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Feasibility for Identifying Mineralogical and Geochemical Tracers for Vermiculite Ore Deposits

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ABSTRACT

A review of the geological, industrial, and health literature on vermiculite ore deposits indicates that mineralogical or chemical fingerprints may exist that would allow linking vermiculite in consumer products to a particular source ore deposit. Two characteristics of vermiculite suggest that pursuit of a set of tracers could be successful. First, vermiculite deposits are formed in geochemically distinct, ultramafic environments that may concentrate a unique set of minor or trace elements. Second, vermiculite is a mineral with particularly high cation exchange capacity and is amenable to sequestering and retaining trace elements. A two-phase approach toward identifying suitable tracers is recommended. The first phase would include a screening study of a small set of samples from the few major sources that serve the U.S. market. The screening study would determine whether enough variation exists among ore deposits to yield measurable differences in diagnostic minerals or elements. The screening study would also evaluate whether diagnostic characteristics can be detected in a few selected vermiculite products. If a screening study successfully identifies potential tracers, a second-phase detailed study would use a large set of samples to determine whether tracer variability among ore deposits is greater than variability within a deposit. The second phase would also determine a range of vermiculite products in which characteristics can be measured.

INTRODUCTION

Vermiculite is used as a component of many consumer products sold in the northwestern states within the jurisdiction of Region 10 of the U.S. Environmental Protection Agency. These states include Washington, Oregon, Idaho, and Alaska. EPA investigations at a major U.S. source of vermiculite at Libby, Montana, have shown that asbestiform amphibole minerals occur as accessory minerals in vermiculite ore (Atkinson and others, 1982). Asbestiform minerals have also been reported at other commercial vermiculite deposits. Some of these occurrences are reported at concentrations less than those found at Libby, but most are at poorly known or unknown concentrations. The asbestiform component of vermiculite ores may not be completely removed in the preparation of consumer products, as shown by recent testing of vermiculite garden products (USEPA, 2000). In order to evaluate risk of exposure to asbestos in vermiculite-containing materials, it is important to know which materials contain asbestiform accessory minerals.

As used in this report, asbestos refers to varieties of serpentine and amphibole minerals that have asbestiform characteristics (see Glossary). Asbestiform is used to describe minerals that have a fibrous form with relatively small fiber thickness, large fiber length, flexibility, easy separability, and a parallel fiber arrangement.

Direct analysis of asbestos content can be straightforward when the mineral is concentrated enough to allow easy identification and quantification. However, analysis of very low, but potentially hazardous, concentrations of asbestos in consumer products may require multiple, expensive techniques in order to achieve both certainty in mineral identification and high confidence in reported concentrations. If the presence of unacceptable concentrations of asbestos in commercial vermiculite is largely confined to that derived from only one or a few discrete sources or mines, then some low-cost means of determining the source of vermiculite in consumer products would be advantageous as a tool in screening for products that likely contain asbestos. An efficient screening tool could thereby allow more focused use of expensive asbestos-specific analytical methods on those products from problematic sources.

The goal of this report is to determine if it is a reasonable assumption that a chemical or mineralogical characteristic of vermiculite ore can be used as a tracer to identify the source of vermiculite in consumer products. The goal is not to identify a specific tracer, but rather to determine if pursuit of a tracer might be successful. Specific objectives include the following:

- Conduct a literature search of the occurrence and characteristics of vermiculite, with emphasis on diagnostic features of ore deposits,

- Evaluate the variability of the compositional characteristics of vermiculite ore in light of potential mineralogical or geochemical tracers, and

- Recommend whether additional work or analytical techniques might be successful in identifying a tracer for the source of vermiculite in consumer products.

BACKGROUND

Methods of Vermiculite Formation

Vermiculite is a secondary mineral formed primarily by the alteration of mica, and less commonly by alteration of pyroxene, amphibole, olivine, chlorite, or other clay minerals (de la Calle and Suquet, 1988, p. 455; Bush, 1976, p. 150). Weathering, alteration by ground water, and hydrothermal processes have been proposed as mechanisms for vermiculite formation. Industrial grade vermiculite deposits are believed to be formed both by weathering and ground water alteration of macroscopic mica particles of biotite or iron-bearing phlogopite (Hindman, 1994).

Geochemical environments in which vermiculite forms are generally associated with ultramafic rocks rich in magnesium silicate minerals. Three categories of deposits are common and are described in more detail below (see Overview of Vermiculite Ore Deposits, page 4).

Ore Minerals and Parent Minerals

Vermiculite and its precursors (parent minerals) are part of a broad class of platy minerals called sheet silicates (Table 1). Vermiculite can display a range of compositions depending on the composition of the original parent minerals and the progress of chemical changes during weathering. Table 1 provides a comparative list of the ideal compositions of vermiculite, its micaceous parent minerals, and a selection of other associated minerals that can be found in vermiculite ore deposits. The ideal composition of vermiculite is a magnesium iron aluminum silicate hydroxide hydrate. The hydrate refers to structural water that occurs between silicate layers. In addition to structural water, vermiculite also contains non-structural water in an amount depending on porosity and relative humidity.

The most common parent minerals of industrial vermiculite are phlogopite and biotite mica (Table 1). These two mica minerals are part of a solid solution series of potassium magnesium iron aluminum silicate hydroxides that ranges from a magnesium-rich end member of phlogopite to more iron-rich biotite. Besides vermiculite, another common mineral that forms from mica is mixed-layer mica/vermiculite. In the mixed-layer minerals, interstratified mica and vermiculite can occur with variable amounts of either component in either a random or regular sequence of mixed layers. If the interstratification of biotite and vermiculite is regular the mineral is called hydrobiotite (Brindley and others, 1983). By analogy with hydrobiotite, mixed-layer phlogopite/vermiculite has been referred to as hydrophlogopite by Schoeman (1989, p. 7).

Some disagreement occurs over whether mixed-layer mica/vermiculite can be formed by hydrothermal processes as well as by lower temperature weathering or ground water alteration. Roy and Romo (1957) pointed out that vermiculite was unlikely to form above 200^{O} C. Boettcher (1968) suggested that although vermiculite appeared to be a weathering product at the large commercial deposit at Libby, Montana, hydrobiotite may have formed by hydrothermal alteration. Libby (1975), on the other hand, demonstrated that both hydrobiotite and vermiculite formed by weathering in large commercial deposits in the Enoree district, South Carolina.

The industrial or commercial use of the term “vermiculite” is broader in meaning than the mineralogical definition. Industrial vermiculite refers not only to ideal vermiculite but also to the mixed-layer phases that are interstratified with biotite and phlogopite; that is, hydrobiotite and hydrophlogopite. This report retains the mineralogical meaning of vermiculite as the unstratified mineral and will refer to it as distinct from hydrobiotite and hydrophlogopite (see Glossary).

Product Minerals

Prior to industrial and consumer use, vermiculite is concentrated (beneficiated) by any number of methods that can include screening, floating, or grading. Beneficiated ore is then thermally or chemically treated to spread apart the macroscopic platy layers like an accordion in order to make a lightweight, porous product. This process is called exfoliation or expansion. The commonly used thermal treatment for exfoliation physically expands the layers by flashing, or very rapidly boiling, the interlayer water to steam. The characteristics of the product minerals after the exfoliation process depend on the parent minerals and the length of time the product is held at high temperature.

Industrially exfoliated vermiculite may therefore include partly or completely dehydrated vermiculite or mixed-layer mica/vermiculite. Industrial vermiculite may also include the parent minerals, biotite or phlogopite, which may have been ineffectively removed during beneficiation. Consequently, the mineralogical characteristics of vermiculite in the product materials may depend as much on the beneficiation and exfoliation processes as on the original ore. For example, the relative amount of vermiculite, mixed-layer mica/vermiculite (hydrobiotite or hydrophlogopite), and parent mica (biotite or phlogopite) strongly depends on the efficiency of beneficiation, and on the temperature and duration of heating during exfoliation.

Several other major, minor, and trace minerals in the original ore may also occur as minor or trace minerals in the exfoliated vermiculite product. Minerals that are mined along with ore but are generally unwanted in the final ore product, are known as gangue. Table 1 includes a selection of minerals in addition to vermiculite, that may be common in vermiculite ore. The presence of gangue in vermiculite products depends on the efficiency of the beneficiation process. Examples of studies that have documented the presence of non-vermiculite minerals in beneficiated or exfoliated vermiculite products are discussed below in Accessory Minerals (see p. 14).

OVERVIEW OF VERMICULITE ORE DEPOSITS

For ease of reference in discussion of ore deposits, the usage of several terms is noted here; see the Glossary for additional terms. In this report, a mineral occurrence refers to a concentration of a particular mineral or minerals in earth materials, regardless of the degree of concentration. A mineral deposit refers to a mineral occurrence that might be concentrated enough to be economic; an ore deposit is economic. Economic deposits are those that are concentrated enough to be profitable to mine. Mines occur at deposits that have undergone some extractive development of ore. Ore is the naturally occurring earth material from which valuable minerals can be extracted. Ore minerals are that part of ore that is of economic value, whereas gangue is that part of ore without value.

This report reviews the mineralogical and geochemical characteristics of vermiculite and some of the associated minerals by focusing primarily on deposits that are either within the United States, or which are likely to be the source of imports to the U.S. (Figure 1, Table 2). Within the United States, vermiculite deposits occur in twenty of the fifty states (Bush, 1976), but ore has been mined in only six states, and in the last quarter century, only from Montana, South Carolina, and Virginia. As of 1998, the major operating vermiculite mines in the U.S. included the W.R. Grace mines near Enoree, South Carolina, and the Virginia Vermiculite Ltd. mines near Woodruff, South Carolina, and Louisa County, Virginia (Potter, 1998). In addition, the Elk Gulch deposit operated by Stansbury Holdings Corporation and Dillon Vermiculite L.L.C. near Dillon, Montana, has produced small amounts of ore sporadically since 1990 (Berg, 1997).

For many years, the W.R. Grace mine (Rainy Creek) at Libby, Montana was the world’s largest producer of vermiculite, but since the mine’s closure in 1990, the Palabora deposit near Phalaborwa, Transvaal, Republic of South Africa has become the world’s largest producer (Hindman, 1994). In 1998, the United States producers sold approximately 170,000 tons of vermiculite while the U.S. imported approximately 68,000 tons. Approximately 60% of the imports came from Palabora in South Africa and 35% from Xinjiang Province in China (Potter, 1998). The Libby closure eliminated the only domestic source of coarse-sized concentrates with flakes greater than 2 mm across, and by the end of 1991 essentially all such coarse vermiculite was obtained from foreign sources (Hindman, 1994).

Economic vermiculite deposits commonly occur in ultramafic intrusive rocks, such as coarse-grained pyroxenites, and metamorphic bodies containing biotite schists and gneisses. The ore is generally 20-35% vermiculite (Hindman, 1994). Most vermiculite deposits are associated with ultramafic igneous or metamorphic rocks cut by igneous intrusions of silicic, alkalic, and carbonatitic rocks. While the deposits can be grouped into three categories following the classification system described by Bush (1976), below, there are strong similarities among all three.

> **Type 1.** The largest deposits form in large ultramafic intrusive bodies, some of which are zoned, and are cut by intrusions of syenite, carbonatite, or both. Examples are Libby, Montana and Palabora, South Africa.
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> **Type 2.** Deposits occur in small to large unzoned dunite, pyroxenite, or peridotite intrusive bodies that are cut by pegmatite, syenite, or granite. These deposits vary in size, but most are small. They are characteristic of the Blue Ridge region of the southeastern U.S. Examples are the North Carolina deposits. None of the currently active mines in the U.S. are found in Type 2 deposits.
>
> **Type 3.** The most common deposits of this type are found in layered ultramafic schist that has been cut by pegmatite, less commonly by pyroxenite or peridotite. This type includes the second largest productive district in the U.S., in the Piedmont of South Carolina. Examples are the Enoree district, South Carolina; Louisa County, Virginia; and most of the deposits in Colorado, Wyoming and Texas.

Type 1 Examples

Libby, Montana

The Rainy Creek mine in the vermiculite deposit at Libby, Montana (Figure 1) was the major commercial source of vermiculite in the world for many years. Detailed mapping by Boettcher (1966) shows that the vermiculite is found within a concentrically zoned complex of igneous intrusions that include biotite pyroxenite and biotitite, a rock made up of almost pure biotite. Both of these ultramafic intrusions are cut by alkaline pegmatites. In addition, Boettcher (1966) describes late-stage hydrothermal veins that are widely distributed in the igneous complex and adjacent rocks. Most of the biotite has been altered to hydrobiotite and vermiculite. The pegmatites have altered the pyroxenite to fibrous soda-rich amphiboles along their contacts with the pyroxenite. Alteration zones are generally less than a foot wide and are reported by Boettcher (1966, p. 82) to be composed mainly of “mass-fiber tremolite,” an amphibole in asbestiform habit.

