Antigorite

Is It the Forgotten Asbestos?

By Sean M. Fitzgerald & Elizabeth A. Harty

In many countries (not including the U.S.), asbestos use is banned due to associated health effects. However, in some regions of the world ongoing asbestos use persists thanks to its commercially useful qualities such as fire resistance, the ability to add tensile strength to materials, insulator potential and, in some cases, resistance to corrosion (Dodson & Hammer, 2011). The dangerous health consequences of asbestos make the discussion of alternative mineral sources a significant topic. Is an alternate, asbestos-like mineral available that can accomplish the same level of product enhancement without posing hazards to workers and consumers?

Asbestos is a term heard daily via U.S. media, thanks to the abundance of litigation centered on this topic. The word alone evokes thoughts of potentially painful, even terminal health effects due to exposure. Occupational safety and health (OSH) professionals understand that asbestos refers to six specific fibrous minerals that were regulated: one serpentine and five amphiboles, which are hydroxylated fibrous magnesium silicates (Dodson & Hammer, 2011). These minerals are still in commercial use today under government regulations (NIOSH, 2010, 2011). Ironically, asbestos is a label that has left the impression in some sectors of the OSH community that other hydroxylated fibrous magnesium silicates are not being used in commercial products.

When these minerals were regulated in the 1970s, it was determined that only those fibrous amphiboles and serpentines with commercial application would be assigned the label asbestos. Other minerals with similar crystal habits were not subject to regulation since these minerals were not expected to enter the commercial product supply and, thereby, expose the public and workforce to possible toxic effects (Baumann, Abrosi & Carbone, 2013; Walton, 1982).

Has this regulatory approach (or lack thereof) left industry unaware that it may be including asbestiform (having the form or appearance of asbestos) and potentially toxic mineral sources in products? The serpentine mineral antigorite is raising this question among the health-research and geological communities (Baumann, Maurizot, Robineau, et al., 2011; Cardile, Lombardo, Belluso, et al., 2007; Fitzgerald, 2013; Pugnaloni, Giantomassi, Lucarini, et al., 2010).

NIOSH (2002) recognizes the need to consider that carcinogenic potential may not be restricted to the six regulated asbestos minerals alone. As far back as 1990, NIOSH (2002) commented to MSHA:

> [T]here was no scientifically valid health evidence to exclude from an asbestos standard cleavage [the

IN BRIEF
- **The SH&E concerns of antigorite and its use in products are explored.**
- **Health researchers, academics and some in the geological community are raising questions about antigorite's asbestiform properties.**
- **The authors conducted some testing to determine what consumer products may contain antigorite. Fibrous silicate materials were found in all seven products tested.**

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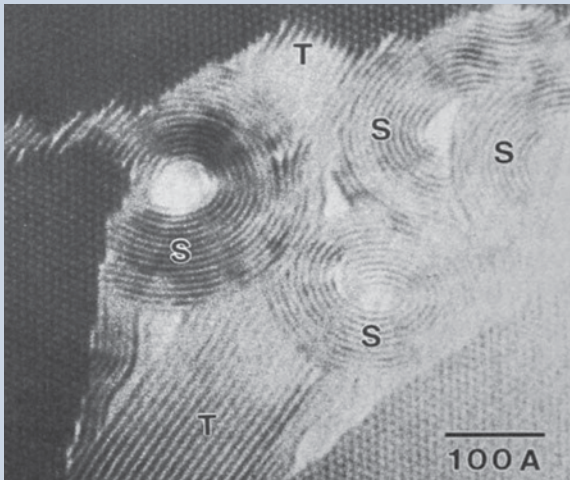


PHOTO 1 COURTESY DAVID R. VEBLEN/MINERALOGICAL SOCIETY OF AMERICA

Photo 1: Antigorite, chrysotile and talc. Cross-section perpendicular to fiber length of amphibole, talc (T) and serpentine (S) intergrowths under high-resolution transmission electron microscopy. Notice the flat talc sheet structure (parallel lines in cross-section), and the serpentine when scrolled is chrysotile. Also note the wavy structure under leftmost scroll, demonstrating the corrugated structure of antigorite.

splitting or dividing along definitive crystalline planes] fragments from the nonfibrous analogs of the asbestos minerals if they meet the microscopic definition of a fiber.

Methods such as light microscopy can be used to identify what is or is not asbestos based on length-to-width aspect ratios and overall fiber length. NIOSH (2002) has further stated that nonasbestiform analogs of the asbestiform minerals can cleave [split] during their handling and generate microscopic-sized fibers (i.e., fragments > 3:1 aspect ratio and > 5 µm in length) that are indistinguishable from the six (asbestiform) asbestos minerals when using phase contrast optical microscopy.

