

# Use of Malachite Green Stain as an Auxiliary Technique for Differentiation of Asbestiform Sepiolite From Chrysotile Asbestos<sup>1</sup>

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## KEYWORDS

Asbestos, central stop dispersion staining (CSDS), chrysotile, clays, kaolinite, malachite green stain, montmorillonite, polarized light microscopy (PLM), sepiolite, transmission electron microscopy (TEM)

## ABSTRACT

Most matrixes submitted to environmental laboratories for asbestos analysis are considered routine and do not present unique analytical challenges. Occasionally, materials are encountered that contain non-regulated asbestiform minerals, which can be misidentified as asbestos. The clay mineral sepiolite,  $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$ , can be asbestiform and is used as a substitute to chrysotile,  $Mg_3Si_2O_5(OH)_4$  in some applications. Asbestiform sepiolite is structurally, compositionally and optically similar to chrysotile, which can exhibit a variability that complicates differentiation. The similarity of sepiolite to chrysotile, combined with chrysotile compositional variability, can result in false positives. Malachite green stain (1) is a relatively simple and quick technique for differentiation of sepiolite from chrysotile in conjunction with polarized light microscopy (PLM) analysis.

## INTRODUCTION

The clay mineral sepiolite was first described in 1847 from an occurrence in Bettolino, Baldissero Canavese, Torino Province, Piedmont, Italy (2). The

mineral name is derived from the Greek *sepiou*, based on a perceived resemblance to porous cuttlefish bone. (1) Shortly after its discovery, the ease in which massive forms could be carved made it suitable for manufacture of meerschaum pipes. Sepiolite has been mined since the 1940s, but it is a relatively uncommon clay mineral and most deposits are small. Due to its unique properties, it has been used in drilling fluids, kitty litter, polymer fillers, pharmaceutical carriers, joint compounds and pesticides (3).

In 1989, the U.S. Environmental Protection Agency issued a ban on products containing asbestos (4). Regulation of chrysotile asbestos in the late 1980s meant that manufacturers needed to find suitable substitutes for numerous applications. Discovery of a few small commercially viable deposits of asbestiform sepiolite led to testing of physical properties in order to assess feasible use of the mineral as a chrysotile substitute (5). Research and development over the years has resulted in the use of fibrous sepiolite for chrysotile in gaskets and other products that once contained chrysotile.

During routine PLM analysis of a gasket, a fibrous mineral was observed at a level greater than 1%. The mineral was morphologically similar to chrysotile, but had refractive indexes slightly lower than is typical of most chrysotile observed in building materials. Malachite green, a clay stain typically used to differentiate smectite from kaolinite, was applied to several of the fibrous mineral bundles. Adsorption of the stain indicated that the mineral was a fibrous clay (sepiolite) asbestos substitute, not chrysotile. In this

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**Table 1: Comparison of Sepiolite and Chrysotile Optical and Structural Properties**

Mineral	Formula	Lattice System	Cell Dimension	Mg:Si Ratio	Refractive Indexes*	Optic Sign	Sign of Elongation	2V	Birefringence
Chrysotile	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Orthorhombic/ monoclinic	a=5.313, b=9.12, c=14.64	7:10	1.493-1.549 (alpha) 1.517-1.571 (gamma)	Biaxial negative	Positive	20 — 60	0.010
Sepiolite	Mg <sub>4</sub> Si <sub>4</sub> O <sub>15</sub> ·6H <sub>2</sub> O	Orthorhombic	a=13.43, b=26.88, c=5.281	5:10	1.52 (alpha) 1.53 (gamma)	Biaxial negative	Positive	20 — 70	0.010

\*Sources: webmineral.com, mindata.org, National Voluntary Laboratory Accreditation Program (NVLAP) and *Handbook of Mineralogy*. Refractive index data for chrysotile includes NVLAP range for acid treated/affected specimens.

paper, the similarities that could result in the misidentification of sepiolite as chrysotile, along with the staining procedure used to distinguish the two minerals, are discussed.