The pyroxenite surrounding the biotitite contains the vermiculite ore zone, which consists of mostly diopside, hydrobiotite, and apatite. Fibrous amphibole is found both in veins and disseminated throughout the intrusive rock in thin layers along cleavage planes of the pyroxene. Thin veins (approximately one inch) are common throughout the deposit, while thicker veins with quartz cores are less common (Bassett,1959). Boettcher (1966, p. 103) notes for late-stage hydrothermal veins that, “Most of the tremolite in the small stringers is cross-fiber material, but the bulk of this mineral is a compact, mass-fiber variety...” The fibrous minerals were sufficiently abundant that early in the history of the Libby deposit, several companies were active in the development of tremolite asbestos deposits along with the vermiculite in the Rainy Creek complex (Boettcher, 1966, p. 7).

The mineralogical characteristics of the varieties of amphibole asbestos at Libby are currently under study (G. Meeker, USGS, personal communication, 2000). The widespread amphibole was described as tremolite and “soda-rich tremolite” by Boettcher (1966, p. 102). Boettcher also described another amphibole, asbestiform richterite, as occurring in an unusual tabular body within the complex that also contains vanadium-rich pyroxene, plus strontianite, barite, and copper and zinc sulfides. Larsen (1942) reported an analysis for richterite that was included in the dissertation by Boettcher (1966) as well as in the compilation by Deer, Howie, and Zussman (1997). Wylie and Verkouteren (2000) reviewed the amphibole nomenclature with respect to asbestiform amphiboles from Libby, and found reference to “tremolite, actinolite, soda tremolite, richterite, and winchite.” In their own analyses of two samples from Libby, Wylie and Verkouteren (2000) identified asbestiform winchite as defined under the most current amphibole nomenclature of Leake and others (1997), but stated that the mineral could have been called a soda tremolite, sub-calcic actinolite, or richterite under older naming conventions. Because of the variability in chemical composition that may be common among amphibole minerals, determination of the full range of fibrous amphibole varieties that exist at Libby awaits a more complete study of many more samples representative of the whole mine, and the use of current nomenclature.

With respect to other characteristic minerals at Libby, the unusual vanadium-rich pyroxenes are also associated with some of the hydrothermal veins in the complex, as are some rocks high in titanium. Fluorapatite is a common accessory mineral throughout the Libby deposit and is found enclosed in the pyroxene grains and in the books of vermiculite, hydrobiotite, and biotite. A magnetite-rich zone surrounds the vermiculite zone, but the ore zone itself is described as being relatively low in iron (Boettcher, 1966).

A few studies have specifically examined fibrous minerals in raw, beneficiated, and exfoliated ore from Libby. Rohl and Langer (1977) reported the presence of chrysotile asbestos in addition to amphibole asbestos in Libby ore. A study by the EPA (USEPA, 1980) reported asbestiform tremolite as a contaminant in the exfoliated vermiculite product from Libby at a concentration of at least 1%. A subsequent detailed mineralogical study commissioned by the

EPA looked at various grades of beneficiated ore and found fibrous tremolite-actinolite at a concentration of 2-7%, with the higher concentrations being in the finer-sized grades of unexfoliated vermiculite (Atkinson and others, 1982). A sample of “head feed” from the Libby mill contained 21-26% fibrous tremolite-actinolite (Atkinson and others, 1982). Moatamed and others (1986) later reported fibrous amphibole identified as actinolite at a maximum concentration of 2% in unexfoliated vermiculite ore from Libby and 0.6% in the exfoliated product, both collected at an exfoliation plant in Utah.

Palabora, South Africa

Potter (1998) reported that 65% of vermiculite imported into the U.S. in 1996 came from South Africa. The Palabora mine, near the town of Phalaborwa in the Republic of South Africa (Figure 1), is the source of the imported vermiculite. The Palabora deposit has many features in common with the Libby deposit. The Palabora Igneous Complex is also a zoned deposit with ultramafic rocks (pyroxenite) at its core. Here the ultramafic deposits were also intruded by alkalic rocks, most of which are syenitic in composition.

One significant difference between the Palabora deposit and the Libby deposit is that the primary mica at Palabora is phlogopite rather than biotite, and the mixed-layer mica/vermiculite alteration product that forms the vermiculite ore is hydrophlogopite rather than hydrobiotite (Palabora Mining Company, 1976; Schoeman, 1989; Evans, 1993). Minor hydrobiotite is present at Palabora but is not mined, as it is finer-grained, and thus of a lower economic grade (Schoeman, 1989).

There are three separate open-pit mines in the Palabora Complex. Along with the vermiculite mine, there is a copper mine (also known as Loolekop) which has byproducts of magnetite, apatite, gold, silver, zirconium, uranium, and nickel as well as a pit in the world’s largest igneous phosphate (apatite) deposit. The relationship among these deposits is not well understood, but some work has shown that copper sulfide liquid was present early in the crystallization sequence (Evans, 1993).

The vermiculite is mined from a coarse-grained zoned ultramafic body that consists of phlogopite-serpentinite rock enveloped by phlogopite-diopside rock. Apatite at Palabora is so abundant in some of the rock types that it is found in economic concentrations over large areas, but apatite content in the ultramafic rocks is quite variable (Palabora Mining Company, 1976).

Carbonatites are a source of rare earth elements (REE), and at Palabora, they have been evaluated for potential economic extraction. It is not clear whether the rare earth elements are found specifically in the vermiculite orebody or are restricted to the separate Loolekop orebody. The Loolekop copper orebody contains uranothorianite (a variable oxide of uranium and thorium) and baddeleyite (zirconium oxide with a trace of hafnium) (Palabora Mining Company, 1976). While these minerals are present in small amounts, both are considered economically recoverable. It was not determined if these unusual minerals exist within the vermiculite ore deposit.

No mention of fibrous minerals in the Palabora deposit was noted in the geological literature, but some reports were found in the industrial and health literature. In a report contracted by Mandoval, Ltd., Chatfield and Lewis (1979) examined vermiculite ore from Palabora for chrysotile asbestos fibers. They suggest that chrysotile-like fibers (about 2 ppm) in South African ore are instead rolled-up scrolls of vermiculite. These scrolls are described as forming at the cracks in vermiculite plates, becoming tubular in appearance, and forming bundles similar to chrysotile (Chatfield and Lewis, 1979, 1980).

Moatamed and others (1986) also found what they described as "rolled vermiculite" fibers from Palabora ore sampled from a rail car at a plant in Utah that used vermiculite in chemical processing. In addition, they reported the presence of actinolite and rare anthophyllite fibers with a low length-to-width ratio. According to Moatamed and others (1986, p. 214), the unexfoliated ore they analyzed contained 0.4% fibrous amphibole. However, elsewhere the report describes the South Africa sample as being distinguished by "a near absence of fibers" (p. 215). The method used for quantification was listed as X-ray diffraction, which leaves some uncertainty as to whether the percentage reported includes solely fibrous, or both fibrous and non-fibrous, amphibole.

In an article evaluating the health of South African vermiculite workers, baghouse dust at Palabora is described as containing small amounts of asbestos fibers (Hessel and Sluis-Cremer, 1989). The mineralogy of the fibers was not determined, but the authors state that it "may be tremolite" (p. 22). Both the statements regarding asbestos in baghouse dust and its likely mineralogy are cited as personal communications, with no additional documentation. Fiber counts in the mill air filter samples were done in 1987, and eight samples varied from 0.27 to 0.80 f/ml, which, according to Hessel and Sluis-Cremer (1989, p. 22), are similar to counts measured in Libby around 1980. It is important to note that the measurement of fibers per milliliter of air sampled is a measure of potential exposure at the mill and not an estimate of the amount of fibrous minerals present in the ore or in consumer products. Exposure measurements are affected by the milling methods, indoor air control, personnel movements, and other factors as well as the abundance of fibers in the ore.

The Palabora ore is described in an EPA report as being "essentially free of asbestiform fibers" (USEPA, 1980, p. 4), a statement based on the work of Chatfield and Lewis (1979). Analyses of the ore for asbestiform minerals have been commissioned by Mandoval, the European distributor of Palabora ore. A recent such report by the Institute of Occupational Medicine in Edinburgh (IOM, 2000) includes analyses from samples of six grades of commercial vermiculite from Palabora. Samples were analyzed by polarized light microscopy, and reported to have a detection limit of 1 ppm. No amphibole or chrysotile asbestos fibers were reported in any of the samples, and further quantification efforts using electron microscopy and X-ray diffraction were not conducted.

Type 2 Examples

North Carolina Deposits, Blue Ridge Mountains Province

This type of vermiculite occurrence is common, but has not produced any of the large economic deposits. Numerous bodies of dunite and peridotite have intruded metamorphic country rock. Vermiculite is found in veins and lenses along the serpentinized contact between the two rock types. Many of the vermiculite deposits are associated with pegmatites (Bush, 1976).

Unusual accessory minerals include nickel silicates and corundum. Talc is also a common accessory. Anthophyllite is mentioned as a "byproduct" in some deposits and has been mined locally. The anthophyllite is not specifically described as fibrous, but elsewhere "asbestos" (mineralogy unknown) is said to have been mined along with corundum in a vermiculite-containing deposit (Murdock and Hunter, 1946). Chrysotile is reported to occur in one of the deposits in veins and in clusters of fibers. In the Day Book dunite (Figure 1), vermiculite is present as hydrophlogopite outside a talc zone and within a zone of "asbestos" (Kulp and Brobst, 1954).

Type 3 Examples

South Carolina Deposits

The most numerous vermiculite deposits of the United States are in potassic ultramafic intrusions that have been regionally metamorphosed and cut by pegmatites. These deposits are found in several of the belts within the Piedmont physiographic province of the southeastern U.S. The cores of potassic ultramafic bodies are "biotitites," composed almost wholly of biotite. They were intruded as small plutons into biotite gneisses, and they host occurrences of similar vermiculite-bearing rocks as scattered occurrences from Georgia to Virginia (Libby, 1975).

The economic deposits contain primarily hydrobiotite, which is found in the upper portion of the biotite intrusions (Maybin and others, 1990). In his dissertation on the Enoree district (Figure 1), Libby (1975) distinguished two types of vermiculite deposits, which he denoted by the prefixes "V-" and "HB-" to distinguish those that were dominated by vermiculite from those that were dominated by hydrobiotite. The hydrobiotite-bearing deposits have been preferentially mined because of superior commercial properties compared to vermiculite (Libby, 1975, p. 30).

Fluorapatite is a common accessory mineral in the South Carolina deposits. Sphene is an ubiquitous minor phase in the "HB" deposits at Enoree, occurring as wedges between the flakes. Zircon is widely dispersed throughout the plutons (Libby, 1975). Other accessory minerals include talc, chlorite, chromite, rutile, zircon, titanite, corundum, anatase, and amphibole asbestos (Hunter, 1950).

At some of the deposits in the Enoree district, amphibole asbestos has been found associated with the vermiculite. The amphibole, identified by Libby in his dissertation as tremolite, is described as occurring in two forms in the HB-biotitites, as a fibrous variety mantling pyroxene and as stubby euhedral to subhedral crystals. In the V-biotitites, the tremolite is found in the same two forms, but a larger proportion of it is described as being of the fibrous variety (Libby, 1975).

A study commissioned by the EPA (Atkinson and others, 1982) examined samples from two mills that processed ore from some of the mines in the Enoree district. This study, which looked at the fibers using X-ray diffraction, identified some of the tremolite from Enoree as being sodium-bearing. The same study also described the South Carolina samples from the two mills as varying somewhat depending on source location. Tremolite-actinolite and anthophyllite were found as mixed bundles of fibers from the W.R. Grace mill at Enoree and separately at the Patterson mill (Table 2). Bulk samples from both the Grace and Patterson mills were reported as containing “<1%” fibrous minerals (Atkinson and others, 1982). At the Grace mill, some of the vermiculite was intergrown with the amphibole fibers, and some occurred separately in a fibrous habit.

Louisa, Virginia

There is minimal information available in the geological literature describing the Virginia Vermiculite mine in Louisa County, Virginia (Figure 1). The deposits were briefly described long before the mine completed its first year of production in 1979 (Meisinger, 1979). Gooch (1957) described deposits in Louisa County as mafic rocks intruded by a series of small pegmatites. In the same area, he described some lenses of vermiculite that were 20 feet thick and more than 100 feet long. Not long before the opening of the mine, Bush (1976) classified the Louisa deposit as Type 3 and suggested that it may be similar to the South Carolina deposits.

Limited information on asbestos content at the Louisa deposit occurs in the health literature. Rohl and Langer (1977) found both amphibole fibers and chrysotile fibers in all six of the ore samples from the Virginia vermiculite deposit that they examined. The chrysotile asbestos was found both as individual fibers and in bundles. The amphibole was described as varying widely in composition, but with more than half being near the range of compositions for actinolite.

Moatamed and others (1986) sampled Virginia ore collected from a rail car at a plant in Utah that used vermiculite in chemical processing. An ungraded vermiculite sample was reported to contain traces of fibrous amphibole (1986, p. 214), with actinolite “mostly as cleavage fragments with a low length to width ratio (p. 217).” Moatamed and others (1986) reported 1.3% amphibole in both unexfoliated and exfoliated ore, although the report is unclear as to whether these concentration measurements represent total, rather than fibrous amphiboles.

