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LETTER

Amphibole forensics: Using the composition of amphiboles to determine their source, the Libby, Montana, example†

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ABSTRACT

As part of a larger on-going research project, we found amphiboles in soils in Libby, Montana, that were derived from both the former vermiculite mine near Libby and other sources. SEM-EDS spectra of the soil amphiboles from these locations are used to ascertain if the amphiboles came from the vermiculite deposit near Libby, Montana, or some other source. This distinction is possible because amphiboles known to originate from the vermiculite deposit all contain Na and K that can be observed in the EDS spectra. We make this statement with confidence because multiple workers have performed EPMA characterization on over 40 amphiboles collected from the deposit and all are found to contain measureable amounts of Na and K. In this brief communication, we show examples from four locations that contain amphiboles consistent in composition and others that have inconsistent composition when compared to reference amphiboles collected from the vermiculite deposit. Also, we demonstrate the presence of amphiboles consistent in composition with amphiboles known to originate from the deposit in sediment that pre-date mining activity. A full-length publication is in preparation detailing the quantity, distribution, and composition of amphiboles in the Libby Valley, if they are consistent in composition with amphiboles known to originate from the deposit or not, and if they pre- or post-date mining operations.

Keywords: Amphibole, amphibole asbestos, Libby, Montana, EPA, SEM-EDS

INTRODUCTION

Amphiboles form in many geologic settings and as such can vary widely in composition and habit. In certain geological settings, it is possible to use amphibole compositions to determine their source. Geologists have used these sorts of methods for years to unravel the geological development of an area. However these methods could also find use where mining and milling processes may have led to alleged soil contamination, as is the case in Libby, Montana. Currently much of the area has been deemed a Superfund site based on amphibole asbestos contamination from the former vermiculite mine (see Gunter et al. 2007 and references therein). The EPA now contends some areas of Libby were contaminated by mine tailings (used on running tracks at two schools) (U.S. EPA 2001) or vermiculite ore used as attic insulation or amendments in gardens and lawns (U.S. EPA 2002). However, Gunter (2008) recently questioned what is and is not contamination in soils in Libby, based on the following: (1) some of the amphiboles might have been naturally transported from the vermiculite deposit and deposited in Libby soil pre-dating mining, and (2) other amphiboles could occur in the soil and sediment whose source is not the vermiculite deposit.

Issues surrounding the former vermiculite mine near Libby, Montana, have been in the national spotlight for almost a decade, mainly due to the amphibole asbestos occurring in the vermiculite ore. Historically, the amphiboles in the deposit were often referred to as tremolite (see Gunter et al. 2007 and references therein). The amphiboles occur in an alkaline-rich pluton (Larsen and Pardee 1929) and thus their increased Na and K content render them as predominately winchite and richterite, with only minor tremolite, and trace magnesio-riebeckite and magnesio-arfvedsonite (Meeker et al. 2003). As part of a much larger project dealing with the legal issues surrounding the deposit and the possible contamination of soils in the town of Libby, we started collecting soil samples in and around Libby to determine the distribution of amphiboles originating from the vermiculite deposit; our goal was to try and distinguish the pre- and post-mining concentration of these amphiboles in the soil. The deposit is upstream from Libby and the rocks composing it are highly erodible (Larsen and Pardee 1929; Boettcher 1967). The area was also glaciated during Pleistocene times (Larsen and Pardee 1929; Boettcher 1967; Smith 2006). Figure 1 shows that the mine is up-river with respect to Libby, and located in a naturally eroded bowl. Our hypothesis was that sediments derived from the deposit would have been transported downstream and deposited in a glacial lake that covered the current location of Libby (Smith 2006); its approximate shoreline is outlined in Figure 1. During our study the EPA also has posed the question about "background" levels of amphiboles from the deposit (U.S. EPA 2008), which they refer to as "Libby amphiboles." One reason they became concerned was the possibility that these amphiboles could occur in borrow pits where they had obtained "clean" soil to replace the contaminated soil in lawns and gardens in Libby.