#### COMPARISON OF CHRYSOTILE AND SEPIOLITE

Structural and optical data for chrysotile and sepiolite are compared in Table 1. The first observation to be made from this table is that both minerals are magnesium silicates of similar chemical composition and structure. Comparable cell dimensions and Mg:Si ratios could result in erroneous identification by energy dispersive X-ray analysis (EDX) and selected area electron diffraction (SAED) during transmission electron microscopy (TEM) analysis. TEM differentiation could be further complicated by acid leaching of chrysotile (reduced Mg:Si ratios, diffraction degradation) or encounters with chrysotile fibers atypical of standards.

A comparison of the optical properties of chrysotile and sepiolite further exemplifies how fibrous sepiolite could be misidentified as chrysotile. Sepiolite's birefringence, sign of elongation and refractive indexes are within the range of accepted values used for chrysotile identification. Note that chrysotile clearly has compositional variability as evident from its refractive index ranges.

The similarity in birefringence and morphology of fibrous sepiolite compared to chrysotile is shown in Figures 1-4. NIST 1866 SRM and Thetford Mines (Quebec) orthochrysotile are provided as control examples of morphologic and refractive index variability among chrysotile specimens. Figures 4 and 8 are images of

fibrous sepiolite from a gasket for comparison. All specimens exhibit distinct asbestiform morphology with discrete fibrils, parallel sides, curvature and splayed ends. The Thetford Mines chrysotile (Figure 2) is morphologically more similar to the Quincy-sur-Cher (France) sepiolite reference specimen (Figure 1) than the NBS SRM (Figure 3).

A refractive index comparison by means of central stop dispersion staining (CSDS) is shown in Figures 5-9. Differences in the CSDS colors observed for the Thetford Mines orthochrysotile (Figure 7) and the NIST 1866 SRM (Figure 8) is an indication of compositional (magnesium content) variability. An example of change in chrysotile refractive index upon acid leaching as a simulation of alteration is evident from the lighter blue CSDS color shown in Figure 9. Note that the CSDS color of the acid leached chrysotile (Figure 9) is similar to that observed for fibrous sepiolite (Figures 5 and 6), indicating that sepiolite could possibly be miscategorized as altered chrysotile.

#### MALACHITE GREEN STAIN TECHNIQUE

Visual differentiation of minerals in thin section by optical microscopy using staining techniques was routine laboratory procedure in the 1940s and 1950s (7, 8, 9). Mineral stain research proliferated with particular emphasis on clays due to inherently small particle sizes that make speciation by optical properties alone difficult. It was during this period that Faust (1) developed a simple technique for differentiating kaolinite (non-swelling clay) from montmorillonite (a swelling smectite clay) by using a diluted solution of malachite green in nitrobenzene after acidification.

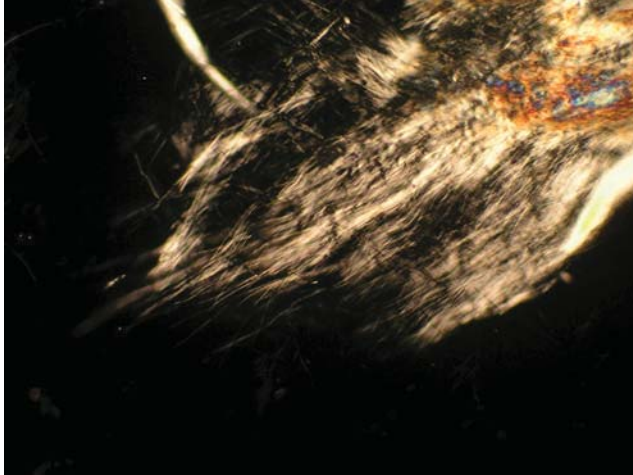


Figure 1. Quincy-sur-Cher fibrous sepiolite reference viewed in crossed polarized light at 200X magnification.



Figure 2. Theftord Mines orthochrysotile viewed in crossed polarized light at 200X magnification.

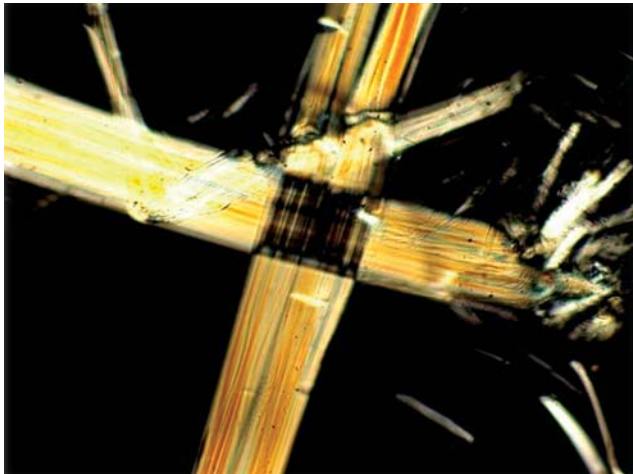


Figure 3. NIST 1866 SRM chrysotile viewed in plane polarized light at 200X magnification.