Dillon, Montana

The Elk Gulch mine, near Dillon, Montana (Figure 1), has produced small quantities of ore intermittently since 1990 (Berg, 1997). The vermiculite occurs with hydrobiotite in pods and stringers along the contact between an ultramafic body and the gneisses it intrudes. A biotite schist developed at the contact of the ultramafic bodies with the enclosing gneiss, and has weathered to form vermiculite (Desmarais, 1976).

The ultramafic body is composed of hypersthene, amphibole (actinolite-tremolite, anthophyllite, cummingtonite), spinel, and olivine. The ultramafic rocks have been prospected for nickel, which has been found, but not in economic concentrations. The deposit contains a distinctive cinnamon-brown anthophyllite (non-fibrous) which may be present in the ore zone as well (R. Berg, personal communication, 2000).

The ultramafic rock has been serpentinized in places and chrysotile asbestos veinlets a few millimeters thick surrounded by massive serpentine are conspicuous locally (Berg, 1995). Analyses performed on drill core samples showed detectable amounts of asbestiform actinolite in one sample, and anthophyllite in another. Additional samples from the ultramafic zone bordering the deposit showed low but detectable amounts (<0.75%) of fibrous actinolite/tremolite and chrysotile asbestos. Transmission electron microscopy (TEM) results indicated asbestiform fibers made up less than 0.1 % of the sample (MDEQ 1999).

A health risk summary report (Behre Dolbear and Company, 2000) conducted for the company developing the mine reported fibrous talc and fibrous biotite as well as chrysotile and asbestiform anthophyllite and tremolite-actinolite. The report estimates that amphibole asbestos minerals make up less than 0.001% (10 ppm) of the ore prior to processing.

Unclassified Examples

Insufficient information is available to place the following deposits into one of the three types described above. They are noted here to indicate the degree to which other deposits are found in similar geologic environments and contain distinctive accessory minerals, such as fibrous amphiboles.

Hafafit, Egypt

In a group of small deposits near Hafafit, Egypt (Figure 1), asbestiform minerals and vermiculite are found where ultramafic rocks which have been altered to serpentinite are cut by pegmatites (El Shazly, 1975a, 1975b). Both asbestos and vermiculite have been mined from the area, but neither are known to be imported into the United States. Phlogopite, hydrophlogopite and vermiculite are found in association with asbestiform anthophyllite and lesser amounts of asbestiform actinolite and tremolite. Other minerals associated with the deposit include serpentine, talc, and apatite.

Russian Deposits

Several types of vermiculite deposits are found in Russia (Vorovikov, 1973). Deposits are found in the Ural Mountains, the Kola Peninsula, Kazakhstan, and other areas (Figure 1). Among these, Vorovikov (1973, p. 172) reported Kovdarsk to be the largest deposit on the Kola Peninsula. Commercial vermiculite deposits are associated with ultramafic intrusions of dunite and pyroxenite as well as alkaline intrusions. The vermiculite minerals are described as alteration products of both biotite and phlogopite (Vorovikov, 1973). One type of deposit is described as being associated with pegmatites, corundum, talc, asbestos and other deposits as well as with veins in serpentinites. The type and concentration of asbestos found in association with the vermiculite is not specified. Vermiculite from the Russian deposits is not known to be imported into the U.S.

Chinese Deposits

Potter (1998) reported that approximately 35% of the vermiculite imported into the US in 1996 came from China, with the remaining 65% coming from South Africa. Using the estimated domestic production for 1996, this would mean that the Chinese imports made up approximately 10% (24,000 metric tons,) of the total vermiculite used in the United States. An industry estimate of Chinese imports for 1998 (Moeller, 2000) reported 40,000 tons (22% of imports) as coming from the Qieganbulake deposit in the Xinjiang Province (Figure 1).

Little information is available in English on the geology or mineralogy of the Chinese deposits. Tongjiang and others (1996a, 1996b) describe phlogopite, vermiculite, and mixed-layer phlogopite/vermiculite in the Weili deposit, Xinjiang, which appears to be one of the few major commercial deposits other than Palabora with phlogopite as the main mica mineral associated with vermiculite. Rongqi and Junchen (1993) describe the same group of minerals at Tseganbrark, Xinjiang.

POTENTIAL TRACERS

A review of the mineralogy and geochemical variability among the major vermiculite deposits may provide a basis for anticipating potentially significant compositional differences. If sufficiently unique, such differences may then provide a fingerprint with which vermiculite in a commercial product may be traced back to a particular ore deposit. Table 3 lists a selected group of minerals, including vermiculite, mixed-layer mica/vermiculite, parent mica, amphiboles, serpentine, talc and apatite found in most if not all vermiculite ore deposits which serve the U.S. market. The relative abundance of these minerals varies somewhat with locality, but they generally are all present. Some pertinent characteristics of the major commercial deposits are discussed first for vermiculite and parent minerals, and then for accessory minerals.

Mineralogy

Vermiculite and Parent Minerals

All of the deposits producing commercially important vermiculite are derived from alteration of a parent mica, either biotite or phlogopite. The presence of either biotite or phlogopite in a vermiculite product would suggest that the ore came from a deposit rich in that particular parent mineral. Phlogopite is reported as the main parent mineral for vermiculite at only one of the major producers for the U.S. market, that at Palabora (Table 3). However, the Weili and other deposits in China, a small but steadily increasing contributor to U.S. vermiculite consumption, apparently also have phlogopite as the main mica parent mineral (Tongjiang and others, 1996b; Rongqi and Junchen, 1993). Phlogopite has been reported as the parent mica for vermiculite deposits in North Carolina, Texas, and Egypt, but these are not current producers for the U.S. market.

The phlogopite/biotite ratio in a vermiculite product may therefore provide a potential signature for the Palabora and at least some of the Chinese ore deposits, provided no other sources of a phlogopite-bearing vermiculite have entered the U.S. market. Color can be a means of distinguishing large flakes of darker biotite from somewhat lighter phlogopite. Since the two minerals are part of a solid solution series that varies mainly in iron content accompanied by only subtle structural change (Brindley and Brown, 1980), the discrimination of phlogopite from biotite can be achieved with chemical analysis. Reflectance spectroscopy can also be a useful method of discrimination (G. Swayze, personal communication, 2000).

Mixed-layer mica/vermiculite, either hydrobiotite or hydrophlogopite, has been reported at all major commercial deposits (Table 3). In fact, there is some evidence that the presence of mixed-layer mica/vermiculite is what makes a vermiculite ore particularly amenable to producing a durable, exfoliated material. For example, Libby (1975) reported that when non-mixed-layer vermiculite is exfoliated, the resulting material tends to be more brittle and subject to pulverization.

Hydrobiotite at some deposits, such as Enoree, is reported to occur in more or less concentrated pods within the orebody (Libby, 1975), potentially leading to distinctive but temporally variable vermiculite/hydrobiotite ratios in the product. The beneficiation process, however, should tend to mix different qualities of vermiculite ore so that a more uniform product results with a less variable vermiculite/hydrobiotite ratio than found in the raw ore. No report has been found for any of the ore producers that would indicate mining or milling procedures specifically attempt to segregate products that have widely different ratios of vermiculite to mixed-layer mica/vermiculite. Therefore a unique ratio of these minerals in a vermiculite product may not be found to be a useful signature.

As previously noted, the process of exfoliation alters the mineralogical characteristics of both vermiculite and mixed-layer mica/vermiculite by removal of water. The degree of dehydration that accompanies exfoliation measurably alters the mineral structure providing a potential useful identifier. The exfoliation process, however, may occur at any of a large number of exfoliation plants across the country rather than at the original mine sites. As many as nineteen exfoliation plants were active in 1999 (Potter, 2000). Since exfoliation plants may receive both domestic and imported ore from a variety of mines, the potentially unique mineralogical effects of exfoliation of a particular ore material may be confounded by different operating conditions at different plants and by mixing with ore from more than one source. Consequently, though the mineralogical structure of vermiculite may be distinctively different in various consumer products, evaluation would be needed to be certain the difference is not due more to the characteristics of the exfoliation process rather than the ore deposit. Other than changes in water content, the chemical compositions of individual mica and vermiculite phases would not be expected to change during exfoliation and could remain potentially unique identifiers of the individual mine sites, as discussed below in the section on Chemical Composition (see p. 15).

Accessory Minerals

The classification of vermiculite ore deposits (see p. 5) emphasizes the zoned nature and distinctive rock types associated with vermiculite deposits, for example ultramafic rocks intruded by alkaline magmas. Zoning derived from magmatic, metamorphic, hydrothermal, or weathering processes would tend to provide a wide variety of minerals within a single ore deposit. On a broader scale, the vermiculite-forming processes as described in the literature for the different commercial ore deposits have a common ultramafic thread, tending to make mineral suites similar from deposit to deposit. Under such conditions, the variability in minerals may likely be as great within a deposit as among deposits.

Table 3 notes that amphibole, serpentine, talc, and apatite accessory minerals have been reported for most ore deposits for which information is available. Perhaps the best potential mineralogical tracers among the accessory minerals are the amphiboles, which are relatively abundant at all sites and which have a wide range of compositions. Additionally, fibrous amphiboles (asbestos), which are the impetus for this evaluation, are reported for all sites though in highly variable and debatable amounts.

Few studies in the literature have sought to contrast in detail both vermiculite and accessory minerals at vermiculite ore deposits. Perhaps the most detailed to date is the study contracted by the EPA that examined material from the W.R. Grace Rainy Creek mine at Libby, Montana, and the W.R. Grace and Patterson mills in the Enoree district, South Carolina (Atkinson and others, 1982). The variability of vermiculite and accessory minerals from raw ore and beneficiated ore, as reported by Atkinson and others (1982), is shown in Figure 2A for Libby and Figure 2B for Enoree samples representing one point in time. The diagrams indicate the change in relative abundance of the minerals as raw ore with 20-40% vermiculite is concentrated into beneficiated ore with 65-95% vermiculite. The data from both localities indicate continued presence of the same accessory minerals in the beneficiated ores, notably amphiboles in the range of 2-16%. Differences in beneficiated ore among localities include a relatively greater proportion of talc and apatite at Enoree, and biotite, pyroxene, and calcite at Libby. Data from Atkinson and others (1982) show that the accessory mineral patterns are carried through to exfoliated ore from the Enoree site (Figure 2B). Though the total amphiboles remain high in beneficiated ore from both localities, the Libby site retains a higher component of fibrous amphibole of up to 7% compared to less than 1% at Enoree (arrows in Figures 2A and 2B). The relative amounts of accessory minerals in beneficiated ore may therefore provide a signature for at least one point in time for ore from a particular site. Accessory minerals can change significantly with location within a deposit, however, leading to variation in the ore as different parts of a mine are developed. Furthermore, dilution with minerals from other material in a mixed consumer product may mask such an accessory mineral signature.

Chemical Composition

Major and Minor Elements

Table 4 lists oxide and element concentrations for vermiculite ore minerals (vermiculite, mixed-layer mica/vermiculite, and mica) from deposits that serve the U.S. market. Values for oxide weight percent in Table 4A are taken from the literature; element concentrations in Table 4B are recalculated from the oxide values. Sources of data include vermiculite, hydrobiotite, and biotite in mine samples from Libby, (Boettcher, 1966); vermiculite, hydrobiotite, and biotite in mine samples from several Enoree deposits (Libby, 1975); vermiculite, hydrobiotite, and phlogopite in orebody samples from Palabora (Schoeman, 1989); hydrophlogopite and phlogopite in mine samples from Tseganbrark, Xinjiang (Rongqi and Junchen, 1993); vermiculite concentrates from Libby (Bassett, 1959); and vermiculite concentrate from Louisa, Enoree, Palabora, and Qieganbulake, Xinjiang (Hindman, 1984).

The limited data set suggests that some gross discrimination among biotite-derived versus phlogopite-derived deposits may be made on the basis of major elements associated with the phlogopite-biotite solid solution series. For example, Figure 3 shows the relationship between the ratio of magnesium to magnesium plus iron [Mg/(Mg+Fe)] versus ferric iron concentration. Ferric iron allows discrimination of the parent mica minerals, biotite (EB and LB in Figure 3) and phlogopite (XP and PP) from the more oxidized vermiculite and mixed-layer mica/vermiculite (uncircled symbols). The Mg/(Mg+Fe) ratio in turn allows some discrimination of the more magnesium-rich phlogopite-derived vermiculite from Palabora and Xinjiang (dashed tie-lines on the right side of Figure 3) from the biotite-derived material at Libby, Louisa, and Enoree (dotted tie-lines). Of commercial ore deposits that serve the U.S., only the imported deposits are largely phlogopite-derived, and hence more enriched in magnesium. These data, therefore, suggest a potentially useful method for discriminating the more magnesium-rich, imported materials from domestic sources.

Not all of this sparse data set would support a general rule for discriminating sources on the basis of major elements, however. For example, one sample of Enoree vermiculite (EV) plots in the magnesium-poor, ferric iron-rich region of Figure 3 as would be expected considering the biotite parent mica, but another sample of Enoree vermiculite plots in the magnesium-rich, ferric iron-poor region more suitable for a phlogopite parent mica. Likewise, the few data points for the mixed-layer mica/vermiculite samples do not all support a general rule on discriminating imports. For example, the only chemical data found for a Palabora mixed-layer mica/vermiculite were for a hydrobiotite (PH in Figure 3) rather than for hydrophlogopite which is described in the literature as the dominant mixed-layer mica/vermiculite at that mine (Schoeman, 1989). Therefore, the utility of major-element relationships among deposits would need more extensive samples and better documentation of samples and analytical methods to support a consistency in patterns.