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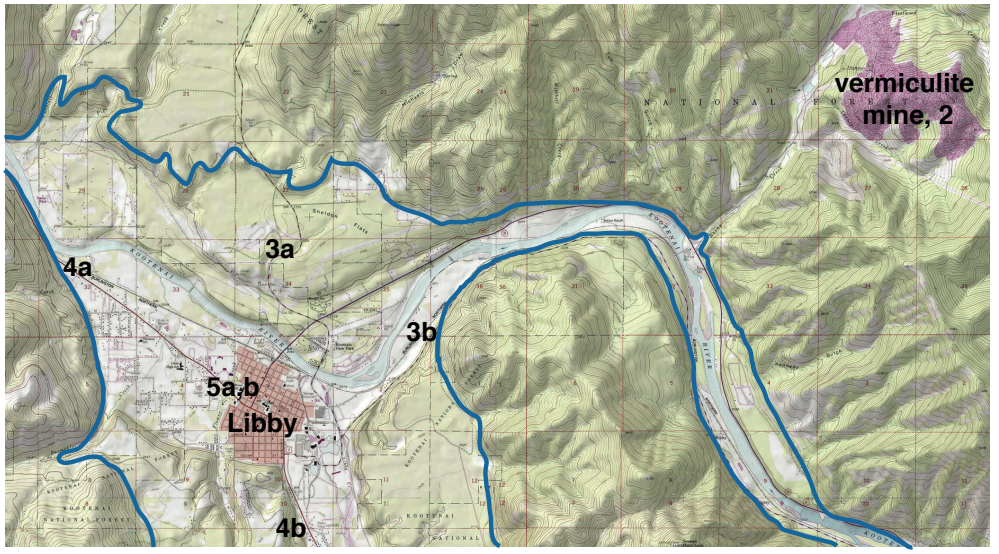

FIGURE 1. A section of a 7.5 min topographic map of Libby, Montana. The blue lines are the approximate boundary of glacial Lake Kootenai. The numbers are sample collection locations keyed to Figures 2–5.

SAMPLE SELECTION AND EXPERIMENTAL METHODS

Sample selection

A series of amphibole samples from the deposit are used as reference materials herein to compare to amphiboles obtained from six soil samples collected at five locations in the Libby area. The soil sample locations are shown on Figure 1 and are referenced to Figures 2–5. Figures 2–5 show amphibole SEM images and EDS spectra for each respective location. The soil samples presented here are a subset of a larger collection of 66 samples from 33 locations, and were chosen to represent the compositions found in the larger suite. The three amphiboles in Figure 2 are from the deposit and represent three species of amphibole: tremolite, winchite, and richterite; note all of which contain observable Na and K in increasing amounts (Sanchez et al. 2008). They were chosen because they represent low, intermediate, and high Na and K content, and are used as our reference amphiboles.

Powder X-ray diffraction

Back-filled cavity mounts were prepared by first sieving the soil to 250 mesh (or <63 μm) and then placing 2 g in a McCrone micronizing mill with 25 mL of methanol for 12 min. Data were collected from 2–42° 2θ with a step size of 0.02° and a count time of 9 s. Scans were also made from 9.5 to 11.5° 2θ with a step size of 0.02° and a count time of 180 s to record the region of the 110 amphibole peak. We used the Rietveld method on the 2–42° 2θ scans to determine the major mineral phases and developed a set of standards (i.e., samples with known added amount of amphibole) for the 9.5 to 11.5° 2θ to obtain detection levels of 0.1% or better (Gunter et al. 2008); however, this method yields only amphibole concentrations and cannot distinguish the compositions of the amphiboles.

Scanning electron microscopy and energy dispersive spectroscopy

Soil samples were prepared for SEM by sieving to 250 mesh (or <63 μm), placing a small amount of material on an aluminum SEM stub covered with carbon tape, and applying a carbon coating. For each elongated mineral particle observed in the SEM, an EDS spectrum was collected at 20 kV accelerating voltage.

RESULTS AND DISCUSSION

We are only reporting herein a small subset of our results from this project, while the larger data set is being analyzed. We feel these results are time-sensitive for Libby, as well as other locations where amphibole asbestos "contamination" may be incorrectly attributed to human activity when natural processes are to "blame," or the offending amphiboles may have come from a non-mining source. As stated in the introduction, our major objective in this study was to determine the amphibole content in soils in the Libby area and to determine what portion of the amphibole were pre- or post-mining (i.e., compare the natural occurrences vs. the contamination from mining). We found all 66 of our samples to contain amphiboles, based on powder X-ray diffraction from tenth's of a percent to several percent (Gunter et al. 2008). What we should have, but did not anticipate was that the majority of the amphiboles (~90%) were not from the Libby vermiculite deposit. The amphiboles originating from the deposit can be distinguished from those not originating from the deposit based on the fact that all of the analyzed amphiboles from the deposit contain Na and K, and Na and K peaks can be seen in the SEM-EDS spectra on amphiboles obtained from soil samples. The ability to use EDS to aid in identification of these amphiboles was also pointed out in Bern et al. (2002) and Eckberg et al. (2007).