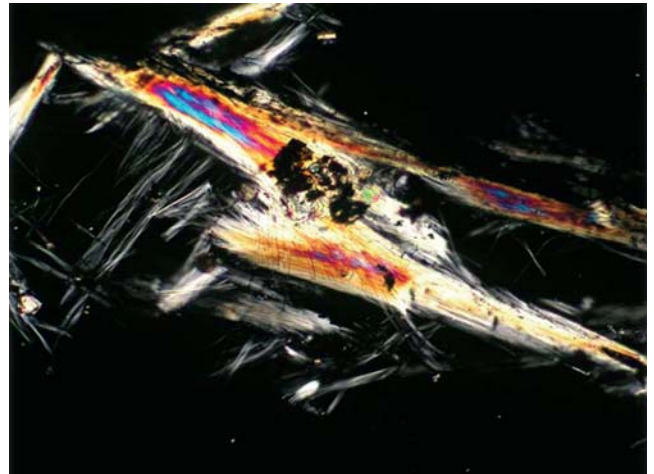


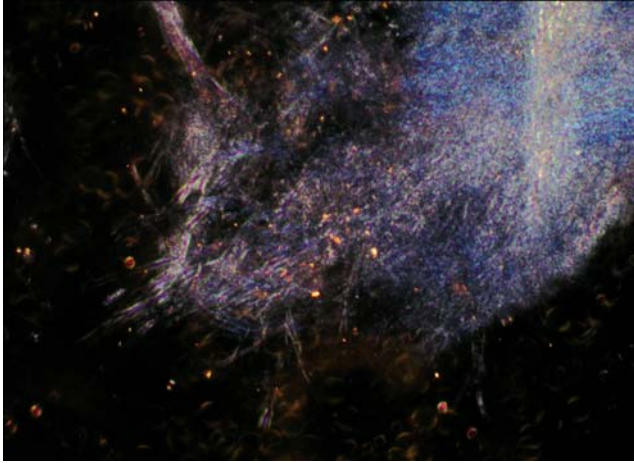
Figure 4. Sepiolite bundle removed from gasket viewed in crossed polarized light at 100X magnification.

In the procedure, clay is dispersed in 10% hydrogen chloride (HCl), an aliquot of the slurry is placed on a microscope slide and taken to dryness on a hot plate at approximately 110 °C. A drop of malachite green in nitrobenzene is placed on the acidified clay, dispersed, and washed to remove excess dye. Faust found that clays with exchangeable cations such as montmorillonite adsorb malachite green and turn a green color. Clays such as kaolinite with little or no exchangeable cations and less adsorption capacity turn yellow. Use of the stain appears to have received little notice until the 1970s, when Palenik (10) extended its application for particle identification by using microchemical techniques in forensic investi-

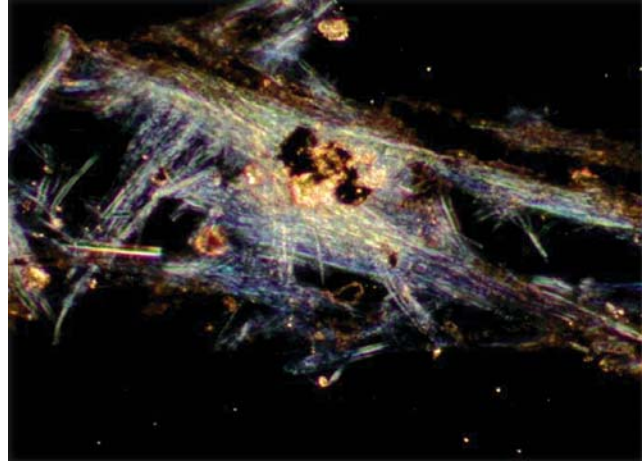
gations. In the 1990s, the stain was applied to quantification of small quantities of montmorillonite in kaolins for quality control of coatings (11). A preliminary finding of application of differentiation of sepiolite from chrysotile using the staining procedure was reported in 2007 (12).