Data for minor elements may also show potentially diagnostic differences among the major deposits. For example, inspection of Table 4 shows that Palabora vermiculite has relatively elevated values for fluoride, whereas Enoree vermiculite may be associated with relatively high aluminum and chromium. Louisa vermiculite has high sodium, and Louisa and Libby vermiculite have high potassium. As with major elements, the significance of minor element relationships for vermiculite among the different deposits cannot be fully determined from these few data, but the patterns suggest that additional analyses could be informative.

Trace Elements

Although major and minor element analyses of vermiculite have been found for some of the ore deposits, to date little information has been found on the trace element content. In general, vermiculite has a high ion exchange capacity, perhaps the highest among layer-silicates, and a mineral structure suitable for sequestering trace elements (McBride, 1994). At least two features of the environment of vermiculite deposits foster the occurrence of elevated trace metals. First, the ultramafic character of the geologic setting in which vermiculite deposits form is commonly associated with a distinctive set of elevated trace elements including titanium, chromium, nickel, and cobalt. Chromium is shown in Table 4B to be elevated in vermiculite at levels greater than 1000 ppm in one or more samples from all of the deposits which have data, with Enoree vermiculite particularly high in chromium (3400 ppm). Maybin and others (1980) found that the South Carolina vermiculite deposits have associated stream sediment and soil anomalies of chromium, nickel and phosphorous and possibly cobalt and copper that are high enough to have possible exploration potential as indicators of vermiculite ore. Murdock and Hunter (1946) reported that North Carolina vermiculite deposits are enriched in nickel and even have nickel silicate minerals associated with them. El Shazly and others (1975a) noted nickel, chromium, and cobalt enrichment in Egyptian vermiculite deposits.

The second trace element feature of potential significance is that vermiculite has been found to have the capability to preferentially concentrate the group of trace elements known as rare earth elements (Pastor and others, 1988). The rare earth elements, including in particular the lanthanide series from atomic number 57 (lanthanum) to 71 (lutetium), with the addition of elements 21 (scandium) and 39 (yttrium) have been found in geochemical studies to be particularly useful in fingerprinting applications. A useful characteristic of rare earth elements is their limited reactivity under conditions at the earth's surface, so that once incorporated into a deposit they are likely to remain present and retain similar relative proportions during weathering processes.

Therefore, the abundance of rare earth and other elements that tend to be less mobile at ambient temperatures may potentially provide a diagnostic signature for vermiculite ore deposits. Fortuitously, carbonatites which are associated with the Palabora deposit, and other alkaline rocks that are in general of the type associated with other vermiculite deposits, are commonly elevated in rare earth elements (Korotev, 1996). Indeed for Palabora, Evans (1993) reported that rare earth elements are sufficiently abundant as to be considered potentially extractable.

Isotope Ratios

No data have been found on stable or radiogenic isotopes for vermiculite deposits. Isotopes have been found to be of use in fingerprinting geologic deposits and may have application with vermiculite ores. No further evaluation of isotopes has been made for the purposes of this report.

Likelihood of Deposits being Chemically Distinctive

Several lines of reasoning argue for vermiculite deposits from widespread locations being chemically distinctive. While the association of vermiculite with ultramafic rocks is a common characteristic that sets the local geologic environment apart from the surrounding regional rock, the deposits differ in detail because of the regional influence. The rock type surrounding each vermiculite orebody is one important regional variable, as is the composition of crosscutting intrusions and the resulting alteration.

As the ultramafic magmas move upward through the earth’s crust, many variables can influence their composition and mineralogy. Potential influences include the composition of the rocks the magmas move through and the degree to which those are assimilated, the sequence and timing of associated fluids of various compositions, and the pressure and temperature conditions under which the rocks crystallize.

Limitations of the Data

While it seems more likely that vermiculite deposits are chemically distinctive rather than identical, the differences could be difficult to detect. Little is known at present about the amount of variability within the deposits. Without this knowledge, it is difficult to determine the number of samples necessary to measure the differences among deposits with enough confidence to provide a predictive tool. Some deposits, such as Libby and Palabora, are zoned on a large scale, but smaller scale differences that would affect trace element chemistry may also exist. Additionally, efforts to link vermiculite consumer products with particular ore deposits may be stymied by the practice of exfoliation plants or distributors mixing ores from different locations and thereby masking or confounding any possibly unique chemical signature.

The limitations suggest that a phased approach to tracer identification is appropriate, whereby an initial study is designed to verify that gross compositional differences occur between deposits. A subsequent more detailed study would determine whether within-deposit variability masks or exceeds between-deposit variability.

RECOMMENDATIONS FOR FURTHER STUDY

This literature review indicates that unique signatures for different vermiculite deposits are not unreasonable, considering the distinctive geologic environments in which vermiculite deposits are formed as well as the geochemical reactivity of vermiculite. Mineralogical and geochemical data are sparse but suggest that a set of chemical signatures may be found, especially among trace element content of either vermiculite minerals or the bulk ore. Furthermore, limited mobility for some of the more likely elevated trace elements suggests that their signature may be retained through the vermiculite milling and exfoliation process and ultimately remain measurable in consumer products.

The mineralogy of a deposit and the major element composition may also have a unique character, though possibly not as distinctive as the trace element content. Nonetheless, any fingerprinting effort should include mineralogy and major element analysis in order to provide a framework in which to place and interpret trace element data.

Analytical Methods

Analytical methods for a tracer analysis should include both mineralogical and chemical methods that can be applied to bulk samples as well as mineral grains. Mineral grains can be analyzed as either concentrates derived from the bulk samples or as individual particles. The reason for emphasis on mineral grains is that vermiculite in some consumer products would be highly diluted by material from sources other than the vermiculite ore deposit. Conceivably, the vermiculite grains themselves, or a particularly abundant accessory mineral such as amphibole, would hold the key to geochemical discrimination.

Table 5 lists a limited selection of methods potentially useful in tracer analysis. A variety of other methods exist, some of which are pointed out below as also particularly suited to the problem. The limited list in Table 5 is not meant to be exclusive, but serves to highlight readily available methods capable of yielding a low-cost approach. Although some methods provide mineral identification and compositional information with the same instrument, generally no single instrument is sufficient for mineral characterization. Therefore a complement of different instrumental techniques would be most appropriate allowing both low and high magnification, and measurement of optical properties, structure, and composition.

A selective set of methods (Table 5) includes optical microscopy (OM) consisting of both stereomicroscopy for sample description and polarized light microscopy for mineral identification, quantitation and textural description; X-ray diffraction (XRD) for mineral identification and qualitative or quantitative abundance; scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) for mineral identification, texture, and semi-quantitative chemical composition; electron probe microanalysis with wavelength dispersive X-ray spectroscopy (EPMA) as well as energy dispersive X-ray spectroscopy for mineral identification, texture, and quantitative chemical analysis; and transmission electron microscopy with energy dispersive X-ray spectroscopy and electron diffraction (TEM/EDS/ED) for identification and quantitative chemical composition of fine-grained fibrous minerals.

Two additional microanalytical techniques not listed in Table 5, but which can achieve low detection limits for rare earth elements in solid samples should be considered; these are secondary ion mass spectrometry (SIMS) and laser ablation - mass spectrometry (LA-ICPMS) (Williams, 1996, p. 344). A rapidly developing method, also not listed on Table 5, that has the advantage of discriminating potentially unique characteristics in bulk samples without having to conduct microanalysis on every sample is high resolution reflectance spectroscopy (Clark, 1999). The method can be applied with lab- or field-based spectrometers or airborne imaging spectrometers. The method relies on identification of distinctive absorption spectra, particularly in the visible and near-infrared part of the energy spectrum. By comparison and calibration with samples previously evaluated by other mineralogical methods, reflectance spectra can be used to characterize unknown material and should be considered as a potentially efficient and quick method for fingerprinting either bulk samples or components of vermiculite ore.

Several methods listed on Table 5 are available for trace element analysis of bulk material, either as ore, mineral concentrates, or consumer products. The most suitable multi-element methods (Table 5) that are commonly used for bulk solid samples include inductively coupled plasma atomic emission spectroscopy and mass spectrometry (ICP-AES, ICP-MS), X-ray fluorescence spectroscopy (XRF), and instrumental neutron activation analysis (INAA). A combination of analytical requirements, such as low-level detection of trace metals including rare earth elements, non-destructive analysis of whole solid samples, minimal specimen preparation, and a throughput of many samples could perhaps be best met with INAA techniques (Marfunin, 1995; Williams, 1996) provided costs are competitive with the other techniques. A disadvantage of INAA would be the inability to analyze some potentially important elements including some of the major species. An advantage of ICP methods over INAA is a much more complete list of available analytes, whereas a disadvantage is the preparation requirement for whole-solid analysis to completely dissolve the specimen. ICP methods using non-whole rock acid digestion preparation could be adapted for tracer analysis, provided a preliminary sensitivity study is conducted to establish minerals left unanalyzed by incomplete acid digestion. Traditional whole-rock XRF analysis of thick specimens also has an advantage of a broad analyte list but preparation requires pulverization and homogenization of the sample and possibly fusion prior to analysis. Thin-film XRF analysis is a technique developed for air-filter samples that could be adapted to other granular material and avoid destructive dissolution preparation required by traditional XRF analysis. In all techniques the detection limits will vary depending on the analyte of interest.

Study Design

The lack of information on compositional variability within vermiculite deposits as well as among different deposits argues for a phased approach in search of useful tracers. Initially, a first-phase screening study should be undertaken to confirm or further evaluate some of the patterns among vermiculite deposits that have been described in this report based on the literature. Some of the assumptions on trace element concentrations, particularly that of elevated chromium, nickel, and cobalt, and the rare earth elements, also need elaboration.

The goal of the first phase would be to verify on the basis of a small set of samples that differences in potentially diagnostic mineralogical or geochemical characteristics among sites are measurable. The first phase would analyze samples from known sources, recognizing that the small number of samples will not fully characterize the variability within any particular source.

The goal of the second phase would be to verify on the basis of a large set of samples that the spatial variability of a potential fingerprint within a source is less than the variability among sources. The second phase would require a statistically significant set of samples that would more fully characterize variability within and among ore deposits and their commercial products.

The design for conducting the second phase would be based on evaluation of variability of first-phase data. If the first-phase variability among all samples is minimal, the study would end. If there are apparent differences among samples, an evaluation would be attempted to determine whether differences could be attributed to different sources. If variability can be attributed more to different sources than to differences within a source, then a more robust second phase would be undertaken.

Recommended objectives for a screening study are to examine a limited set of samples (approximately 35) that would include the following (Figure 4):

- Beneficiated ore from up to three batches each from at least five major deposits that are spatially distant from each other. A batch of beneficiated ore refers here to material produced during a discrete time period. Major deposits are those in ore districts that supply products for use in the U.S. Spatially distant deposits are those in different ore districts.

- Exfoliated products known to have originated from the sampled ore deposits.

- A few consumer products made from vermiculite originating from sampled ore deposits.

- One site each for beneficiated ore and exfoliated product should be duplicated to estimate the combination of sampling and analytical variability.

- Consumer products should be analyzed both as bulk samples and as separated vermiculite concentrate.

Sample volumes for most samples should be sufficient for both the screening analysis and for a detailed second-phase study, if undertaken, in order to minimize repetitive field sampling. Each batch of beneficiated ore should be derived from different mixes of raw ore from spatially different parts of the mine. Where a variety of mixes for beneficiated ore are not available for an individual mine, raw ore samples should be collected to allow lab generation of beneficiated ore using different mixes of raw ore. The purpose of multiple mixes is to account for some degree of within-mine variability in the results.

Recommended analyses for the screening effort should include mineral identification and qualitative estimate of abundance for major, minor and trace phases, and chemical analysis of major, minor and trace elements for both bulk material and for separated vermiculite concentrates. As indicated in Figure 4, mineral identification should proceed from optical microscopy to X-ray diffraction, with feedback of information between the two methods to characterize the mineral content. Mineral separations by size, shape, density, or magnetic methods will aid in identification as well as estimation of abundance.

Once the general mineral content is known, electron microprobe or scanning electron microscope methods should be used to verify mineral species by microchemical and textural analysis of individual grains (Figure 4). Transmission electron microscope analysis could be used to more fully characterize fibrous minerals, but only where such minerals are initially evident from the other observations. Chemical characterization of bulk material should begin after the preliminary identification of the mineral content by microscopy and X-ray diffraction (Figure 4), in order to allow results on the mineral content to be used as a guide in setting up element-specific data objectives. Major and trace element analysis by X-ray fluorescence and additional trace element analysis by instrumental neutron activation would be a suitable approach. ICP methods could be considered if they were accompanied by a separate study to determine the comparative influence of digestion procedures relative to whole-sample composition. Additional innovative microanalytical and reflectance spectroscopic methods should also be considered depending on availability through cooperating investigators.