Figure 1 shows the distribution of the samples in this study as well as the location of the mine and Libby. Figure 2 shows representative samples from the mine. (Details of the samples are given in the figure captions, and EPMA data are given in Sanchez et al. 2008.) They were selected to show low, intermediate, and high Na and K levels. Wylie and Verkouteren (2000), Meeker et al. (2003), Gunter et al. (2003), and Bandli et al. (2003) all present EPMA data that are in the range of the EDS spectra shown here, with the exception of sample 20 in Meeker et al. (2003) that has a Na + K = 0.5, being slightly lower than our sample shown in Figure 2a [where Na + K = 0.7, Sanchez et al. (2008), Table 2b therein]. Of the 43 samples for which EPMA data are available, 0.5 is the lowest and 0.7 is second lowest value. Note all of these spectra were collected on polished samples prepared for EPMA analysis. For the amphibole particles obtained from the soil samples, this is not possible as the samples are too small.

Figure 3 shows two high-aspect ratio amphibole particles; both were collected from lake sediment in road cuts as noted on Figure 1. In each case, we dug back into sediment so as to obtain an undisturbed, natural sample. The particle in Figure 3a has a composition inconsistent with amphibole originating from the deposit, while the particle in Figure 3b is consistent with amphibole originating from the deposit. Figure 4 shows two more amphibole particles that are slightly wider than the ones shown in Figure 3. The deposit amphibole in Figure 4 was collected in lake sediments in a road-cut, while the non-deposit amphibole was collected with a hand auger at a depth of ~1 m, both would represent a pre-mining time period. Notice how the samples in Figures 3 and 4 were collected around Libby; the