#### DIFFERENTIATING SEPIOLITE FROM CHRYSOTILE WITH MALACHITE GREEN STAIN

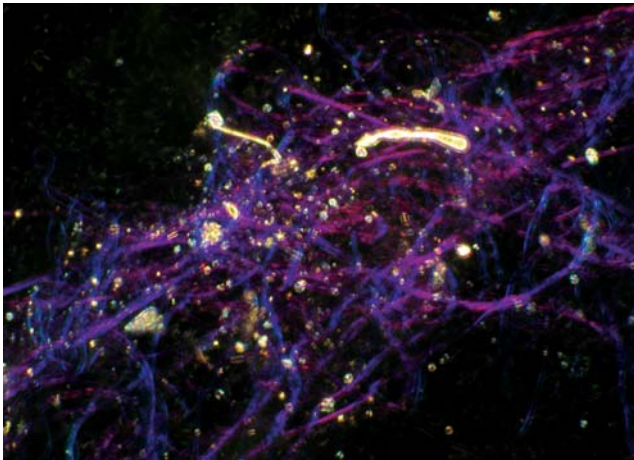
Although sepiolite is a non-swelling clay, it possesses a high surface area and porosity due to a tubular zeolitic water channel in its fibrous structure. The structure of sepiolite accounts for greater adsorptive



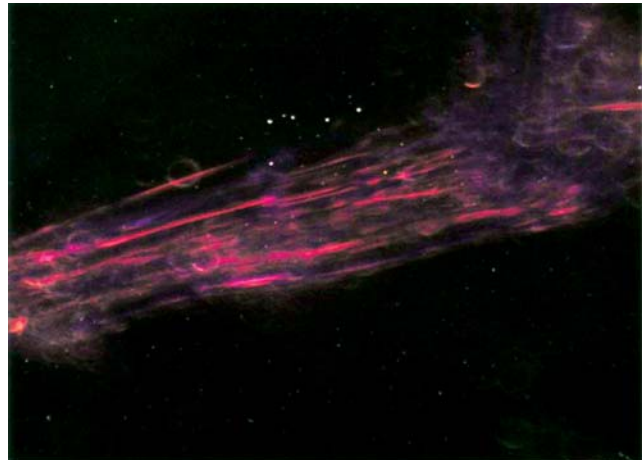
**Figure 5.** Quincy-sur-Cher sepiolite viewed with central stop dispersion staining in Cargille Series E 1.550 refractive liquid at 100X magnification.



**Figure 6.** Sepiolite from a gasket viewed with central stop dispersion staining in Cargille Series E 1.550 refractive liquid at 100X magnification.



**Figure 7.** Thetford Mines orthochrysotile viewed with central stop dispersion staining in Cargille Series E 1.550 refractive liquid at 100X magnification.



**Figure 8.** NIST SRM 1866 chrysotile viewed with central stop dispersion staining in Cargille Series E 1.550 refractive liquid at 100X magnification.

and absorptive capacity than non-swelling clays such as kaolinite. Application of the malachite green stain on sepiolite (in the manner described above) from a gasket and the Quincy-sur-Cher sepiolite control produced a deep bluish green color (Figures 10 and 11). Unaltered chrysotile (no acid leaching) is not sorptive and does not stain (Figure 12). Chrysotile exposed to concentrated HCl for prolonged periods (more than 24 hours) results in higher stain sorptive capacity due to leaching of magnesium after application of the stain (Figure 13). However, the color of the stain is a slightly grayish hue and is uneven, suggestive of alteration effects, not structural staining.