For the full fingerprinting effort, recommended analyses should include mineral identification and quantitative abundance, and chemical composition of both bulk samples and vermiculite grains or other selected minerals such as amphiboles. Results of the screening effort should provide guidance on how to structure the approach toward full fingerprinting, such as selection of sample preparation, additional analytical methods, target minerals, and target elements.

CONCLUSIONS

A review of the literature indicates that many, if not most, commercial vermiculite deposits contain asbestiform accessory minerals. The amount of asbestiform minerals appears to vary substantially from source to source, though documentation in the open literature remains far from adequate to fully evaluate asbestos content at mines. Furthermore, the efficiency of any asbestos removal that might occur during the course of ore beneficiation or other mineral processing activities likely varies from source to source. Without knowing the characteristics of the vermiculite source, the risk from asbestiform minerals in a vermiculite product can only be determined by relatively expensive asbestos analysis of each product. To help anticipate potential risk in vermiculite products, a low-cost mineralogical or geochemical means of determining the source of vermiculite would be helpful as a tracer to identify those products more likely to contain asbestiform minerals.

A two-phase approach toward identifying suitable mineralogical or geochemical tracers is recommended using the general study design outlined in this report. The approach accommodates consideration that the success of a tracer study would depend on being able to measure variations in mineralogical or geochemical characteristics among different ore deposits beyond those variations that normally occur within each ore deposit. A first phase is recommended to examine a limited set of samples to verify that enough variability exists among ore deposits to measure differences in diagnostic minerals or elements. If the first phase successfully identifies potential tracers, a second-phase detailed study should use a large set of samples to determine whether tracer variability among ore deposits is greater than variability within a deposit. Both phases should examine the degree to which ore deposit characteristics remain identifiable in samples of vermiculite products.

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GLOSSARY

The definitions of terms as used in this report are derived, where noted, from the numbered references. See also Table 1 for mineral formulae.

[1] Gaines and others (1997)
[2] Guthrie and Mossman (1993)
[3] Jackson (1997)
[4] Leake and others (1997)
[5] Skinner, Ross and Frondel (1988)

Acicular - "Said of a crystal that is needle-like in form." [2]

Actinolite - "An amphibole with the ideal composition $Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$. Actinolite is a species in the Mg-Fe^{2+} series, tremolite - ferro-actinolite, with $0.9 > Mg/(Mg+Fe^{2+}) > 0.5$." [2] Actinolite can occur with different habits, one of which can be asbestiform.

Amphibole - A group of minerals that are hydroxylated chain silicates with Mg, Fe, Ca, and Na as the dominant cation species. These, together with other cations, substitute at specific sites in the crystal structure producing a group of minerals closely related crystallographically and chemically. Fibrous varieties of minerals in the amphibole group occur. Not all members of the amphibole group occur in fibrous form, and those that do may also be found in other habits. [5]

Asbestiform - "An adjective describing inorganic materials that possess the form and appearance of asbestos. Asbestiform is a subset of fibrous, where asbestiform implies relatively small fiber thickness and large fiber length, flexibility, easy separability, and a parallel arrangement of the fibers in native (unprocessed) samples. Often, asbestos fibers occur in bundles, i.e., they are often polyfilamentous." [2]

Asbestos - "A term applied to asbestiform varieties of serpentine and amphibole, particularly chrysotile, 'crocidolite' [asbestiform riebeckite], 'amosite' [asbestiform grunerite], asbestiform tremolite, asbestiform actinolite, and asbestiform anthophyllite. The asbestos minerals possess asbestiform characteristics." [2]

Aspect Ratio - "The ratio of length to width." [2]

Beneficiated Ore - Ore that has been processed in a mill to concentrate the material of commercial interest. In the case of vermiculite, beneficiated ore has had most but not necessarily all of the accessory minerals (gangue) removed. See exfoliated ore.

Beneficiation - "Improvement of the grade of ore by milling, flotation, sintering, gravity concentration, or other processes. The resultant product is a concentrate." [3]

Biotite - “A series of 2:1 layer silicates of ideal composition $K(Mg,Fe)_3Si_4O_{10}(OH)_2$. Phlogopite is the magnesium end-member of the series; annite is the iron end-member.” [2] In this report, biotite refers to a mineral intermediate in the annite-phlogopite series, listed as $K(Fe^{2+},Mg)_3AlSi_3O_{10}(OH,F)_2$ in Table 1. “The biotite composition field is arbitrarily defined as that having Mg:Fe ratios between 2:1 and 1:4, but the division is obscured by substitution of other cations in the octahedral as well as tetrahedral sites.” [1]

Carbonatite - “An igneous rock composed of at least 50% carbonate minerals.” [3]

Chain Silicate - A mineral class consisting of silica tetrahedra linked in one direction. Amphiboles, pyroxenes, and pyroxenoids are included in this class. [2]

Chlorite - A group of platy sheet silicates with the general formula $(R^{+2}R^{+3})_6AlSi_3O_{10}(OH)_8$, where R is usually Fe or Mg. [3]

Chrysotile - A hydrated magnesium silicate mineral that is a member of the serpentine group and is usually asbestiform. [2,4]

Cross Fiber - Aggregate of asbestos in a vein in which parallel fibers or bundles of fibers are oriented perpendicular to the margins of the vein.

Equant - “Said of a crystal having the same or nearly the same dimensions in all directions.” [2]

Exfoliated Ore - Vermiculite ore that has undergone thermal, or less commonly chemical, processing to expand the platy layers like an accordion.

Fiber - A mineral with a highly elongate morphology developed during growth. [2] “A long, thin thread or threadlike solid with distinctive elongate shape that may be natural or synthetic and organic or inorganic in composition.” [5]

Fibrous - Said of a mineral that gives the appearance of being composed of fibers. [2] “Aggregates of any size of individual fibers may form relatively thick fibrous bundles, thus becoming visible to the naked eye.” [5]

Framework Silicate - A mineral class having silicate tetrahedra polymerized in three dimensions. [2] Quartz and feldspar are among minerals included in this class.

Gangue - “The valueless rock or mineral aggregates in an ore; that part of an ore that is not economically desirable but cannot be avoided in mining. It is separated from the ore minerals during concentration.” [1]

Habit - “The shape or morphology that a crystal or aggregate of crystals assumes during crystallization.” [2] Examples of habit are equant, prismatic, acicular, fibrous, and asbestiform.

Head Feed - Ore that has been mined and is at the point of entering the processing system in a mill.

Hydrobiotite - A sheet silicate mineral that is a regular mixed-layer mica/vermiculite. “A regularly ordered, 1:1 mix of biotite/vermiculite.” [3]

Hydrophlogopite - A sheet silicate that is a regular mixed-layer mica/vermiculite. A regularly ordered, 1:1 mix of phlogopite/vermiculite, by analogy with hydrobiotite.

Layer Silicate - A sheet silicate mineral class having silica tetrahedra polymerized in two dimensions. [2] Micas, vermiculite, mixed-layer mica/vermiculite, and the chlorite smectite, and serpentine groups are among minerals included in this class.

Mass Fiber - Aggregate of asbestos in which fibers or bundles of fibers have random orientation.

Mica - A group of sheet silicate minerals that have an ideal electrical charge of -1 per formula unit. [2] The group includes biotite, phlogopite, muscovite, and many others. Mica is the most common precursory or parent mineral that alters to form vermiculite.

Mixed-layer mica/vermiculite - A group of sheet silicate minerals that have a mica component and a vermiculite component mixed in either a regular or random interstratification of layers.

Ore - The naturally occurring material from which a mineral or minerals of economic value can be extracted at a reasonable profit. [3]

Ore Feed - Ore that has been mined, transported to a mill site, and manipulated perhaps by size reduction in preparation for beneficiation; ore just prior to entering a mill for processing.

Phlogopite - “A 2:1 layer silicate with an ideal composition $KMg_3(Si_3\,Al)O_{10}(OH)_2$. Phlogopite is the magnesium end-member of the biotite series.” [2] Phlogopite, listed as $K(Fe^{2+},Mg)_3AlSi_3O_{10}(OH,F)_2$ in Table 1, has relatively less iron than biotite. “Members of the [biotite] series with Mg:Fe ratios of > 2:1 are generally regarded as phlogopites, but the boundary is arbitrary largely because substitutions other than Fe for Mg may also occur.” [1]

Prismatic - “A term used to describe crystals exhibiting aspect ratios greater than one and having parallel sides.” [2]

Raw Ore - Unprocessed ore.

Richterite - An amphibole mineral with an end-member composition $Na(Ca,Na)Mg_5Si_8O_{22}(OH)_2$. [4] Richterite can occur with different habits, one of which can be asbestiform.

Serpentine - A group of common rock-forming minerals that are always derived from alteration of magnesium-rich silicates, especially olivine; including minerals such as antigorite, lizardite, and chrysotile. [3]

Serpentinite - “A rock consisting almost wholly of serpentine-group minerals.” [3]

Sheet Silicate - A platy mineral also called a layer silicate. A mineral class having silica tetrahedra polymerized in two dimensions. Micas, the chlorite group, vermiculite, and the serpentine group are among minerals included in this class.

Tremolite - “A species of amphibole with the ideal composition $Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$. Tremolite is the magnesium-rich end member of the Mg-Fe^{2+} series, tremolite - ferro-actinolite, with Mg/(Mg+Fe2+) > 0.9.” [2] Tremolite can occur with different habits, one of which can be asbestiform.

Ultramafic - An igneous rock composed chiefly of mafic minerals, such as hypersthene, augite, or olivine. [3]

Vermiculite - A sheet silicate with a general formula: $Mg_{0.35+/-}(Mg,Fe^{3+})_3Si_3(Al,Fe^{3+})O_{10}(OH)_2 \cdot nH_2O$. [1] Vermiculite has high exchange capacity and exfoliates like an accordion when quickly heated at high temperature.

Winchite - An amphibole mineral with an end-member composition $(Ca,Na)Mg_4(Al,Fe^{3+})Si_8O_{22}(OH)_2$. [4] Winchite can occur with different habits, one of which can be asbestiform.

FIGURES

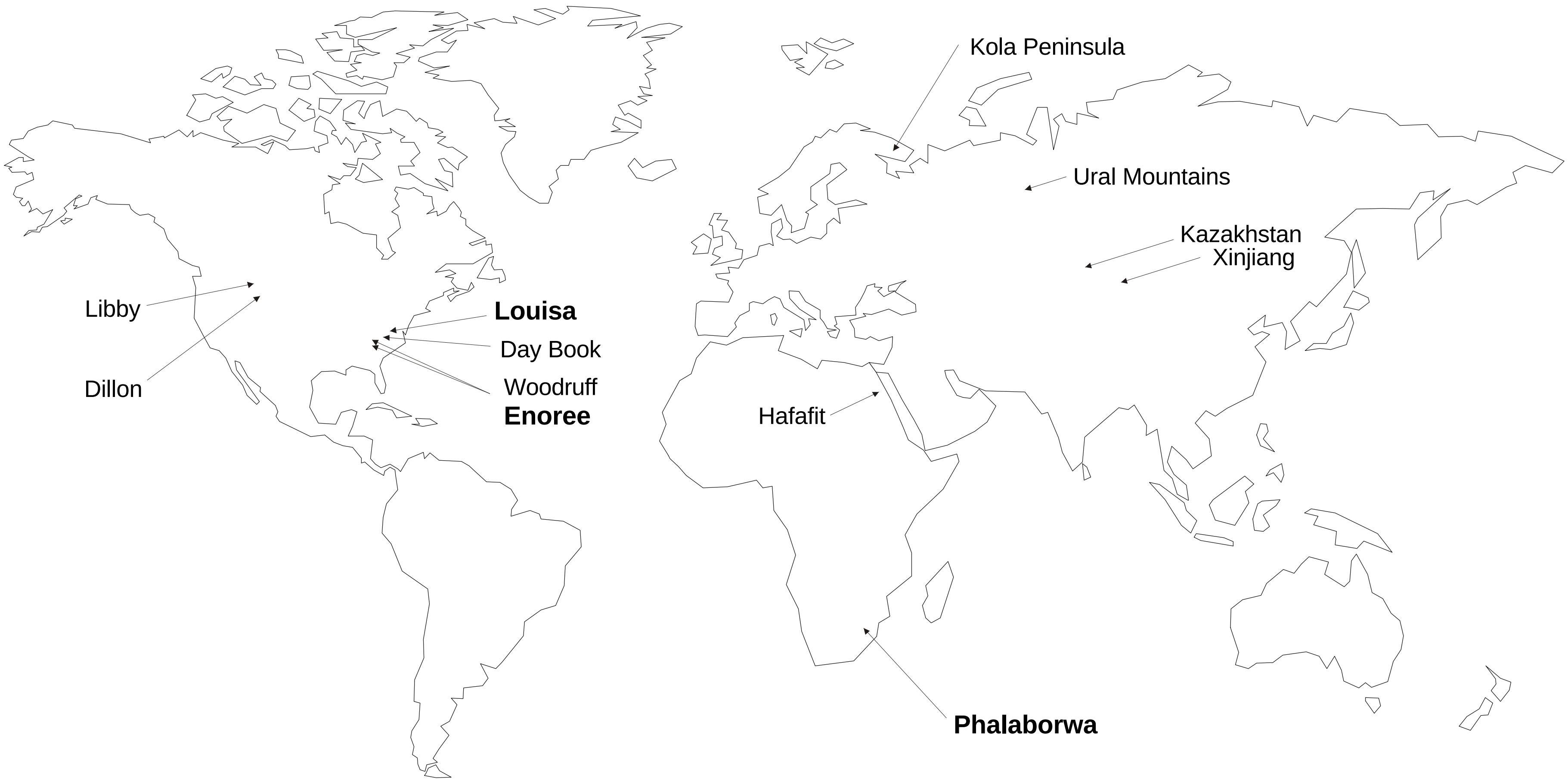

Figure 1. Locations of vermiculite deposits discussed in this report. Current major sources for the U.S. market are in bold, including Louisa, Virginia; the Enoree district, South Carolina; and Phalaborwa, South Africa. A previous major source was at Libby, Montana.

