gram aliquots of five samples, #10b2, #10b3, and three tremolite-spiked #10b3 samples were placed in a cocktail of 24 mL 16M

Fig. 4. A series of ten XRD scans for some of the sample locations described in Table 1, offset vertically from each other, with intensities standardized, peaks of the major phase labeled, and step size for all patterns 0.02° 2θ . The scans in A, taken over longer 2θ ranges with 9 seconds per step, were used to identify the major phases, whereas the scans in B and C, taken over selected 2θ regions where the (110) and (310) amphibole peaks should occur, have longer count-times, 180 second per step. All of the scans in A, B, and C were standardized in 2θ on the brucite peak. A) All of the samples except #7 and #9 are predominantly a mixture of chrysotile and brucite with minor amounts of hydroxalcite, except for #10b2. Talc peaks occur in #6 and #10b2. Minor amounts of magnetite, calcite, and magnesite occur in some of the samples, with #9 being almost pure magnesite, and #7, pure chrysotile. Note that amphibole is not seen in these scans. B) Ten scans from 9.5 to 11.5° 2θ with longer count-times, to examine the samples for the (110) amphibole peak that occurs near 10.5° 2θ . Note that talc can now be seen in several patterns, and hydroxalcite in most. Also, a small amphibole (110) peak occurs in #10b2. C) Ten scans from 27.5 to 29.5° 2θ with longer count-times, to examine the samples for the (310) amphibole peak that occurs near 28.5° 2θ . Note that the only sample that shows a peak in this region is #10b2; however, because the (003) peak for talc overlaps with the (310) amphibole peak, and appears more intense, the peak is probably predominantly due to talc.





HCl and 12 mL 16M HNO₃ in a sealed Teflon bomb. The bombs were then placed in a microwave oven for 30 minutes heating at 1400 kPa and 200°C. This process was used to digest the majority of the minerals in the samples, while leaving tremolite (and any other amphiboles) intact. Unfortunately, this cocktail does not dissolve talc.

Figure 6 shows results of the XRD scans of the five samples performed in the same manner as the scans in Figure 5, except the scans have not been aligned in 2θ on the brucite peak because brucite is dissolved. Likewise, chrysotile is totally removed from all but #10b3 + 0 ppm and #10b3 + 1000 ppm, although peak intensities are drastically reduced. The broad peak that occurs near the center of the scans is of a type commonly referred to as an “amorphous hump” and results from poorly crystalline samples; this is the residue from the

chrysotile. In the 5–40° 2θ scans (Fig. 6A), tremolite is clearly visible at the 1000 ppm level and possibly on the 500 ppm scan. For the longer count-time scan over the (110) peak (Fig. 6B), no tremolite is seen in the unspiked sample or the 100 ppm scan, but distinct peaks occur for the 500 and 1000 ppm samples. On the basis of this set of scans, the amphibole concentration of #10b2 would be between 500 and 1000 ppm, but closer to 500 ppm. Lastly, scans over the (310) region (Fig. 6C) show only a significant tremolite peak for the 1000 ppm sample, with a possible peak for the 500 ppm sample; when compared to Figure 6B, the (110) scans are seen to be more sensitive than the (310) peaks. Notice also the presence of talc in the #10b2 sample, and the occurrence of its (003) peak near the region of the amphibole (310) peak. This fact is another reason to use the (110) peaks for amphibole detection in this talc-containing sample.

PLM (polarized light microscopy)

For each of the ten samples (Table 1), three immersion mounts were made in high-dispersion, index-matching fluid (n = 1.635); this index was chosen because dispersion-staining colors would be produced for anthophyllite, tremolite, and low-Fe actinolite. All three mounts were scanned with central stop dispersion by placing them in a point-counting stage and observing the entire slide; this process took approximately one hour. With this method, materials with a near-match to the fluid appear colored (blue for tremolite) and would stand out in contrast to the other non-matching particles, which are white, all on a dark-field background (Fig. 7A). Each slide contained approximately 10,000 particles, as estimated by observations under low power, counting the number of particles in several fields, and then extending that to the entire slide.

Because each slide contains approximately 10,000 particles, it would contain 100 particles of amphibole if the overall amphibole content was 1% (= 10,000 ppm), 10 particles for 0.1% (= 1000 ppm), and 1 for 0.01%

TABLE 2. THE Ca CONTENT FOR TEN SAMPLES BEFORE AND AFTER MICROWAVE ACID-TREATMENTS, Ca CONTENT FOR THREE ACID-TREATED TREMOLITE-SPIKED SAMPLES, AND CALCULATED MAXIMUM CONCENTRATIONS OF TREMOLITE FOR ALL

Sample	Ca ppm	max. % Tr	max. ppm Tr	Ca ppm	% left	Ca ppm adj.	max. % Tr	max. ppm Tr
#3	175	0.061	610	49*	26.44	13	0.005	50
#6	175	0.061	610	55*	33.67	19	0.006	60
#7	305	0.106	1,060	36*	48.67	18	0.006	60
#9	533	0.186	1,860	92*	39.33	36	0.013	130
#10A	204	0.071	710	96*	35.33	34	0.012	120
#10B	264	0.092	920	76*	37.67	29	0.010	100
#10C	168	0.059	590	44*	35.11	15	0.005	50
#10b1	143	0.050	500	50*	37.33	19	0.007	70
#10b2	1,494	0.521	5,210	1,542	39.67	612	0.213	2,130
#10b3	231	0.081	810	76*	34.50	26	0.009	90
#10b3 + 100 ppm Tr	-	-	-	69	32.67	23	0.008	80
#10b3 + 500 ppm Tr	-	-	-	107	32.17	34	0.012	120
#10b3 + 1000 ppm Tr	-	-	-	1,105	34.67	383	0.134	1,340

