

GRACE



Zonolite
Construction Products Division

TO: A. N. Crawford

DATE: August 31, 1984

FROM: J. R. Hindman

SUBJECT: Commentary on the Chatfield
& Lewis paper, "Development &
Application of Analytical Techni-
que for Measurement of Asbestos
Fibers in Vermiculite"

cc: W. J. McCaig, H. C. Duecker, ~~J. R. Hindman~~

INTRODUCTION

As you requested, I have studied the data and conclusions presented by Chatfield and Lewis concerning "Vermiculite Scrolls". Since their conclusions are based on elemental analysis by energy dispersive x-ray (EDX) methods and crystal structural parameters obtained by selected area electron diffraction (SAED), I should clarify some aspects of the magnesium rich sheet silicate minerals for you first.

SOME BASIC CRYSTAL STRUCTURE

Phyllosilicates are a class of silicate minerals that are characterized by sheets of SiO_4^{-4} and AlO_4^{-5} tetrahedra linked together in a two dimensional array. This is usually referred to as the tetrahedral layer and it is normally attached on the apex side to a layer of di- or trivalent cations and hydroxyl ions in what is referred to as the octahedral layer. The cations in octahedral coordination are surrounded by six hydroxyl ions, or a combination of the oxygen atoms (which are the apices of the $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra) and hydroxyls. In Figure 1, the basic tetrahedral sheet (Si_4O_{10}) and octahedral layer, as brucite $\text{Mg}(\text{OH})_2$, are shown. The symbols of connected triangles and connected parallelograms are used later for the sake of clarity. Ionic substitution in the tetrahedral sheets is usually limited to Al for Si. However, in the octahedral layer one may find Mg, Fe, Al and rarely Li.

In Figure 2, the simplified structures of phlogopite mica, magnesium chlorite, magnesium vermiculite, and chrysotile are shown. By using structural symbols one is able to see that the four structures are elegant in their simplicity. In phlogopite the octahedral layer is sandwiched between two tetrahedral sheets. The strong charge imbalance caused by 25% of the tetrahedral cations being Al^{+3} is compensated for by potassium ions between the tetrahedral-octahedral-tetrahedral sheets. (If there were no aluminum in the tetrahedral layer, there would be no charge imbalance, no potassium, and the structure would be that of talc).

Although phlogopite does not commonly alter to chlorite, the structure of talc-chlorite is shown because of its resemblance to that of vermiculite. In vermiculite the layer which contained potassium before alteration of phlogopite now contains

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exchangeable cations surrounded by water molecules in octahedral coordination. In chlorite, non-exchangeable magnesium octahedrally surrounded by hydroxyls occupy this layer. The two structures are similar in size.

Chrysolite is the simplest structure with layers of one tetrahedral sheet bound to the octahedral sheet and nothing between the layers. The resulting layer to layer distance is about 7.3 A, compared to 10 A for phlogopite and 15 A for vermiculite.

SOME BASIS CRYSTAL CHEMISTRY

In the table below are listed some chemical data for magnesium phyllosilicates. Chatfield and Lewis do not report analyses for Na, K, Ca or Fe and so we will not consider these elements. Remember that Al can substitute in both tetrahedral (Si) and octahedral (Mg) positions.

	<u>% Mg</u>	<u>% Al</u>	<u>% Si</u>
Phlogopite	17.48	6.47	20.19
Chlorite	26.32	nil	20.27
Mg-Vermiculite	17.74	4.11	20.19
NH ₄ -Vermiculite	15.75	4.08	20.01
Chrysotile	30.50	nil	23.49

In the chemical evaluation of the vermiculite scrolls, Chatfield and Lewis measure peak areas of energy dispersive x-ray spectra. While this type of data can be used for qualitative and semi-quantitative work, there are two drawbacks which should be kept in mind: EDAX won't detect lithium, and sodium data is affected by the use of copper-TEM grids. Both Li and Na can enter into the vermiculite structure.

IDENTITY OF VERMICULITE SCROLLS

There are two primary criteria for identifying a mineral phase: chemical composition and crystal structure. Remember in Figure 2 one could see that phlogopite, vermiculite and chrysolite share common building blocks - the tetrahedral and octahedral layers. Thus, it is expected that x-ray or electron diffraction photographs should share common features. Of primary importance is the repeat distances along the "zero layer". Chrysolite must show a reflection at 7.3 A and vermiculite should show a reflection at 14-15 A. The repeat distance in the scrolls

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is 10.2 Å which would indicate a mica structure. There is another reflection appearing between the (002) and the (020) chrysotile positions which could be diagnostic if identified.