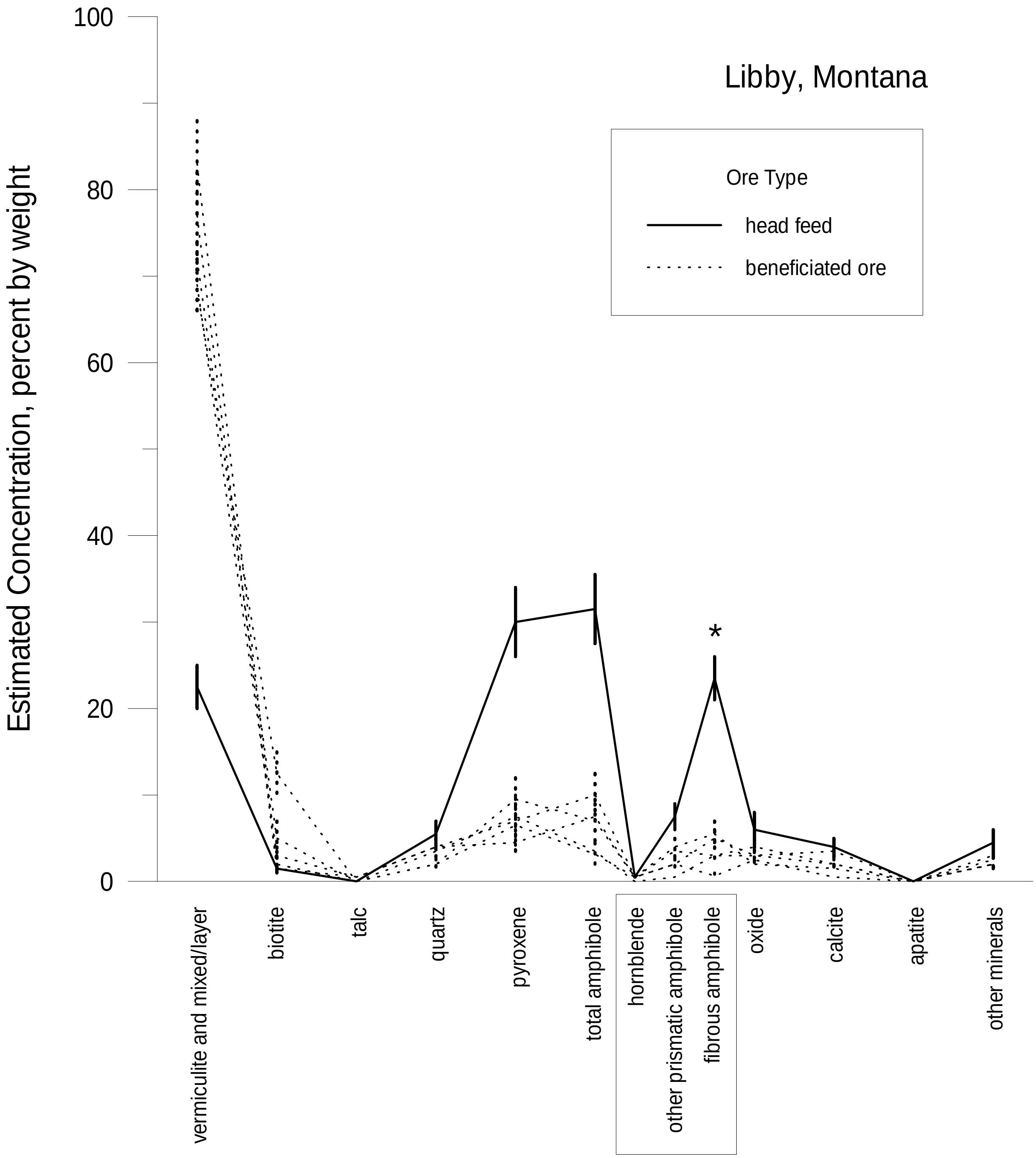

Figure 2A. Mineral composition of vermiculite ore (data from Atkinson and others, 1982). Data include head feed (solid line), and five grades of beneficiated ore (dotted lines) from the W.R. Grace mine at Libby, Montana. The graph shows three types of amphiboles (outlined) that make up total amphiboles. Asterisk indicates fibrous amphiboles.

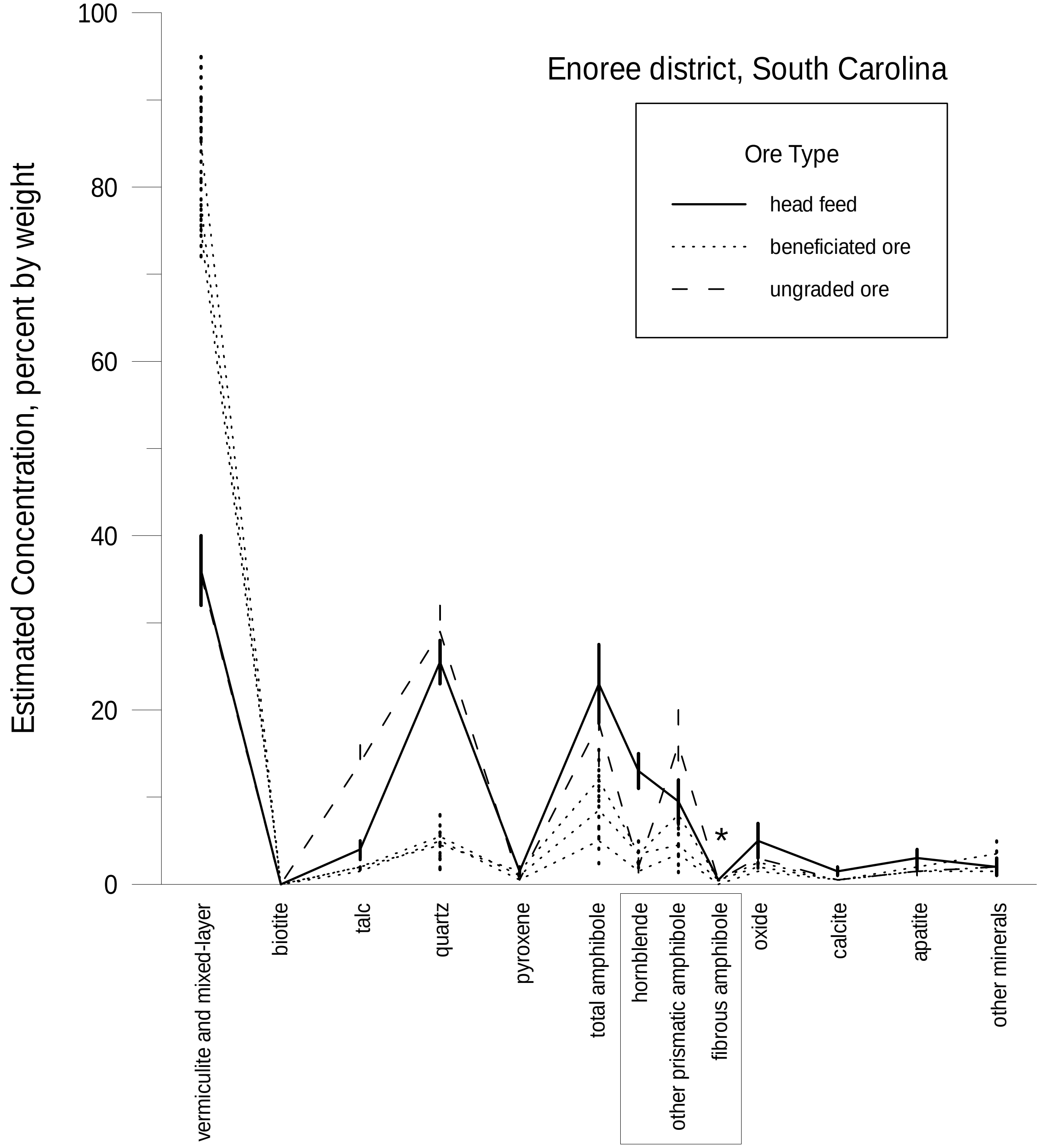

Figure 2B. Mineral composition of vermiculite ore (data from Atkinson and others, 1982). Data include head feed (solid line) and three grades of beneficiated ore (dotted) from the W.R. Grace mill, and ungraded ore (dashed) from the Patterson mill in the Enoree district, South Carolina. The graph shows three types of amphiboles (outlined) that make up total amphiboles. Asterisk indicates fibrous amphiboles which are present, but at a level of less than 1%.

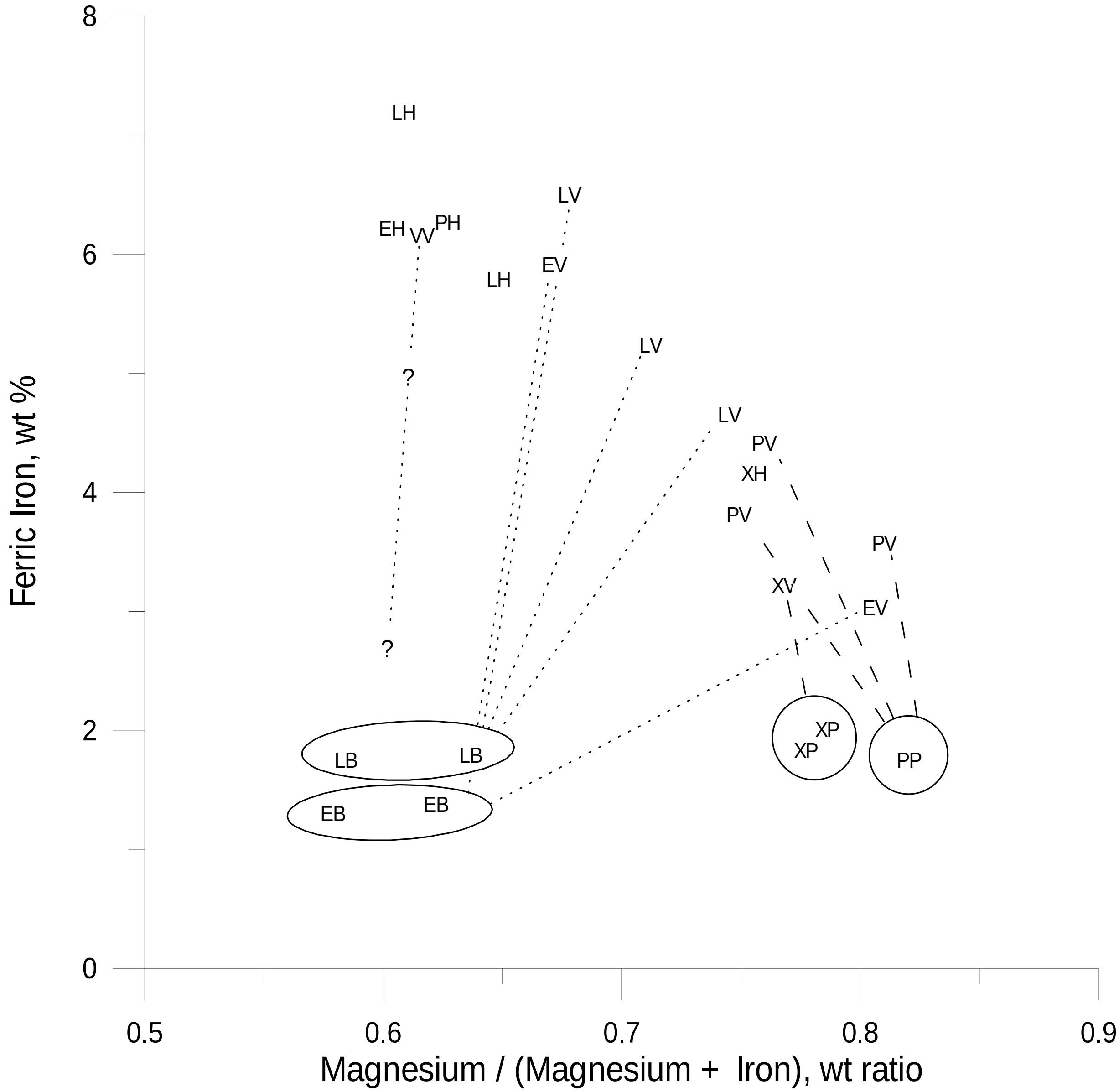

Figure 3. Distribution of magnesium, total iron, and ferric iron in vermiculite, mixed-layer mica vermiculite (hydrobiotite and hydrophlogopite), and mica (biotite and phlogopite). Parent micas are circled; tielines match parent micas with vermiculite from the same localities. Mixed-layer symbols do not have tielines. Data from Table 4.