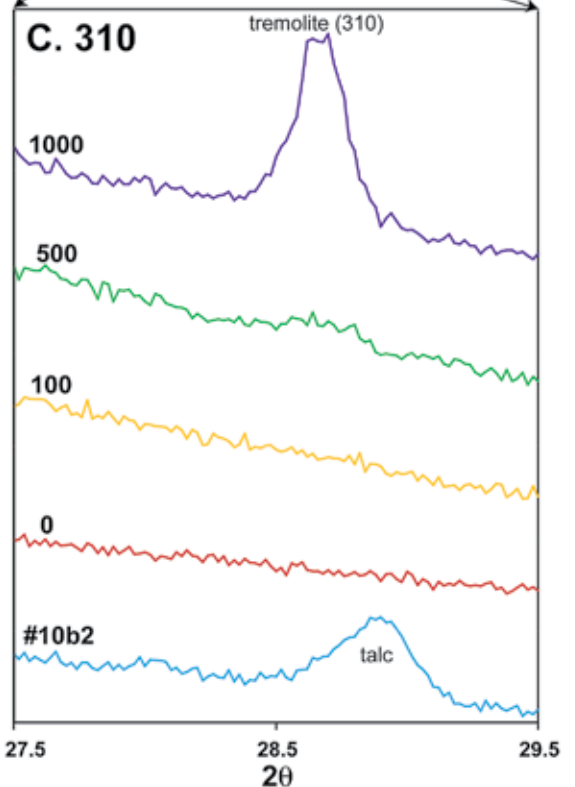
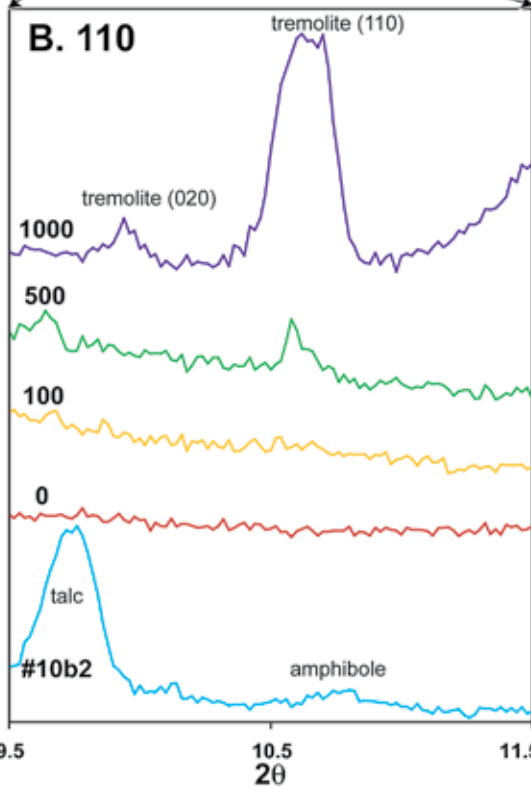
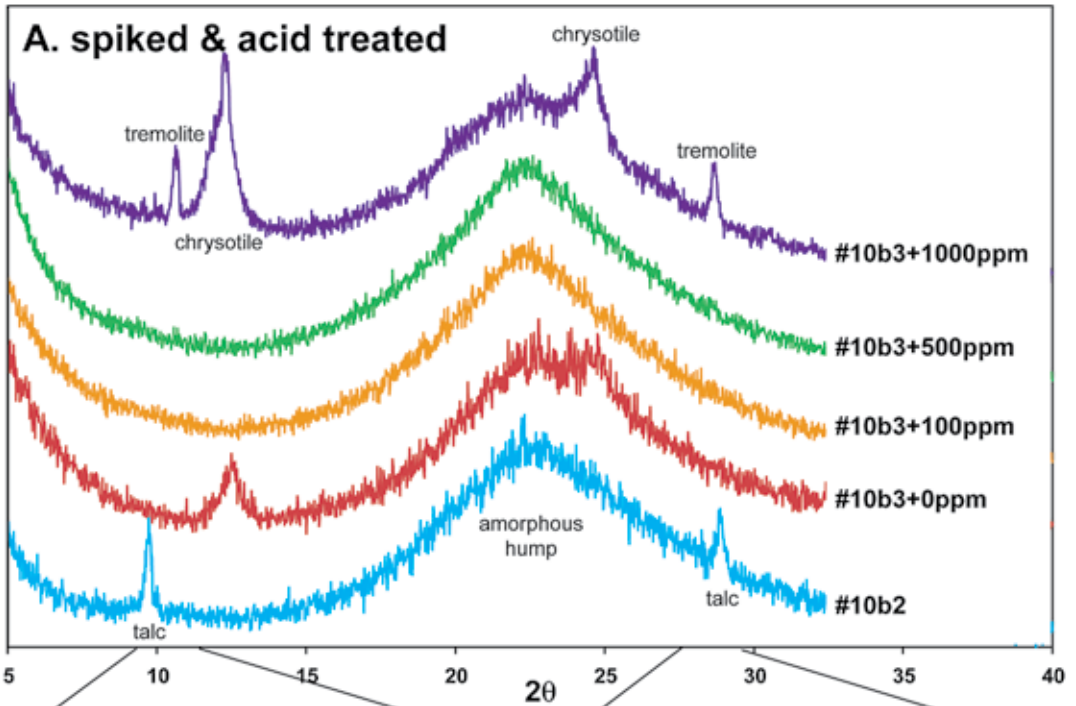
All Ca values are the average result of two separate analyses except those with *. The results are quoted in wt. percent and ppm. Tr: tremolite, adj.: adjusted.