The potential health risks presented by minerals beyond the original six regulated asbestos minerals led NIOSH to explore its application of the definition of asbestiform fibers. This has generated much debate in recent years. Currently, NIOSH (2011) does not define antigorite as asbestos. However, the agency continues to specify that antigorite is a mineral to count as fibrous when it meets the dimensional criteria under microscopic view (NIOSH, 2002, 2011).

Antigorite: A Background

Antigorite (CAS number 12135-86-3) is a fellow serpentine with the widely used chrysotile asbestos (chrysotile) and as noted has chemical makeup consistent with its asbestos kin. These magnesium silicates, $Mg_3Si_2O_5(OH)_4$, differ primarily by their physical arrangement: chrysotile presents in a rolled fashion, while antigorite has a wavy or rippled effect (Photo 1).

In current literature, antigorite is often described as nonasbestiform (IARC, 2012; NIOSH, 2010; however, researchers have identified fibrous configurations of antigorite dating back to Deer, Howie and Zussman's 1966 work. Geologists are now noting this occurrence and are calling for further mineralogical studies (Fitz Gerald, Eggleton & Keeling, 2010; Fitzgerald, 2013; Keeling, Raven & Self, 2010) (Photos 2-4).

For example, in 2005, a routine geological assessment of an abandoned chrysotile mine located in Rowland Flat, South Australia, was conducted as part of a mining rehabilitative program. Curiously, the report concluded that the serpentine variety of asbestos mined for approximately 30 years at this quarry was asbestiform antigorite, not chrysotile as the mine had reported (Fitz Gerald, et al., 2010; Keeling, et al., 2010). The antigorite mined at this quarry demonstrated via electron microscopy the dimensional criteria necessary for an asbestiform classification (Fitz Gerald, et al., 2010; Keeling, et al., 2010). Asbestiform antigorite has been confirmed in quarry and mining products found in Europe, Australia-Oceania and North America (Baumann, et al., 2011; Cardile, et al., 2007; Fitzgerald, 2013).

This trend of asbestiform descriptions of antigorite has compelled the public health community to consider the biological impact of the often overlooked mineral. For example, Australian geologist John Keeling reported to the author that he helped NIOSH procure a 10 kg sample of asbestiform antigorite from Rowland Flat. As chrysotile was the serpentine mineral mined as asbestos, the scientific community is just now recognizing that not only is antigorite often a constituent of the material mined as chrysotile asbestos, but it has also been found to exhibit asbestiform morphology on its own.

Named after the Antigorio Valley in the picturesque Piedmont region of Italy, the mineral antigorite has inspired some compelling biological studies by Italian academics in recent years (Cardile, et al., 2007; Pugnaloni, et al., 2010). Fibrous antigorite has demonstrated toxicity at the cellular level that appears to parallel asbestos (Cardile, et al., 2007). In vitro epithelial cell viability has shown

Photo 2: Asbestiform antigorite from Granada, Spain (upper), and Rowland Flat, South Australia (lower).

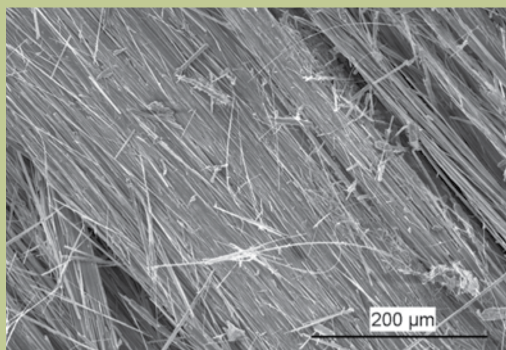


Photo 3 (left): Asbestiform antigorite, from Rowland Flat, South Australia; SEM.

Photo 4: Asbestiform antigorite identified in a closed quarry near Rowland Flat, South Australia. From the 1940s to 1978, the asbestos was identified first as an amphibole variety of asbestos and later as chrysotile asbestos. This past decade, John Keeling, mineral systems team leader of the Geological Survey of South Australia, identified the strong presence of asbestiform antigorite in the quarry.

vulnerability in the presence of fibrous antigorite (Pugnaloni, et al., 2010). Most recently, cases of mesothelioma have been reported to be environmentally associated with the fibrous mineral in New Caledonia (Baumann, et al., 2011).