## CONCLUSIONS

Sepiolite is a fibrous clay mineral that can crystallize in an asbestiform habit. The physical properties of asbestiform sepiolite make it useful as an asbestos substitute for some applications. The structural, chemical and optical properties are similar to chrysotile, which can lead to false positives by analysts not familiar with sepiolite. Utilization of malachite green stain following the Faust technique can serve as a useful and quick auxiliary technique to PLM analysis for differentiating sepiolite from chrysotile in some instances. Chrysotile affected by acid leaching may present an interfer-

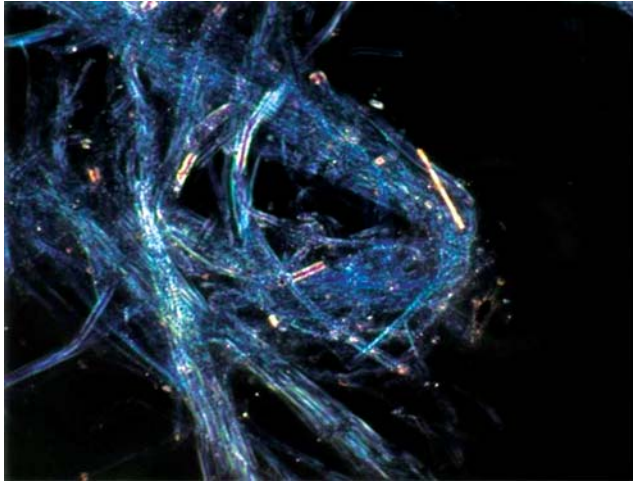


Figure 9. NIST SRM 1866 chrysotile after 24 hours in concentrated hydrogen chloride, viewed with central stop dispersion staining in Cargille Series E 1.550 refractive liquid at 100X magnification.

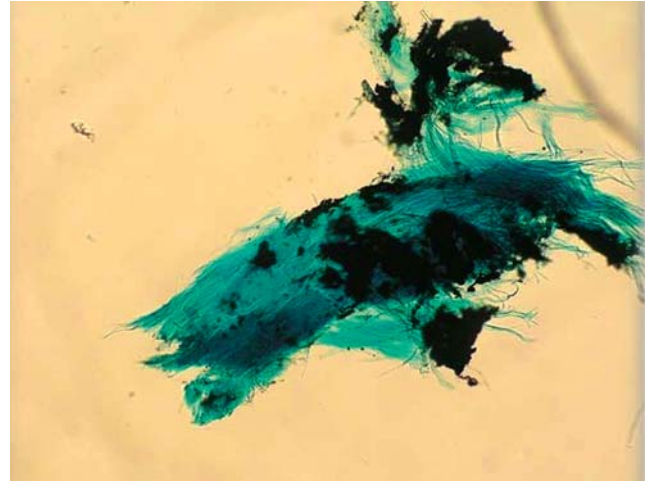


Figure 10. Malachite green stained sepiolite from a gasket, viewed in plane polarized light at 100X magnification.



Figure 11. Malachite green stained Quincy-sur-Cher sepiolite control, viewed in plane polarized light at 100X magnification.

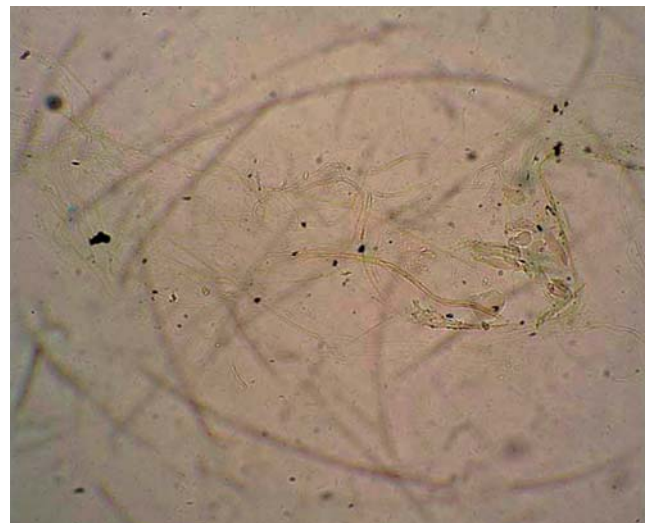


Figure 12. Thetford Mines chrysotile showing lack of stain sorption, viewed in plane polarized light at 100X magnification.

ence as it can sorb malachite green stain. Comparison of reference slides used as controls, however, should facilitate differentiation of sepiolite from acid leached/ altered chrysotile during staining investigations.

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**Figure 13.** Malachite green stained NIST SRM 1866 chrysotile leached for 24 hours, viewed in plane polarized light at 100X magnification.

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