FIG. 5. Seven stacked XRD scans of samples #10b2, #10b3, and five tremolite-spiked #10b3 samples run in the same manner as the three series of scans shown in Figure 4 and used to determine the amount of amphibole in #10b2 and the detection limit for tremolite. Sample #10b2 is on the bottom, followed by the amphibole-free #10b3 (labeled 0 ppm) and then by five tremolite-spiked samples with increasing amounts of tremolite on the upper scans. A) All six of the #10b3 samples appear identical except for the upper two, where the tremolite (110) and (310) peaks appear. B) The (110) peak appears for the tremolite-spiked samples containing more than 100 ppm, and the areas of these peaks correlate with the amount of tremolite added to the samples. C) The (310) peak for tremolite appears in all of the samples above 100 ppm, and its area also correlates well with the amount of tremolite added.

TABLE 3. CHEMICAL COMPOSITION* OF THE TREMOLITE SAMPLE USED FOR SPIKING IN THE XRD EXPERIMENTS AND AS THE STANDARD FOR EDS

SiO ₂	58.87	Si <i>apfu</i>	7.94
Al ₂ O ₃	0.43	Al	0.03
TiO ₂	0.02	Ti	0.00
FeO	4.13	Fe	0.47
MgO	22.45	Mg	4.52
MnO	0.11	Mn	0.01
CaO	13.66	Ca	1.97
Na ₂ O	0.23	Na	0.03
K ₂ O	0.10	K	0.01
Mg / (Mg + Fe)	0.91		
K _{0.01} (Na _{0.01} Ca _{1.97}) (Mg _{4.52} Fe _{0.47} Mn _{0.01}) (Al _{0.03} Si _{7.94} O ₂₂) (OH) ₂			

* as determined by X-ray-fluorescence analysis. The formula is calculated on the basis of 23 atoms of oxygen per formula unit.



(= 100 ppm). Because three slides (or 30,000 particles) were observed for each sample, three particles would be seen if the sample contained 0.01% amphibole, 30 for 0.1%, and 300 for 1.0%. Given these sorts of numbers and careful observations of the slides, it would seem reasonable that a microscopist could see 15–30 particles of amphiboles in the three slides; this would result in a lower level of detection of 0.05–0.1% (= 500 to 1000 ppm). With this method, no amphibole was found in any of the ten samples at a lower level of detection at 500 to 1000 ppm. However, based on the positive identification of amphibole in #10b2 by X-ray diffraction, more slides with higher concentrations of particles were made for this sample, and some amphibole particles were indeed found after several hours of searching (Figs. 7A and 7B). PLM was also used to help isolate some of these particles for chemical and morphological analysis after a digestion method was used to concentrate them. (This method is discussed in the section on SEM below.) Figure 7C shows a single crystal of an amphibole from a digested sample of #10b2 mounted on the end of a glass fiber with red fingernail polish and immersed in an index-matching fluid. This is the same particle as that shown in Figure 8B, also discussed in the SEM section. On the basis of morphological observations with the PLM (Brown & Gunter 2003), all the amphibole particles seem nonasbestiform (*i.e.*, they lack the ability to be separated into fibers). Also, optically the particles exhibit single-crystal characteristics (*i.e.*, sharp and inclined extinctions).

FIG. 6. XRD scans of #10b2, #10b3, and three tremolite-spiked #10b3 samples after microwave acid-treatment. This treatment leaves talc and the amphiboles unchanged, but in general destroys the crystallinity of chrysotile and brucite, which accounts for the large amorphous hump between 15 and 30° 2 θ . (The same operating conditions exist as in Figures 4 and 5, except that scans could no longer be standardized in 2 θ with the brucite peak.) A) Brucite is removed from all the samples, whereas some residual chrysotile remains in #10b3 + 0 ppm and #10b3 + 1000 ppm. The only crystalline phase that now appears in #10b2 is talc. There is a hint of the (110) peak of tremolite in #10b3 + 500 ppm, and both the (110) and (310) peaks clearly occur in the 1000-ppm-spiked sample. B) These high count-time scans show clear (110) peaks for tremolite in the 500- and 1000-ppm-spiked samples, and no peak in the unspiked sample (*i.e.*, the 0 ppm one) or the 100 ppm sample. Thus, on the basis of the intensities of these peaks, #10b2 would seem to have less than 500 ppm amphibole. C) In this set of scans, the (310) tremolite peak is clear in the 1000 ppm sample with a slight indication of the peak in the 500 ppm scan, but it is absent from the 100 ppm and unspiked scans. These scans are less useful to determine the amphibole content for #10b2 because of the overlap of the (003) talc peak with the (310) amphibole peak.

SEM-EDS (scanning electron microscopy with energy-dispersive spectroscopy)

On the basis of the results from the XRD above, #10b2 contains between 500 and 2000 ppm amphibole, and from the optical data (*i.e.*, the indices of refraction), the amphibole could be either anthophyllite, tremolite, or a low-Fe actinolite. Thus, chemical analysis was required to determine the amphibole species. However, because the amphibole particles are small (Fig. 7) and in very low concentrations, we needed to develop a method to concentrate them. This was accomplished with a more aggressive digestion method than that used in the XRD analysis and modified from that of Addison & Daveis (1990). A 0.25 gram sample of #10b2 was placed first in 100 mL of 16M HCl and boiled for one hour. After rinsing in deionized water, the remaining residual was placed in 100 mL of 4M NaOH and boiled for one hour. This process dissolved most of the other mineral matter, thus concentrating the amphibole. Next, individual grains of amphibole could be isolated from the residue (as was done for the PLM samples above and shown in Fig. 7).