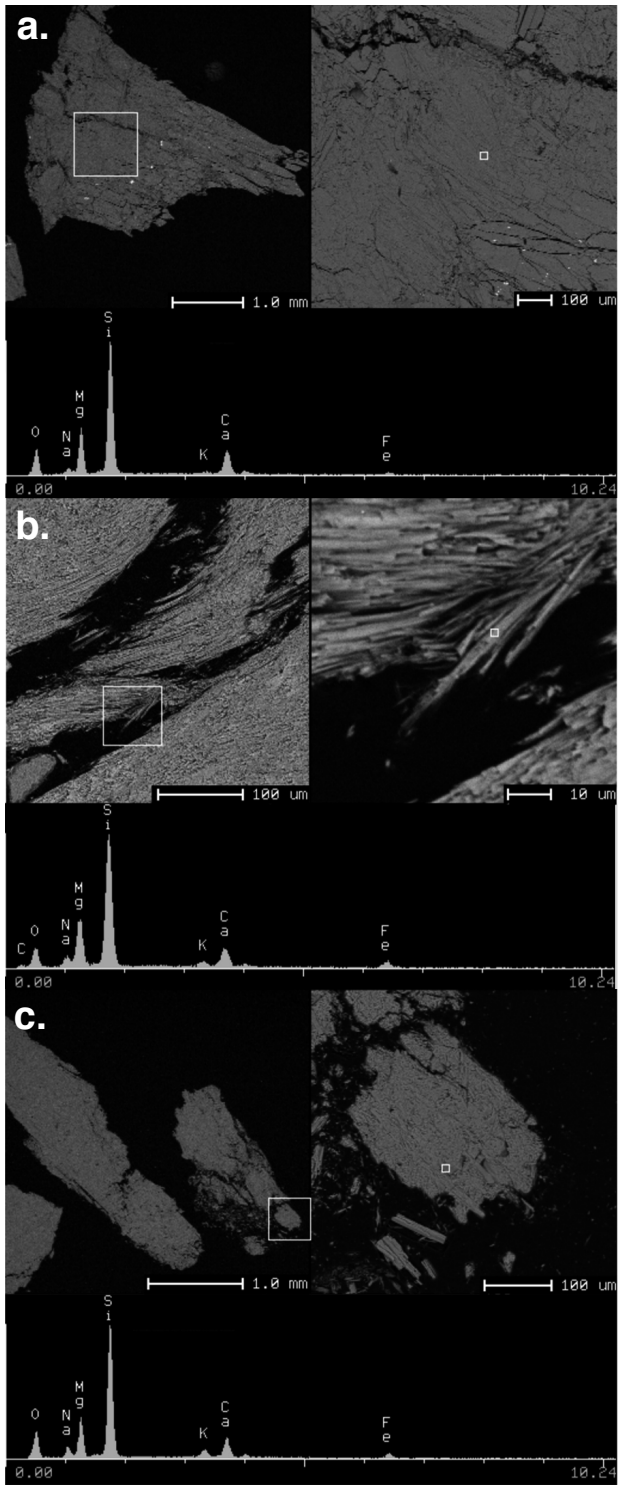

Figure 2. Three sets of SEM images and associated EDS spectra obtained on polished samples of amphiboles from the former vermiculate mine near Libby, Montana: (**a**) Butte 2, (**b**) float, and (**c**) Harvard 1. (Names correspond to those used in Sanchez et al. 2008.) For each, the left image is at lower magnification and contains a box that represents the higher magnification image to the right. The small box on the right image coincides to the locations of the SEM beam, and in turn, the area analyzed in the EDS spectra immediately below the images. Note how the Na and K contents increase from **a** to **b** to **c**.

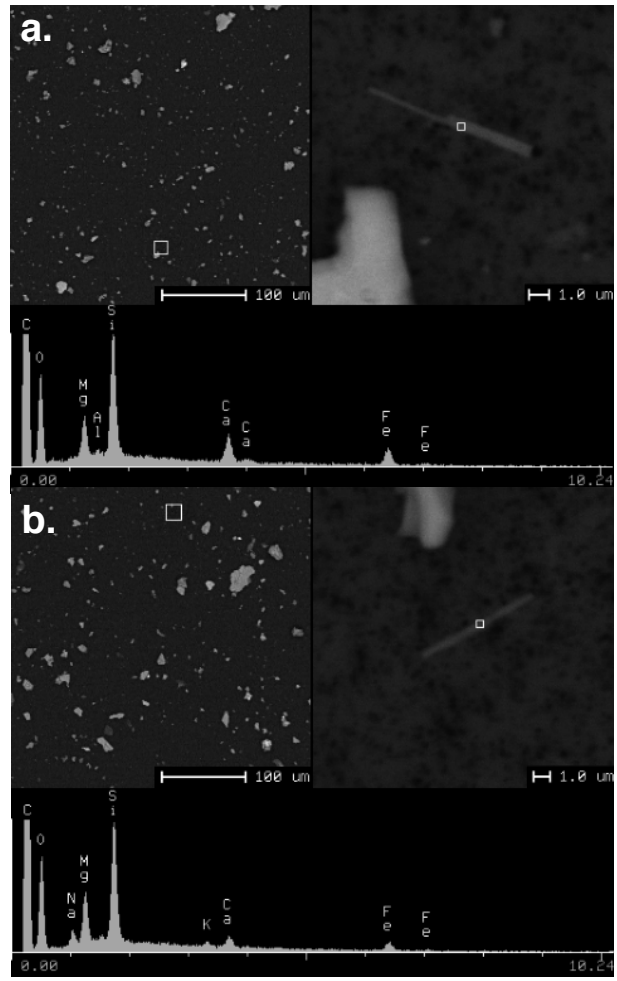

Figure 3. Two sets of SEM images and associated EDS spectra obtained on amphibole particles collected in road cuts of lake sediments located at 3a and 3b on the map in Figure 1. Note the upper EDS spectra is Na and K free, while the lower one contains Na and K, and resembles the EDS spectra shown in Figure 2.

sample in Figure 5 was collected in town just below the grass roots in a schoolyard. Note here that, again, the upper sample is Na and K free (i.e., it has a composition inconsistent with those from the deposit), while the lower sample contains Na and K and has similar composition to those from the deposit. Thus, our results to date demonstrate the ability to distinguish particles with compositions consistent with reference amphiboles obtained from the former vermiculite deposit from amphibole particles with compositions inconsistent with those known to be from the deposit.