	Mica	Mixed-Layer Mica/Vermiculite	Vermiculite
Libby	LB	LH	LV
Louisa	?	?	VV
Enoree	EB	EH	EV
Palabora	PP	PH	PV
Xinjiang	XP	XH	XV

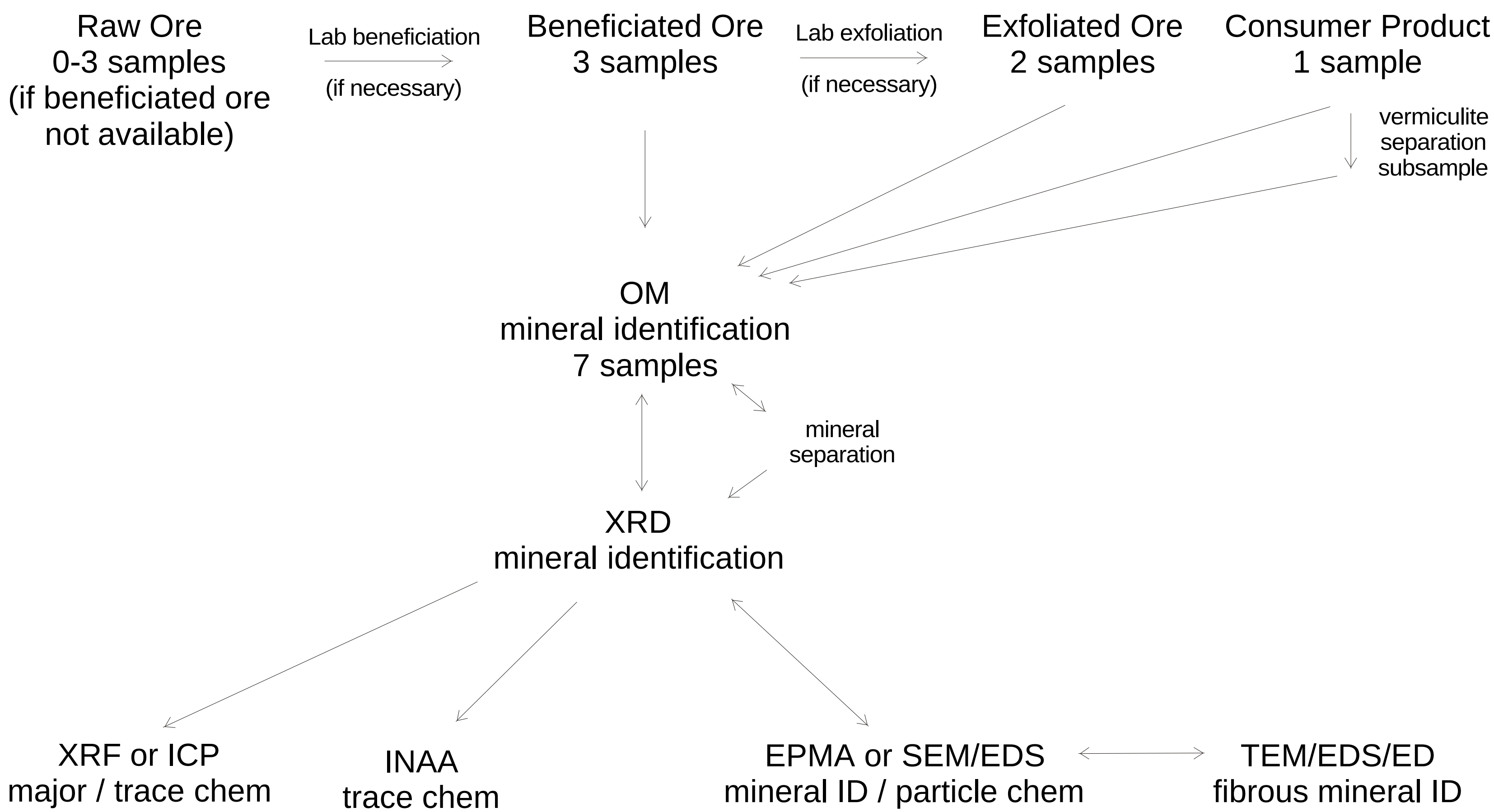

Figure 4. Analytical approach for the screening phase of a tracer analysis. Seven samples, not counting duplicates, are shown for materials derived from a single vermiculite ore deposit. Where beneficiated or exfoliated materials are not available in the field, raw ore would be collected for lab beneficiation. As many as 35 samples would be derived from 5 vermiculite mines. See Table 5 for methods.

TABLES

Table 1. Vermiculite and some associated minerals. Formulae are from Gaines and others (1997), except for those noted in footnotes and for amphiboles, which are taken from Leake and others (1997).

MINERAL	IDEAL FORMULA
SHEET SILICATES	
Industrial Vermiculite	
Vermiculite	$Mg_{0.35+/-}(Mg,Fe^{3+})_3Si_3(Al,Fe^{3+})O_{10}(OH)_2 \cdot n\ H_2O$
Hydrobiotite *	$K(Mg,Fe)_6(Si,Al)_8O_{20}(OH)_4 \cdot n\ H_2O$
[Hydrophlogopite] *	$KMg_6(Si,Al)_8O_{20}(OH)_4 \cdot n\ H_2O$
Mica	
Biotite **	$K(Fe^{2+},Mg)_3AlSi_3O_{10}(OH,F)_2$
Phlogopite **	$KMg_3AlSi_3O_{10}(F,OH)_2$
Annite	$KFe^{2+}{}_3AlSi_3O_{10}(OH,F)_2$
Muscovite	$KAl_2AlSi_3O_{10}(OH,F)_2$
Serpentine	
Antigorite	$(Mg,Fe^{2+})_3Si_2O_5(OH)_4$
Chrysotile ***	$Mg_3Si_2O_5(OH)_4$
Other Clay Minerals	
Talc	$Mg_3Si_4O_{10}(OH)_2$
Smectite group	$(Na,Ca,K)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2 \cdot n\ H_2O$
Chlorite group	$(Al,Fe,Mg,Mn,Ni)_{5\text{-}6}(Al,Si,Fe)_4O_{10}(OH)_8$
Kaolinite	$Al_2Si_2O_5(OH)_4$
CHAIN SILICATES	
Pyroxene	
Augite	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$
Diopside	$CaMgSi_2O_6$
Rhodonite	$(Mn^{+2},Fe^{+2},Mg,Ca)SiO_3$
Amphibole	
Magnesiohorneblende	$Ca_2(Mg_4(Al,Fe^{3+}))Si_7O_{22}(OH)_2$
Anthophyllite ***	$Mg_7Si_8O_{22}(OH)_2$
Tremolite ***	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Actinolite ***	$Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$
Richterite ***	$Na(Ca,Na)Mg_5Si_8O_{22}(OH)_2$
Winchite ***	$(Ca,Na)Mg_4(Al,Fe^{3+})Si_8O_{22}(OH)_2$
Grunerite [Amosite ***]	$Fe^{2+}{}_7Si_8O_{22}(OH)_2$
Riebeckite [Crocidolite ***]	$Na_2(Fe^{2+}{}_3,Fe^{3+}{}_2)Si_8O_{22}(OH)_2$

MINERAL	IDEAL FORMULA
FRAMEWORK SILICATES	
Quartz	SiO_2
Feldspar	
Alkali feldspar subgroup	$(K,Na)AlSi_3O_8$
Plagioclase series	$(Na,Ca)(Si,Al)_4O_8$
OTHER SILICATES	
Olivine group	$(Mg,Fe^{2+})_2SiO_4$
Garnet group	$(Ca,Fe,Mg,Mn)_3(Al,Fe)_2(SiO_4)_3$
Titanite [Sphene]	$CaTiSiO_5$
Zircon	$ZrSiO_4$
OXIDES	
Magnetite	$Fe^{2+}Fe^{3+}{}_2O_4$
Hematite	$\alpha\text{-}Fe_2O_3$
Chromite	$Fe^{2+}Cr_2O_4$
Rutile	TiO_2
Anatase	TiO_2
Pyrolusite	MnO_2
Spinel	$MgAl_2O_4$
Corundum	Al_2O_3
CARBONATES	
Calcite	$CaCO_3$
Dolomite	$CaMg(CO3)_2$
Strontianite	$SrCO_3$
SULFATE	
Barite	$BaSO_4$
PHOSPHATE	
Apatite	$Ca_5(PO_4)_3(F,OH,Cl)$

Notes:

[Brackets] Mineral names in brackets are informal in that they are not recognized by the International Mineralogical Association (IMA), though they occur in the literature. The informal names are used here for ease of reference.

* Mixed-layer minerals. The formula for hydrobiotite is generalized from that in Gaines and others (1997): $K(Mg,Fe)_3Si_3AlO_{10}(OH)_2$ / $Mg_{0.35+/-}(Mg,Fe)_3Si_3AlO_{10}(OH)_2 \cdot n\ H_2O$.
The formula for hydrophlogopite is also generalized by analogy with that for hydrobiotite.

** Biotite and phlogopite are common parent minerals of vemiculite and mixed-layer mica/vermiculite (hydrobiotite or hydrophlogopite). Biotite is also a series name extending from annite, which is iron-rich, to phlogopite, which ideally lacks iron. Members of the series with Mg:Fe ratios greater than 2:1 are generally regarded as phlogopites, though the boundary is arbitrary (Gaines and others, 1997).

*** Mineral may commonly occur with an asbestiform habit.

Table 2. Locations of mines that produced vermiculite for use in consumer products in the United States during the last 10 years. Major producers are listed in bold. Data are taken from Potter (1998 and earlier).

LOCATION OF MINES	COMPANY	STATUS
MONTANA		
Libby	**W.R. Grace & Co.**	**Closed**
Dillon	Stansbury Holdings Corp.	Active, limited production
VIRGINIA		
Louisa County	**Virginia Vermiculite, Ltd.**	**Active**
SOUTH CAROLINA		
Enoree district*	**W.R. Grace & Co.**	**Active**
Enoree*	Patterson Vermiculite Co.	(not determined)
Woodruff*	Virginia Vermiculite, Ltd.	Active
	Carolina Vermiculite Co.	Active
SOUTH AFRICA		
Phalaborwa	**Palabora Mining Co., Ltd.**	**Active**
CHINA		
Xinjiang Province* (several mines)	China Xinjiang Metals & Minerals Imp & Exp Corp	Active
Other Provinces*	(not determined)	(not determined)

* Location may represent multiple mines.

Table 3. Minerals associated with selected vermiculite deposits.

Vermiculite Deposits	Vermiculite^	Biotite	Phlogopite	Total amphibole	Fibrous amphibole	Total serpentine	Chrysotile serpentine	Talc	Apatite	References	Other Minerals and Comments
Libby, Montana	**	*		**	**	*	*	*	**	1, 4, 13 14, 19, 21 23	(Apatite is fluorapatite), vanadium-rich pyroxene, strontianite, barite, copper and zinc sulfides. Diopside, augite, hornblende, sphene, magnetite, hematite, quartz, . Locally, carbonate and feldspar are intergrown with vermiculite. Antigorite reported in head feed (13); mention of chrysotile (19, 13), very low abundance.. Amphibole asbestos reported as tremolite-actinolite (13), sodium tremolite and richterite (4), winchite (23).
Palabora, South Africa	**		*	*	*	**	See Notes	NR	**	5, 7, 8 10, 14, 17	See text for minerals assoc. with the Igneous Complex, but not necess. with the vermiculite deposit. Some describe chrysotile, others say it is scrolls of vermiculite (5); rare anthophyllite fibers reported (14). The mica at Palabora is phlogopite rather than biotite.
North Carolina deposits	**	*	*	**	See Notes	**	*	**	NR	9, 11, 16	Nickel silicates, corundum, chlorite. Fibrous amphibole and chrysotile are reported as abundant in individual deposits.
Enoree district, South Carolina	**	*		**	*	*	*	*	**	12, 13	(Apatite is fluorapatite), sphene, zircon, chlorite, chromite, rutile, titanite, corundum, anatase, hornblende, magnetite, hematite, rhodonite, pyrolusite, quartz, feldspar. Tremolite-actinolite and anthophyllite occur mainly in prismatic form.
Louisa, Virginia	**	*		**	*	NR	*	NR	NR	14, 19	No detailed geologic reports were found describing this deposit. Traces of fibrous amphibole reported (14).
Dillon, Montana	**	*		**	*	**	*	*	NR	2, 3, 15	Magnetite, spinel, and olivine (in the ultramafic bodies), garnet and chlorite in vermiculite ore zone. Fibrous tremolite, actinolite, anthophyllite, and fibrous talc and biotite (2).
Xinjiang Province, China	**		*	I	I	I	I	I	I	18, 20	No detailed geologic reports were found describing these deposits.
Hafafit, Egypt	**		*	**	**	**	NR	*	*	6	Amphibole asbestos minerals include primariliy anthophyllite with lesser tremolite and actinolite.
Russia (Urals, Kola Peninsula)	**	*	*	I	See Notes	I	I	*	I	22	Several amphibole minerals of unspecified habit, including Na-rich species, reported at many deposits. Unspecified type of asbestos reported to occur with some deposits.