To ascertain if the particles consist of amphibole or partially digested chrysotile, individual crystals were mounted on glass fibers and immersed in 1.635 high-dispersion liquid. The partially digested chrysotile particles were observed to have considerably lower indices of refraction. Figure 7C shows a near-index match for an amphibole. Next, the glass fiber – crystal combination could be transferred to an SEM equipped with EDS to gain insight into the chemical composition of the sample. Figures 8A and 8B show the spectra and images of two amphibole grains from #10b2 obtained in this manner. The sample in Figure 8A contains significant amounts of Mg and Si (with minor Al), so it probably is anthophyllite, $Mg_7Si_8O_{22}(OH)_2$, whereas the sample in Figure 8B contains Ca, Mg, Fe, and Si, and probably belongs to the tremolite–actinolite solid-solution series. On the other hand, a partially digested sample of chrysotile was observed to contain mainly Si and O because the Mg was leached from its structure. Lastly, Figure 8C shows the EDS spectrum of the NIST standard tremolite. Whereas the NIST tremolite is somewhat similar to the sample shown in Figure 8B, it is difficult to tell whether the sample in Figure 8B is tremolite or actinolite. To make this distinction, more precise and accurate chemical data must be obtained.

Before proceeding, a brief review of amphibole nomenclature extracted from Leake *et al.* (1997) as it applies to these three species is warranted. First, the distinction between anthophyllite and the tremolite–actinolite series is based on Ca content. If Ca is less than 1.0 atoms per formula unit (*apfu*), our sample would be classified as anthophyllite. If Ca is greater or equal to 1.0 *apfu*, the sample would belong to the tremolite–actinolite series. The distinction between tremolite and actinolite is made on the basis of the value

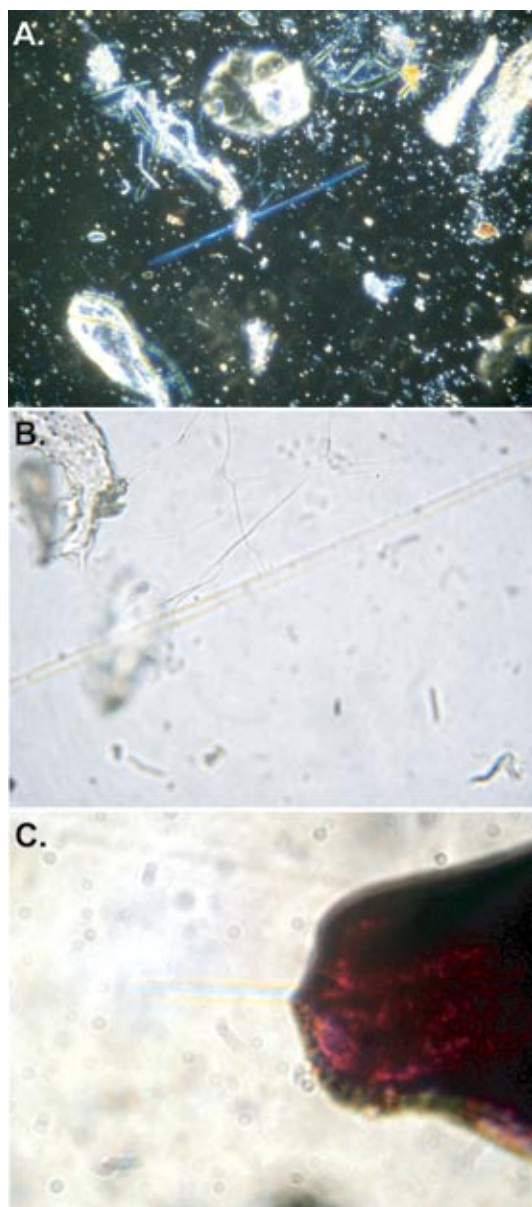


FIG. 7. PLM photographs of amphibole from sample #10b2 in 1.635 index of refraction liquid, none of which display the asbestiform habit. A) A central stop-dispersion image of a grain mount showing an elongate single crystal of amphibole with chrysotile; the blue color indicates that the amphibole matches the liquid (the field of view is approximately 300 μm , and the amphibole particle is approximately 3 μm wide). B) Same sample as in A, but in plane-polarized light and a higher magnification (the field of view is approximately 100 μm). C) An amphibole particle approximately 8 μm wide mounted on the end of a glass fiber and slightly defocused, showing the colored Becke lines (the field of view is approximately 300 μm).

obtained from the relationship $\text{Mg\#} = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$. If the value Mg# is between 1 and 0.9, the sample would be tremolite, and if it is between 0.9 and 0.5, it would be classified as actinolite. Thus, to distinguish between these three species, we need to determine their chemical compositions and, by using the values of Ca and Mg#, in turn determine the species. However, first we needed to determine whether the digestion process affected the composition of the amphibole, and to develop and test a method to accurately, precisely, and reproducibly determine the compositions of these amphiboles.

To chemically analyze these samples, the residuals on the filter paper were dried and then carbon-coated. Next, the samples were placed in the SEM at 20 keV accelerating voltage and analyzed for Si, Fe, Mg, Ca, and O by a standardless ZAF method. In Table 4, we show the chemical data for a natural sample and one that had gone through the digestion process. These data are the mean result of five analyses, with the standard deviations for each in parentheses. From these results, it appears that the digestion process does not affect the composition because the corresponding values are within experimental uncertainty, as expressed by the standard deviation. Note that the tremolite used in Table 4 is the same as that used to spike the XRD samples, and relevant chemical data are given in Table 3. However, in Table 3 we give the chemical data in terms of weight percent oxides, which in turn are calculated to atoms per formula unit (*apfu*). The *apfu* values are required to determine the amphibole species. The data in Table 4 are given in terms of atom weight percent, and again need to be converted to *apfu*.