In addition to the safety and health concerns of antigorite, it is important to understand the research that is exploring new potentials for the mineral. The gap of mineral supply created by the declining use of asbestos has established a wider market for the lesser-known antigorite. With the long-running assumption that the mineral is wholly nonasbestiform, mines, quarries and manufacturers may be building their commercial futures on erroneous reports, which adds to the significance of this topic. For example, current antigorite-related product descriptions found on a Canadian mine's website highlight its asbestos-like applications (Northfil, 2014).

While the OSH professional community is familiar with the traditional uses of asbestos, it is important to note that antigorite is also being targeted for use in an application with significant environmental consequence: carbon dioxide (CO_2) sequestration (Krevor & Lackner, 2011). Research is underway worldwide to identify economical means to neutralize CO_2 emissions from coal-burning electricity generation facilities (Power, Wilson & Dipple, 2013) to thereby reduce the growing industrial carbon footprint. Since magnesium, which is found in serpentine minerals such as antigorite, readily bonds with CO_2, this abundant natural resource is a logical place to look for the raw materials to drive the chemical equation in a favorable direction.

Indeed, specific research is considering the neutralization of CO_2 within redesigned storage facilities containing serpentinite mine tailings (Power, et al., 2013). Furthermore, chrysotile mines and quarries that have been closed due to their toxic hazards are being tapped as potential sources of serpentinite magnesium should the sequestration application prove economically feasible (Gale, 2000; Krevor & Lackner, 2011).

At Scientific Analytical Institute Inc., antigorite is often found during product testing for asbestos (Fitzgerald, 2013). The asbestos-forming minerals are closely related to antigorite, and as noted, the antigorite itself can be asbestiform. It is not unusual in the asbestos laboratory to see fibrous antigorite in talc samples (Fitzgerald, 2013; Photos 5 and 6, p. 46). Where there is abundant chrysotile, intergrowths of antigorite occasionally occur. To properly identify these intergrowths, which are considered interferences, accredited laboratories must maintain antigorite reference materials for their review (Richmond, 2006). Microscopists must familiarize themselves with antigorite to ensure successful asbestos identification.

Study Materials & Methods

Given the implications of antigorite as a potential hazard, the authors conducted some testing to determine what consumer products may contain antigorite. An online search for antigorite listed in an MSDS as an ingredient or natural contaminant revealed products available to any consumer.

Knowing that antigorite can present in a green marbleized fashion, the authors decided to pursue products sold as such. Green "marble" floor tiles were purchased at a home improvement store, and a mortar and pestle set made of similar material was purchased at a retail home decorating center (Photos 7 and 8, p. 47). Two mineral (rock) samples were purchased through eBay (Photo 9, p. 47); these products were advertised as the mineral antigorite (although one rock was described as originating in Canada's famous Jeffrey Mine). Wood and window glazing products intended for do-it-yourself use, as well as nail-hole and scratch-filling products, were purchased at a major retail center.

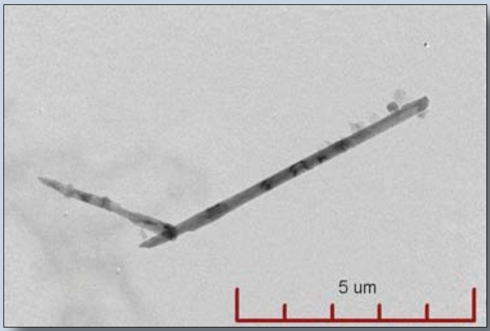


Photo 5: Antigorite fibers found in a talc product.

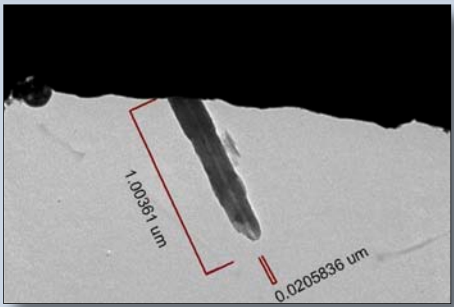


Photo 6: Antigorite-chrysotile fiber in talc product showing hollow center of scroll as a 200 nm tube.

PS EXTRA

To view additional photos provided by the authors, visit www.asse.org/psextra.

The MSDS (obtained from the manufacturer's website) differed slightly for each of the window glazing and blending stick products tested, although all three originated from the same manufacturer. The first glazing product listed CAS number 12135-86-3, the MSDS identification number for (nonasbestiform) antigorite, as a potential contaminant of the ingredient talc (CAS number 14807-96-6). This manufacturer labels CAS number 12135-86-3 as "nonfibrous serpentine," the group name for antigorite. The blending stick product used to repair blemishes in wood also lists antigorite as a naturally occurring contaminant of talc. CAS number 12135-86-3 is referenced on this product's MSDS, but in this case the name provided is "nonasbestiform antigorite." Only the third product that was assessed lists antigorite (CAS number 12135-86-3) as an ingredient in the product.