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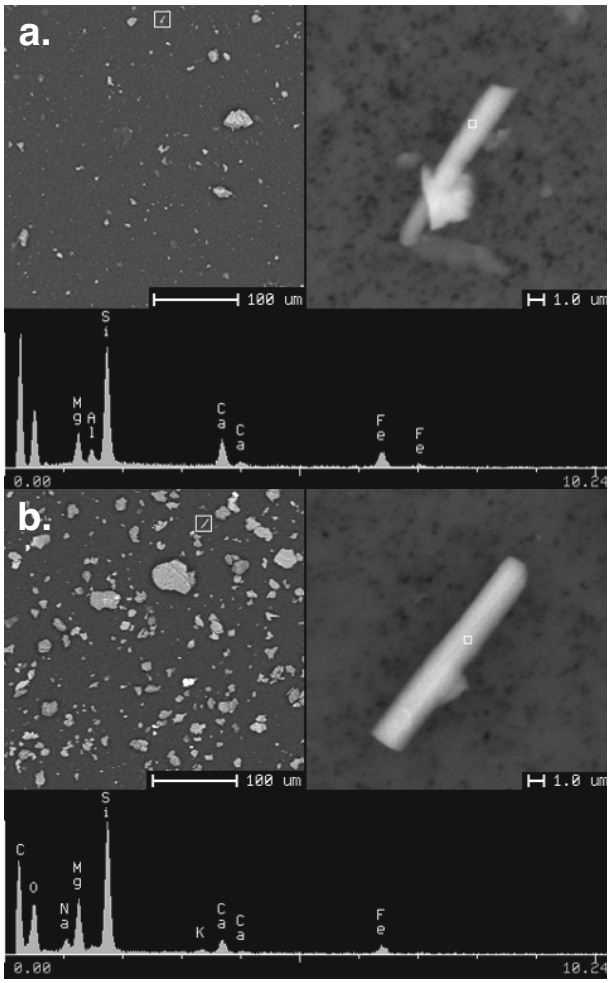

FIGURE 4. Two sets of SEM images and associated EDS spectra obtained on amphibole particles occurring at 4a and 4b on the map in Figure 1. These samples have similar EDS spectra to those shown in Figure 3, but the particles are wider. The upper EDS spectra is Na and K free, while the lower one contains Na and K and resembles the EDS spectra shown in Figure 2.

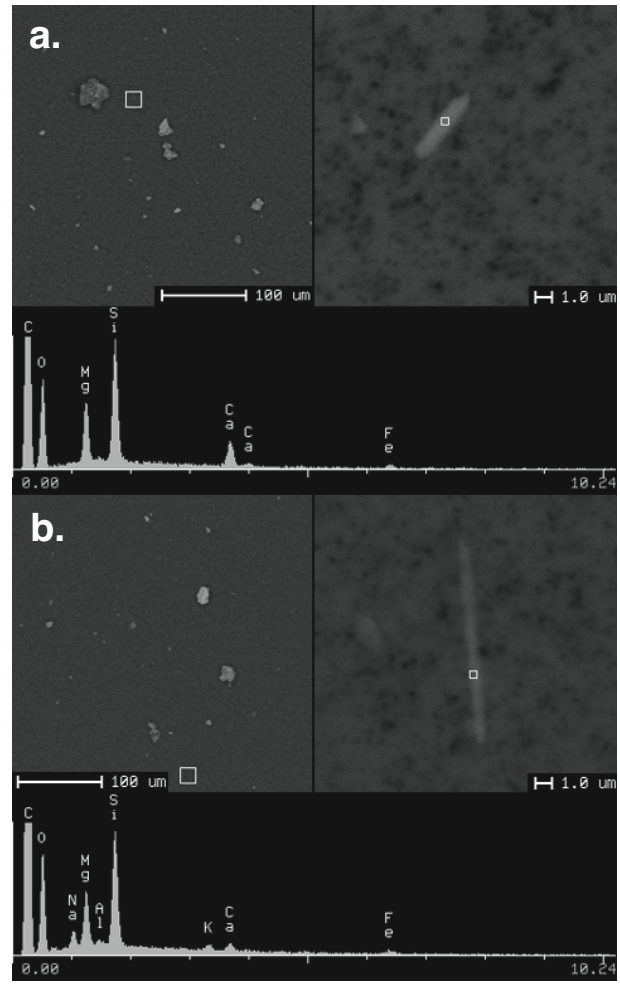

FIGURE 5. Two sets of SEM images and associated EDS spectra obtained on amphibole particles collected at location 5a and 5b on the map in Figure 1. The upper amphibole is not associated with the vermiculite deposit, while the bottom one is, based on the Na and K contents.

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