The first column in Table 5 labeled "XRF" is the tremolite standard used with its chemical data converted to atom percent (to match the output data from the SEM-EDS system). Comparing these data to those in Table 4, one notes some lack of agreement, especially for Fe, Mg, and Ca. The SEM-EDS analysis provides high precision (*i.e.*, it is reproducible and has low standard deviations), but to obtain higher accuracy, a standardization method is required. To accomplish this, the tremolite standard of known composition was analyzed, and "factors" were derived to improve

TABLE 4. NON-STANDARDIZED ATOM WEIGHT PERCENT BEFORE (NATURAL) AND AFTER (DIGESTED) FOR THE TREMOLITE (TABLE 3) AS DETERMINED BY SEM-EDS

	natural	digested
Si atom %	21.64 \pm 0.08	21.82 \pm 0.08
Fe	0.53 0.08	0.67 0.09
Mg	13.60 0.38	13.47 0.25
Ca	3.27 0.30	2.96 0.20
O	60.95 0.03	61.08 0.04

The values given are the mean results of five spot-analyses on a single particle.

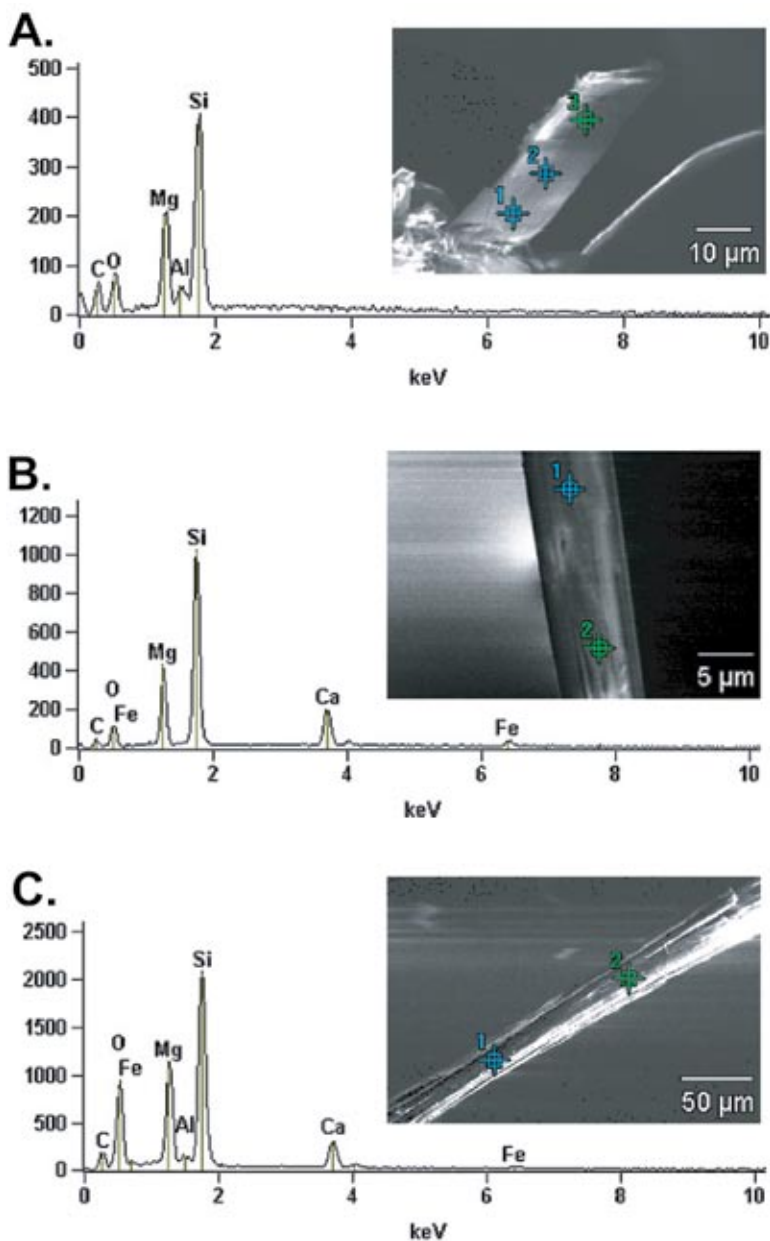


FIG. 8. SEM photographs and EDS results for three particles of amphibole: A and B from sample #10b2, mounted on glass fibers, with indices of refraction matching an amphibole, and C, a NIST tremolite. The numbers on the samples indicate the spots analyzed, with the green spot being associated with the SEM-EDS spectra shown. A) The EDS data indicate that this particle is an Mg amphibole, probably anthophyllite. B) This is the sample shown in Figure 7C; the EDS data would indicate that this is a Ca-Mg-Fe amphibole, probably actinolite or tremolite. C) The EDS data from the NIST tremolite are similar to the pattern in Figure 7B, possibly with less Fe.

TABLE 5. RESULTS FOR THE TWO SAMPLES OF TREMOLITE USED FOR STANDARDIZATION

atom %	XRF	std 1A	factor 1A	std 1B	factor 1B	factor 1	std 2A	factor 2A	std 2B	factor 2B	factor 2
Si	20.91	21.65 0.06	0.9658	21.64 0.09	0.9663	0.9661	21.59 0.08	0.9685	21.46 0.11	0.9744	0.9715
Fe	1.23	0.58 0.06	2.1207	0.55 0.07	2.2364	2.1786	0.50 0.03	2.4600	0.52 0.03	2.3654	2.4127
Mg	11.89	14.14 0.20	0.8409	14.21 0.26	0.8367	0.8388	14.78 0.18	0.8045	14.80 0.13	0.8034	0.8040
Ca	5.20	2.80 0.08	1.8571	2.79 0.09	1.8638	1.8605	2.47 0.11	2.1053	2.48 0.11	2.0968	2.1011
O	60.55	60.83 0.03	0.9954	60.82 0.05	0.9956	0.9955	60.75 0.08	0.9967	60.74 0.05	0.9969	0.9968