The products were analyzed for asbestos following the analytical procedures described in the EPA Test Method EPA/600/R-93/116, Method for the Determination of Asbestos in Bulk Building Materials. The samples were examined by polarized light microscopy and/or transmission electron microscopy (TEM), prepared in accordance with the matrix reduction sections of EPA/600/R-93/116. TEM analyses were conducted on a JEOL 2000FX TEM equipped with an energy-dispersive X-ray analyzer detector and selected area electron diffraction at magnifications up to 50,000 times.

To remove organics, a representative quantity of the suspect product was placed in a muffle furnace for approximately 12 hours at a temperature between 400 and 500 °C. Next, the sample was dissolved in hydrochloric acid and water to remove any acid and/or water-soluble materials (e.g., carbonates, gypsum, salts). The organic and acid soluble-reduced sample was then filtered through a 0.2 µm polycarbonate filter, weighed and resuspended in water to deposit aliquots of the residue on a 0.2 µm mixed cellulose ester (MCE). The final MCE filter was dried, collapsed with acetone and coated with carbon in a vacuum evaporator. The fibers and solids collected on the carbon-coated filter replicate were transferred onto copper grids for TEM analysis.

Study Results

Fibrous silicate materials were found in all seven products tested for antigorite or related materials in this study. One product was found to contain both asbestiform antigorite and chrysotile asbestos; one contained asbestiform antigorite; two contained tremolite asbestos; two contained both tremolite and chrysotile asbestos; and one revealed no antigorite or regulated asbestos, but was found to contain abundant aluminosilicate fibers (clay).

Specifically, both eBay-purchased products revealed examples of the mineral chrysotile asbestos, and one rock also had smaller amounts of tremolite asbestos (tremolite). Neither was found to contain antigorite, even though the materials were advertised as such (Photo 10). The floor tile sample contained asbestiform antigorite along with chrysotile and anthophyllite asbestos (Photo 11).

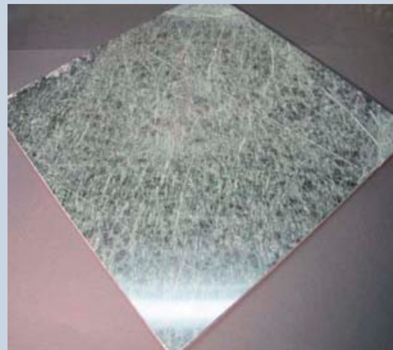
Highly asbestiform antigorite and tremolite were present in the mortar and pestle set, and tremolite was found in two of the do-it-yourself products that listed antigorite on their MSDS as a potential contaminant and ingredient. Coincidentally, the glazing products did not contain any form of antigorite (Photo 12, p. 48). Last, clay and talc fibers were present in the blending stick product but no antigorite contamination was identified.

OSHA (2004) defines an asbestos-containing material as any material that contains more than 1% asbestos. Given this definition, it is important to note the estimated percentages of asbestiform material in the assessed products. The eBay antigorite rock material was nearly 100% chrysotile. The second eBay antigorite rock contained at least 1% tremolite and 40% chrysotile. The mortar and pestle contained at least 5% asbestiform antigorite and the marble floor tile contained 10% chrysotile and 20% asbestiform antigorite. Both glazing compounds contained quantifiable tremolite, but the amounts were less than 1%. The asbestiform antigorite was observed with length-to-width aspect ratios in excess of 10:1, making it countable as asbestos by any counting method.

Discussion

The authors expected to find some form of antigorite in all products; however, the test results indicate the complex relationship among regulated asbestos and the unregulated antigorite. It is evident that MSDS inaccuracies occur and that while antigorite may be listed as an ingredient, another regulated asbestos mineral may be present instead. The presence of tremolite in the products was in some cases unexpected. However, since the geology of antigorite and tremolite are closely

PHOTOS 5-12 COURTESY SEAN FITZGERALD/SCIENTIFIC ANALYTICAL INSTITUTE INC.



(Left to right) Photo 7: Mortar and pestle set purchased from a kitchen supply retailer. This product was sold as a marble mortar and pestle, suitable for use in preparing foods.

Photo 8: Example of floor tile sold as "green marble."