The chemical data obtained by EDAX is not as satisfying as one would like. The Mg/Si and Al/Si peak area ratios obtained from the scrolls are too low for vermiculite and phlogopite, and don't match other magnesium phyllosilicates. If the EDAX data is acceptable and the assumption of a mica structure is correct, then we have a fascinating enigma. The enigma can be explained if the Palabora mill uses froth flotation in its mineral processing.

It is well known that ammonium ions can replace cations in the exchangeable layer of vermiculite. The ammonium vermiculite crystal structure is smaller than that of magnesium or calcium vermiculite and is similar to that of biotite or phlogopite. The probability of finding NH_4^+ in a cationic flotation circuit is quite good.

It is not uncommon to add soluble silicate compounds to reagent schemes. At Libby fluorosilicic acid is used; and sodium silicate is commonly added at other locations. When one considers the size of a vermiculite scroll one can see how a coating of silicate-organic reagent could add Si in a non-crystalline form and add an EDAX invisible coating of organic molecules. Whether or not this coating would cause a vermiculite platelet to curl is not clear, but this organic layer "jelly rolled" into the scroll would account for the low electron scattering power mentioned by Chatfield and Lewis.

In summary, vermiculite scrolls may be ammonium vermiculite containing residual flotation reagent.

EXFOLIATION STUDY

On page 331, Chatfield and Lewis referred to a study of fibers/scrolls collected from samples after expansion in a muffle furnace. The results of this study would be interesting since chrysotile decomposes to olivine, Mg_2SiO_4 at about 600° C. One would also expect that a major change in NH_4 -vermiculite might take place before reaching that temperature.

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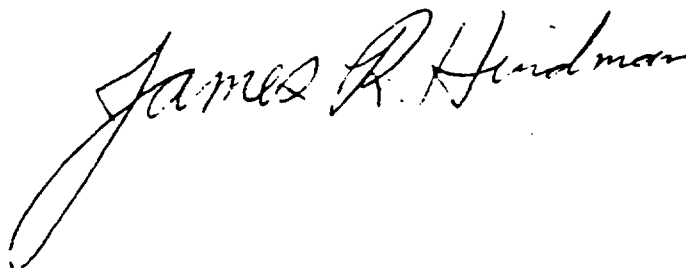
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CONCLUSIONS

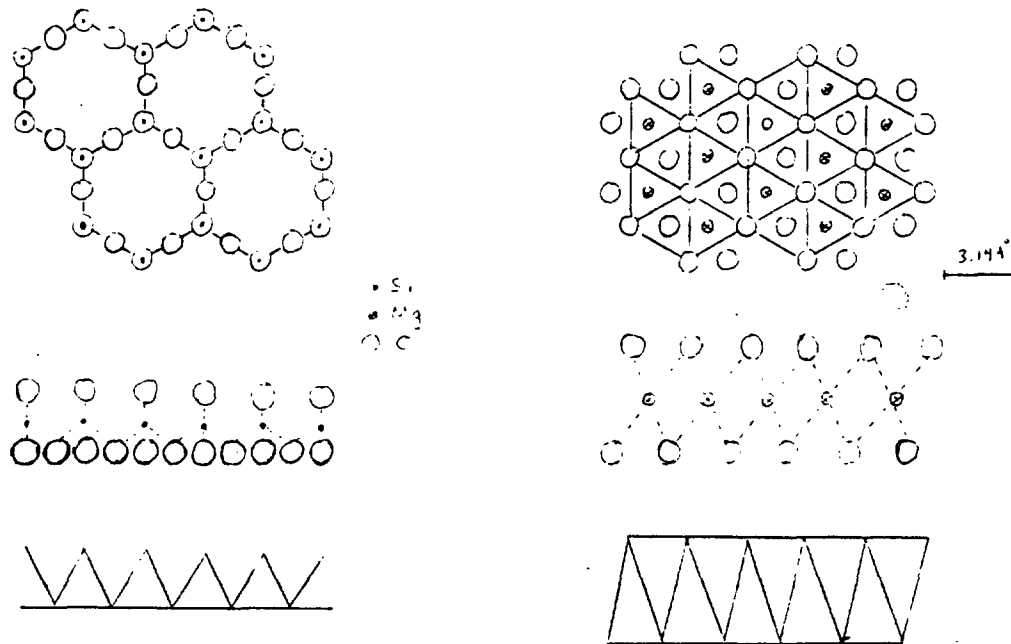
Chemical and electron diffraction data presented by Chatfield and Lewis indicate that vermiculite scrolls are similar to a mica structure and may be NH_4 -vermiculite. The NH_4 -vermiculite scrolls could be formed by the action of NH_4^+ ions and soluble silicate reagent components present in the Palabora mill. This analysis, if correct, would have obvious implications for LTEV products and fiber counts. The electron diffraction data presented by Chatfield and Lewis do not indicate the presence of chrysotile in those vermiculite scrolls studied.