The atom % given is the mean of five spot-analyses, and the number shown on the second line is the corresponding standard deviation. The first column (labeled XRF) is the known composition, and the derived factors are determined by dividing the XRF data by the SEM-EDS data. Factor 1 was used for particles 1–5 and std1, and factor 2 was used for particles 6–12 in Table 6.

accuracy and standardize the chemical data. In Table 5, we give these factors for two standards that are shown in Figure 9 and labeled as std1 and std2. The method developed herein was to analyze five points on std1 (std1A), then run unknown samples 1–5 (Fig. 9), and restandardize on std1 (std1B) to arrive at factor 1. Then, the amount of each of the elements in percent for 1–5 was multiplied by this factor. The upper part of Table 6 lists the observed atom weight percent for Si, Fe, Mg, Ca, and O for the first five amphiboles (*i.e.*, 1–5) shown in Figure 9. The lower part of the table lists the values in *apfu* that were obtained by first multiplying each atom percent by factor 1 (Table 5) for each element and then converting the standardized atom percent to values in *apfu*. Next, as a check on the method, three points were measured on std1 (Fig. 9), and the results are listed in Table 6 in the column labeled std1. Finally, the process was repeated with a new different standard (std2) and amphibole particles 6–12 measured. Again, those data are given in Table 6.

Given the *apfu* values for each of the twelve amphiboles in Table 6, the Mg# and Ca values are used to determine the amphibole species. As can be seen at the bottom of Table 6, five of the samples are anthophyllite and seven are actinolite. Also, note the std1 is correctly classified as tremolite. It is also worth comparing the chemical formula for the amphibole standard obtained by the standardization method used herein obtained by SEM-EDS data with that obtained by XRF and seeing how well they agree. The last two rows in Table 6 represent the sizes of the particles and their aspect ratios. Morphologically, most of the particles in Figure 9 are nonasbestiform. However, the analyzed particles shown in samples 4, 5, and 10 may be morphologically asbes-

tiform, but it is difficult to tell at this magnification and image resolution.

Ca content and maximum tremolite

Another independent method was developed to predict the maximum tremolite content in a chrysotile ore. The method uses the Ca content of the sample as a predictor for tremolite, as suggested by Williams-Jones *et al.* (2001), because few other minerals in the sample contain Ca, and some that do (*e.g.*, calcite or magnesite) can be removed by pre-treating the samples with acids that will not affect the tremolite. This method works as follows: given a 1% tremolite – 99% chrysotile mixture, the Ca content can be related to the amount of tremolite as follows:

$$\begin{aligned}
 &1\% \text{ tremolite} + 99\% \text{ chrysotile} = \\
 &1\% [\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2] + 99\% [\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4] = \\
 &0.02 \text{ Ca} + 3.02 \text{ Mg} + 2.06 \text{ Si} + 9.15 \text{ O} + 3.98 \text{ H} = \\
 &0.8016 (\text{Ca weight}) / 282.4649 (\text{total weight}) = \\
 &0.28\% \text{ Ca} = 1\% \text{ tremolite} = 0.28\% \text{ Ca} = \\
 &2,800 \text{ ppm Ca}
 \end{aligned}$$

Thus, if one measured the Ca content in a mixture of tremolite and chrysotile and found the sample to contain 0.28% Ca, that value would equate to 1% tremolite. Likewise, 2.8% Ca would equate to 10% tremolite and 0.028% Ca would equate to 0.1% tremolite. In general, the conversion between measured Ca ppm and maximum percent tremolite is the slope of the blue line shown in Figure 10, which is 0.000349. Thus, given a measured Ca in ppm, that number can be multiplied by 0.000349 to find the corresponding maximum percent tremolite.