Photo 9: Antigorite sample purchased from eBay, as it appeared upon shipment.

related and often occur together, the presence of one where another is named is not novel. In other words, it is reasonable to expect materials that include antigorite to also contain regulated asbestos minerals. In addition to the concerns about regulated asbestos present in some of the products tested, the presence of asbestiform antigorite in accessible commercial products lends weight to the growing interest among health researchers.

Equally as difficult to navigate are the CO_2 mitigation applications that might involve antigorite in the future. The growing interest in CO_2 sequestration and capture is an important global health endeavor. This topic will continue to arise as the world attempts to think green and reduce its carbon footprint. However, could this pursuit cloud the interest to promote occupational and public safety? With the political issues surrounding climate change, will safety-conscious regulators be in the minority if antigorite is confirmed as an asbestiform toxin?

The potential uses and dangers of antigorite make this a priority concern for the OSH professional community. Health researchers, some American and Italian academics, and some in the geological community are beginning to raise questions about antigorite's asbestiform properties.

It is important to consider potential risks to those who reside near antigorite quarries and mines. It is also important to assess how safe this mineral is for workers who directly handle and transport it. Furthermore, what risks do consumers using antigorite-based or antigorite-intended products face? Perhaps it is also time to reconsider which minerals should be included in the grouping known as asbestos. Antigorite is well worth considering for further study and not left as the asbestos forgotten. **PS**

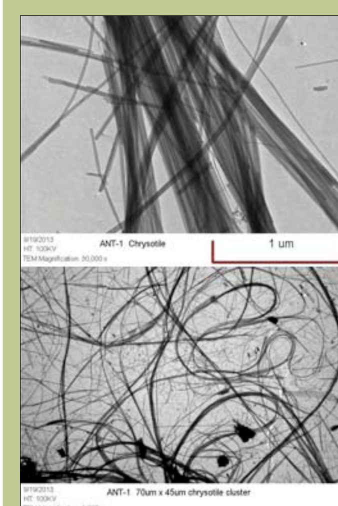


Photo 10: Antigorite sample purchased through eBay. Photo (top) of mineral sample under TEM magnification at 30,000 times. Photo (bottom) of mineral sample under TEM magnification at 1,200 times. Under TEM magnification abundant chrysotile asbestos fibers are present in the mineral sample advertised as "antigorite."

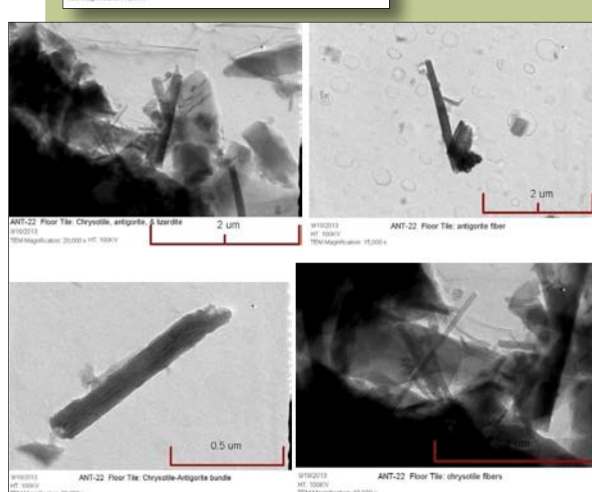


Photo 11: TEM analysis: Fibers of chrysotile and antigorite found in floor tile. The tile contained 10% chrysotile asbestos and 20% asbestiform antigorite.

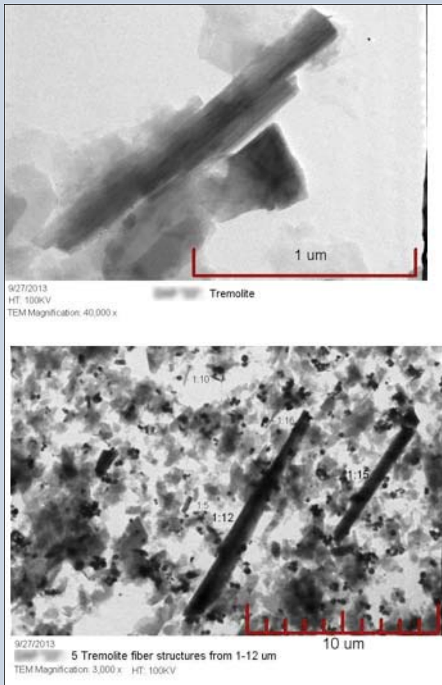


Photo 12: Window glazing: antigorite sample. Tremolite asbestos fibers in TEM analysis of window glazing. The product's MSDS lists antigorite as an ingredient. In this sample set, no antigorite was present; however, tremolite asbestos fibers were identified.

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