Explanation

^ vermiculite includes mixed layer mica / vermiculite.
** mineral is abundant.
* mineral is mentioned in literature as being associated with the vermiculite deposit.

NR mineral is not reported, may or may not be present.
I insufficent information available in literature.
Deposits in bold type are either producing mines in the US or major importers to the US.

References: 1. Bassett, 1959; 2. Behre Dolbear and Co., 2000; 3. Berg, 1995; 4. Boettcher, 1966; 5. Chatfield and Lewis, 1979, 1980; 6. El Shazly, 1975a; 7. Evans, 1993; 8. Hessel and Sluis-Cremer, 1989; 9. Hunter, 1950; 10. IOM, 2000; 11. Kulp and Brobst, 1954; 12. Libby, 1975; 13. MRI, 1982; 14. Moatamed et al, 1986; 15. Montana DEQ, 1999; 16. Murdock and Hunter, 1946; 17. Palabora Mining Co, 1976; 18. Potter, 1998; 19. Rohl and Langer, 1977; 20. Rongqi and Junchen, 1993; 21. USEPA, 1980; 22. Vorovikov, 1973; 23. Wylie and Verkouteren, 2000.

Table 4. Chemical composition of vermiculite, mixed-layer mica/vermiculite, and mica from selected ore deposits. Dashes indicate no analysis conducted.

A. Oxide weight percent from listed references.

LOCALITY AND MINERALS	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	Cr_2O_3	MnO	NiO	Li_2O	Rb_2O	SrO	Cs_2O	BaO	F	Cl	P_2O_5	H_2O+	H_2O-	H_2Otot	Oxide tot	REFERENCE
Libby, Montana																									
vermiculite	38.64	14.94	9.29	--	22.68	1.23	--	7.84	--	0.29	--	--	--	--	--	--	--	--	0.28	--	--	--	5.29	100.59	1
vermiculite	35.57	11.47	7.49	0.34	22.57	0.73	--	0.96	1.06	0.18	0.06	0.02	--	--	0.01	--	0.10	--	--	0.06	9.01	10.11	19.12	99.74	2
vermiculite	35.43	11.30	6.65	0.27	23.56	0.39	--	0.14	0.91	0.26	0.05	0.01	--	--	0.01	--	0.03	--	--	0.05	9.47	11.26	20.73	99.79	2
hydrobiotite	35.60	11.85	10.28	0.81	20.17	1.44	0.16	3.17	1.13	0.03	0.08	--	--	0.0129	0.005	0.00041	0.17	0.21	--	0.07	7.56	7.20	14.76	99.95	2
hydrobiotite	36.77	11.57	8.28	0.98	20.04	1.94	0.12	3.84	1.02	0.27	0.08	--	--	0.0158	0.01	0.00050	0.19	0.30	--	0.06	6.69	7.80	14.49	99.98	2
biotite	38.63	13.08	2.50	8.75	19.94	0.18	0.26	10.00	1.55	0.23	0.14	--	--	0.04	0.005	--	0.45	0.30	--	0.06	3.52	0.30	3.82	99.94	2
biotite	39.10	13.30	2.56	7.23	21.55	0.12	0.23	10.05	1.21	0.25	0.10	--	--	0.03	<0.005	--	0.35	0.35	--	--	3.74	0.06	3.80	100.23	2
Louisa, Virginia																									
vermiculite	38.34	12.85	8.80	--	16.38	1.12	1.72	6.63	1.66	0.23	0.14	--	0.01	--	--	--	--	--	--	--	--	--	10.66	98.54	3
Enoree district, South Carolina																									
vermiculite	38.66	17.36	8.45	--	20.04	0.75	--	4.24	--	0.50	0.07	--	--	--	--	--	0.12	--	--	--	--	--	8.71	98.90	3
vermiculite	39.79	10.96	4.33	0.66	24.42	0.90	--	0.28	0.43	0.15	0.07	0.02	--	0.003	0.01	--	0.02	0.52	--	0.17	6.39	10.25	16.64	99.37	4
hydrobiotite	38.63	13.43	8.89	1.13	17.93	1.28	--	5.48	1.39	0.08	0.19	0.02	--	0.059	0.01	--	0.08	0.78	--	0.09	4.17	5.92	10.09	99.56	4
biotite	40.30	12.43	1.86	9.28	19.42	0.42	--	8.82	2.32	0.10	0.17	0.07	--	0.049	0.01	--	0.43	0.63	--	0.03	2.66	0.30	2.96	99.29	4
biotite	40.23	12.95	1.97	7.72	20.15	0.43	--	9.56	2.14	0.07	0.17	0.03	--	0.063	0.01	--	0.17	0.86	--	0.02	2.76	0.34	3.10	99.64	4
Phalaborwa, South Africa																									
vermiculite	39.37	12.08	5.45	1.17	23.37	1.46	0.80	2.46	1.25	--	0.30	--	0.03	--	--	--	--	--	--	--	--	--	11.20	98.94	3
vermiculite	38.53	8.35	6.31	0.64	25.74	--	--	4.73	1.12	0.12	0.03	--	--	--	--	--	--	0.92	--	0.01	14.58	--	14.58	101.08	6
vermiculite	35.93	9.05	5.11	0.16	26.15	0.50	--	0.16	0.93	0.48	0.02	--	--	--	--	--	--	0.67	--	0.05	11.32	10.36	21.68	100.89	6
hydrobiotite	38.74	10.38	8.96	1.98	21.77	--	0.27	7.82	2.11	--	0.04	--	--	--	--	--	--	0.53	--	--	7.50	--	7.50	100.10	6
phlogopite	40.25	10.45	2.50	2.18	26.11	--	0.25	10.35	1.15	0.07	0.02	--	--	--	--	--	--	0.62	--	--	6.48	--	6.48	100.43	6
Xinjiang Province, China																									
vermiculite	41.20	12.68	4.60	1.54	24.22	0.93	1.61	5.97	1.38	--	0.05	--	--	--	--	--	--	--	--	--	--	--	5.82	100.00	3
hydrophlogopite	36.30	12.45	5.95	0.37	22.82	0.68	1.10	3.70	1.32	--	0.04	--	--	--	--	--	--	--	--	--	6.62	8.08	14.70	99.43	5
phlogopite	39.38	14.44	2.87	2.40	23.61	0.95	2.50	10.40	1.49	--	0.03	--	--	--	--	--	--	--	--	--	1.11	0.34	1.45	99.52	5
phlogopite	38.35	15.44	2.62	2.76	23.02	0.63	3.70	10.20	1.34	--	0.03	--	--	--	--	--	--	--	--	--	1.06	0.35	1.41	99.50	5

OXIDES, wt percent

References 1 - Bassett (1959) 2 - Boettcher (1966) 3 - Hindman (1984) 4 - Libby (1975) 5 - Rongqi and Junchen (1993) 6 - Schoeman (1989)

Table 4 (continued). Chemical composition of vermiculite, mixed-layer mica/vermiculite, and mica from selected ore deposits.
Dashes indicate no analyses conducted.
B. Element concentration in parts per million (ppm), calculated from oxide weight percent. Symbols listed are used in Figure 3.

LOCALITY AND MINERALS	ELEMENTS, ppm																					SYMBOL	DESCRIPTION
	Si	Al	Fe tot	Fe^{3+}	Fe^{2+}	Mg	Ca	Na	K	Ti	Cr	Mn	Ni	Li	Rb	Sr	Cs	Ba	F	Cl	P		
Libby, Montana																							
vermiculite	181000	79100	65000	65000	--	137000	8800	--	65100	--	2000	--	--	--	--	--	--	--	--	2800	--	LV	concentrate
vermiculite	166000	60700	55000	52400	2600	136000	5200	--	8000	6400	1200	460	160	--	--	80	--	900	--	--	260	LV	RCSa-59
vermiculite	166000	59800	48600	46500	2100	142000	2800	--	1200	5500	1800	390	80	--	--	80	--	270	--	--	220	LV	RC-level 12
hydrobiotite	166000	62700	78200	71900	6300	122000	10300	1200	26300	6800	210	620	--	--	120	40	3.9	1500	2100	--	300	LH	RCSAa-36
hydrobiotite	172000	61200	65500	57900	7600	121000	13900	890	31900	6100	1800	620	--	--	140	80	4.7	1700	3000	--	260	LH	RCSp-49
biotite	181000	69200	85500	17500	68000	120000	1300	1900	83000	9300	1600	1100	--	--	370	40	--	40000	3000	--	260	LB	RCB-12
biotite	183000	70400	74100	17900	56200	130000	860	1700	83400	7300	1700	780	--	--	270	<40	--	3100	3500	--	--	LB	RCSp-55
Louisa, Virginia																							
vermiculite	179000	68000	61600	61600	--	98800	8000	12800	55000	10000	1600	1100	--	46	--	--	--	--	--	--	--	VV	concentrate
Enoree district, South Carolina																							
vermiculite	181000	91900	59100	59100	--	121000	5400	--	35200	--	3400	540	--	--	--	--	--	1100	--	--	--	EV	concentrate
vermiculite	186000	58000	35400	30300	5100	147000	6400	--	2300	2600	1000	540	160	--	30	80	--	180	5200	--	720	EV	A-24V
hydrobiotite	181000	71100	71000	62200	8800	108000	9100	--	45500	8300	550	1500	160	--	540	80	--	720	7800	--	390	EH	Y-26V
biotite	188000	65800	85100	13000	72100	117000	3000	--	73200	13900	680	1300	550	--	450	80	--	3900	6300	--	110	EB	A-48B
biotite	188000	68500	73800	13800	60000	122000	3100	--	79400	12800	480	1300	240	--	580	80	--	1500	8600	--	74	EB	Y-35B
Phalaborwa, South Africa																							
vermiculite	184000	63900	47200	38100	9100	141000	10400	5900	20400	7500	--	2300	--	140	--	--	--	--	--	--	--	PV	concentrate
vermiculite	180000	44200	49100	44100	5000	155000	--	--	39300	6700	820	230	--	--	--	--	--	--	9200	--	44	PV	VOD orebody
vermiculite	168000	47900	37000	35700	1200	158000	3600	--	1300	5600	3300	150	--	--	--	--	--	--	6700	--	220	PV	VOD orebody
hydrobiotite	181000	54900	78100	62700	15400	131000	--	2000	64900	12600	--	310	--	--	--	--	--	--	5300	--	--	PH	sw of Loolekop
phlogopite	188000	55300	34400	17500	16900	157000	--	1900	85900	6900	480	150	--	--	--	--	--	--	6200	--	--	PP	VOD orebody
Xinjiang Province, China																							
vermiculite	193000	67100	44100	32200	12000	146000	6600	12000	49600	8300	--	390	--	--	--	--	--	--	--	--	--	XV	Qieganbulake
hydrophlogopite	170000	65900	44500	41600	2900	138000	4900	8200	30700	7900	--	310	--	--	--	--	--	--	--	--	--	XH	Tseganbrark v-5
phlogopite	184000	76400	38700	20100	18700	142000	6800	19000	86300	8900	--	230	--	--	--	--	--	--	--	--	--	XP	Tseganbrark v-1
phlogopite	179000	81700	39800	18300	21500	139000	4500	27000	84700	8000	--	230	--	--	--	--	--	--	--	--	--	XP	Tseganbrark v-3

Table 5. Description of methods useful for identifying tracer constituents in vermiculite ore. See text for additional innovative methods not listed here.

Method	Data Objectives	Material: Bulk *	Material: Grain
OM	Optical Microscopy **	x	x
	Grain morphology, size, habit, color, surface and boundary texture		
	Refractive indices and other optical crystallographic properties		
	Other crystallographic properties		
	Mineral identification by optical properties		
	Qualitative mineral abundance and quantitative concentration		
XRD	X-ray Diffraction	x	x
	Mineral identification by structure		
	Qualitative mineral abundance and quantitative concentration		
SEM/EDS	Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy	x	x
	Grain morphology, size, habit, color, surface texture		
	Mineral identification by chemical composition		
	Qualitative mineral abundance and quantitative concentration		
EPMA	Electron Probe Microanalysis with Wavelength and Energy Dispersive X-ray Spectroscopy	x	x
	Grain size, habit, boundary texture		
	Mineral Identification by quantitative chemical composition		
TEM/EDS/ED	Transmission Electron Microscopy with Energy Dispersive X-ray Spectroscopy and Electron Diffraction		x
	Grain size, habit, internal texture		
	Mineral Identification by chemical composition and structure		
XRF	X-ray Fluorescence Spectroscopy	x	
	Chemical composition		
INAA	Instrumental Neutron Activation Analysis	x	
	Chemical composition		
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy	x	
	Chemical composition		
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry	x	
	Chemical composition		

* Bulk material includes bulk samples of raw ore, beneficiated ore, exfoliated ore, consumer products, and mineral concentrates from all of above.

** Optical microscopy includes both low-power stereomicroscopy with reflected light, and polarized light microscopy with transmitted light.