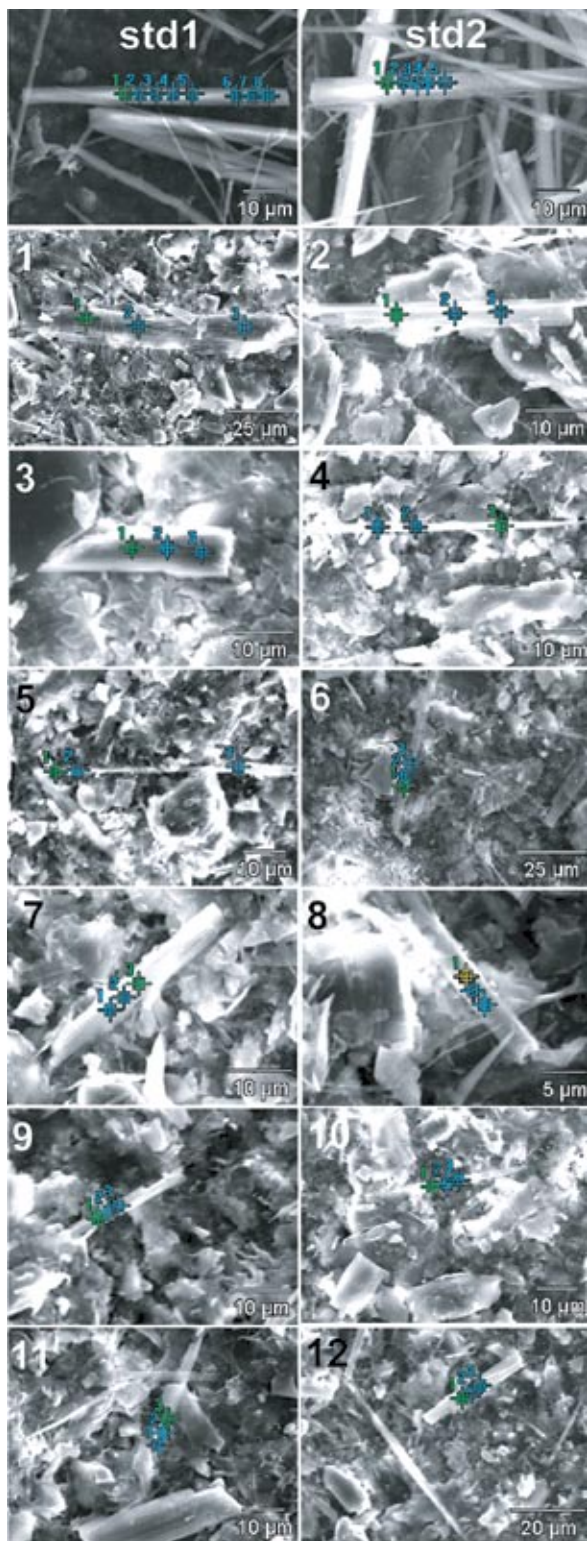


FIG. 9. SEM photographs of two tremolite standards (std1 and std2 with standardization results given in Table 5) and twelve particles from sample #10b2 after digestion; the standardized chemical data are given for each the twelve particles in Table 6. Note the five spots on std1 and std2; data from these were averaged to obtain the “factors” given in Table 5. Also, note that the three extra spots on std1 correspond to the “std1” entry in Table 5. The results in Table 5 were based on the average results of three analyzed spots on each of the 12 grains and were used to determine the species name of the amphibole. Only samples 4, 5, and 10 do not clearly display a nonasbestiform habit.

TABLE 6. RAW EDS CHEMICAL DATA OF ATOM WEIGHT PERCENT (ATOM %) AND STANDARDIZED *apfu* (ATOMS PER FORMULA UNIT) FOR 12 PARTICLES FROM SAMPLE #10b2 AND std1

	1	2	3	4	5	std1	6	7	8	9	10	11	12
Si atom %	22.18	21.81	22.77	23.42	23.09	21.52	22.57	21.94	21.59	24.30	22.52	22.47	22.19
	0.23	0.05	0.18	0.87	0.27	0.08	0.27	0.09	0.18	1.59	0.29	0.14	0.10
Fe	0.70	1.24	2.01	0.92	1.15	0.49	1.43	0.85	0.69	0.59	0.88	1.11	0.68
	0.12	0.05	0.16	0.16	0.27	0.01	0.92	0.06	0.07	0.02	0.07	0.10	0.09
Mg	13.61	15.67	10.49	12.22	10.38	14.51	10.96	15.81	16.64	11.44	14.68	14.32	13.24
	0.84	0.07	0.50	1.66	1.10	0.10	3.72	0.14	0.25	2.86	0.33	0.45	0.36
Ca	2.42	0.37	3.34	1.73	3.82	2.71	3.77	0.43	0.28	1.52	0.65	0.86	2.81
	0.37	0.09	0.14	0.40	1.09	0.03	2.99	0.03	0.03	0.47	0.12	0.15	0.15
O	61.09	60.89	61.39	61.71	61.55	60.76	61.28	60.97	60.80	62.15	61.26	61.24	61.09
	0.12	0.04	0.09	0.44	0.14	0.04	0.14	0.04	0.10	0.80	0.15	0.07	0.05
Si <i>apfu</i>	8.10	7.99	8.28	8.47	8.37	7.91	8.26	8.07	7.96	8.76	8.24	8.22	8.14
Fe	0.58	1.03	1.65	0.75	0.94	0.41	1.30	0.78	0.63	0.53	0.80	1.01	0.62
Mg	4.31	4.99	3.31	3.84	3.27	4.63	3.32	4.81	5.08	3.41	4.45	4.34	4.02
Ca	1.70	0.26	2.34	1.21	2.67	1.92	2.98	0.34	0.22	1.19	0.51	0.68	2.23
O	23	23	23	23	23	23	23	23	23	23	23	23	23
Mg#*	0.88	0.83	0.67	0.84	0.78	0.92	0.72	0.86	0.89	0.87	0.85	0.81	0.87
species**	Act	Ath	Act	Act	Act	Tr	Act	Ath	Ath	Act	Ath	Ath	Act
l × w	86×13	41×5	28×6	61×2	58×1	60×4	61×536×12	24×3	22×3	39×2	10×2	32×5	
aspect ratio	3	8	5	31	58	15	12	3	8	7	20	5	6

* Mg# = Mg/(Mg + Fe), ** Act: actinolite, Ath: anthophyllite, Tr: tremolite. The standardization factors are given in Table 5, and the process to calculate chemical formulas (bottom of the table) from raw data (top of the table) is explained in the text. Also, given at the bottom of the table are the species names and the size of the particle. The sample numbers correspond to the particles in Figure 9. Below each value of atom %, we report the standard deviation.

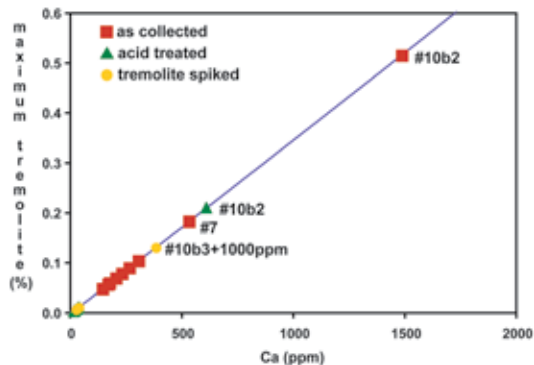


FIG. 10. Plot of calculated maximum content of tremolite in the ten natural samples (red squares), the same ten samples after microwave acid-treatment (green triangles, see text for details), and three tremolite-spiked samples (yellow circles) as a function of measured Ca content. The blue line represents the idea relationship between observed Ca and maximum content of tremolite. The data plotted in the figure are shown in Table 2, and only three samples are directly labeled on the graph and discussed in more detail in the text. Also, note how the ten natural samples (shown with red boxes) all have drastically decreased in tremolite content after microwave acid-treatment (shown by the green triangles).

With this method, we make several assumptions, all of which will tend to overpredict the amount of tremolite-asbestos: 1) no other Ca-bearing minerals are present, 2) all the tremolite in the sample is asbestiform, and 3) the ore contains only chrysotile and not minerals with lower molecular weight. To demonstrate the latter, if the mixture was 1% tremolite and 99% brucite, the following relationship would hold:

$$\begin{aligned}
 &1\% \text{ tremolite} + 99\% \text{ brucite} = \\
 &1\% [\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2] + 99\% [\text{Mg}(\text{OH})_2] = \\
 &0.02 \text{ Ca} + 1.04 \text{ Mg} + 0.08 \text{ Si} + 2.22 \text{ O} + 2.00 \text{ H} = \\
 &0.8016 (\text{Ca weight}) / 65.8603 (\text{total weight}) = 1.22\% \text{ Ca} \\
 &1\% \text{ tremolite} = 1.22\% \text{ Ca} = 12,200 \text{ ppm Ca}
 \end{aligned}$$

From the above, 1.22% Ca now equates to 1% tremolite, and this relationship overpredicts the tremolite content by a factor of approximately 4 if the sample were the heavier chrysotile. Or stated another way, for the 1% tremolite – 99% chrysotile mixture, $0.000349 * 2,800 = 1.0\%$, whereas for the 1% tremolite – 99% brucite mixture, $0.000349 * 12,200 = 4.3\%$ tremolite, thus significantly overpredicting the amount of tremolite. Lastly, recall that brucite is a major component of the chrysotile ores.

To test this method, all ten samples were sent to a commercial lab (Actlabs in Phoenix, Arizona) to have the Ca content determined by AA (atomic absorption) spectroscopy. Also sent to the lab were the ten samples plus three spiked samples that were treated in the microwave oven as described above to remove Ca-bearing minerals. The AA method requires the solid samples to be completely dissolved in a liquid. Approximately 1 gram of each of the 23 samples was dissolved in hydrofluoric acid and then diluted to 100 mL with deionized water. Next, the samples were run through the AA spectrometer to determine Ca content (see right-hand columns in Table 2).

For the ten untreated samples, the maximum amounts of tremolite were calculated and range from a low of 0.050% (sample #10b1) to a high of 0.521% (sample #10b2), with the latter sample being the only sample found to contain any amphibole by XRD. These values are too high because there are other Ca-bearing minerals in the samples. For instance, calcite was shown to occur in #9 based on its XRD pattern (Figs. 4A, C). Also, magnesite, $MgCO_3$, often can contain trace amounts (*i.e.*, less than 1%) of Ca, and this was confirmed on our samples by SEM-EDS.

To alleviate the concern for some of these Ca-bearing minerals and to increase the sensitivity of this method, a set of samples were acid-treated in the microwave as described above. The XRD patterns of these samples (Fig. 6A) show that these carbonate minerals were removed. Also, as shown in Table 2, approximately two-thirds of most of the samples was dissolved, thus increasing the sensitivity. The next column in Table 2, "Ca (ppm) adjusted," are the Ca values from these samples adjusted for the weight lost during the digestion process. For this suite of samples, the maximum amounts of tremolite range from 0.005% (#1 and #10C) to 0.213% (#10b2). Thus, the maximum amounts of tremolite are considerably lowered after the dissolution process. Lastly, three tremolite-spiked standards were run, and there is partial agreement between the known amount of tremolite added and that predicted to occur by the Ca content. For the 100 ppm sample, the method predicted 80 ppm tremolite, for the 500 ppm sample, 120 ppm, and for the 1000 ppm sample, 1340 ppm. Figure 10, a plot of all the data in Table 2, mainly shows how the maximum amount of tremolite is lowered by the acid treatment and that #10b2 is the only sample to contain a significant amount of a Ca-bearing amphibole.

DISCUSSION

A combination of analytical methods was used on bulk samples collected from the former Carey Canadian mine to identify the mineral phases present. These methods depart from those routinely used by commercial laboratories to identify asbestos and even from the methods commonly used for amphibole determination.

For instance, commercial PLM lab technicians will typically only look at a few numbers of points (not 30,000) to determine asbestos content of a sample. By looking at more points, the PLM detection limit can be lowered from 1% to as low as 0.05%. TEM methods also are commonly used, but given gram-scale bulk samples, it is more logical to use bulk-scale methods such as XRD or the Ca-content method, because these methods allow one to examine larger portions of the sample and to minimize the errors associated with counting a few particles and extrapolating to larger size of sample. Such methods as TEM are, however, useful where small sample sizes are all that are available, such as with air samples. Routine powder XRD methods are commonly quoted with detection limits of 1–2% (*e.g.*, Williams-Jones *et al.* 2001); however, it was clearly shown in Figures 4 to 6 that detection limits are at least 500 ppm (*i.e.*, 0.05%) and possibly as low as 100 ppm.

Of the ten samples analyzed, one was found to contain amphibole above the 100 ppm detection limit of these methods. On the basis of calibrated XRD methods, it would appear that this sample contains between 500 to 1000 ppm amphibole and could contain no more than 0.2% (*i.e.*, 2000 ppm) tremolite based on Ca content as a proxy for tremolite, although the latter method is most certainly an overestimate, as explained in the text. The standardized SEM-EDS approach showed approximately half of the amphiboles in the one sample to be anthophyllite and the other half to be actinolite, with no confirmed tremolite. Morphology observations with the SEM and PLM did not reveal any clearly asbestiform amphiboles.

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