J.R.HINDMAN:ch
Attachments: Figures 1 and 2

A handwritten signature in cursive script, reading "James R. Hindman". The signature is written in dark ink and is positioned to the right of the typed name and attachments.

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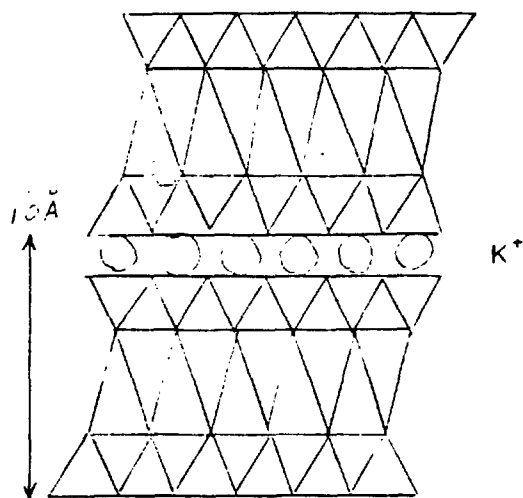
FIGURE 1. THE BASIC BUILDING BLOCKS OF SHEET SILICATES: THE
TETRAHEDRAL LAYER (LEFT) AND THE OCTAHEDRAL LAYER (RIGHT)



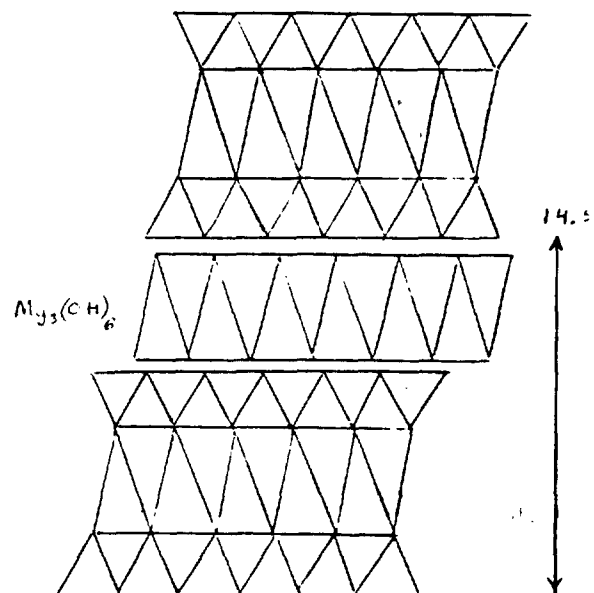
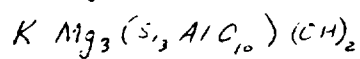
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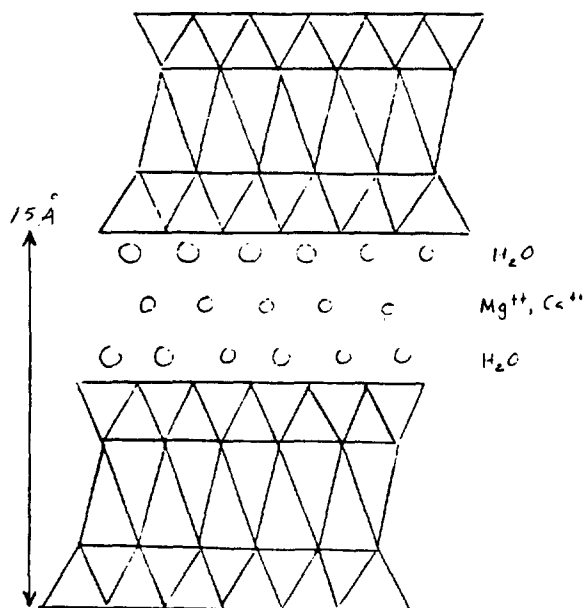
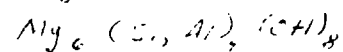
FIGURE 2. THE GENERAL STRUCTURES OF FOUR MAGNESIUM PHYLLOSILICATE MINERALS



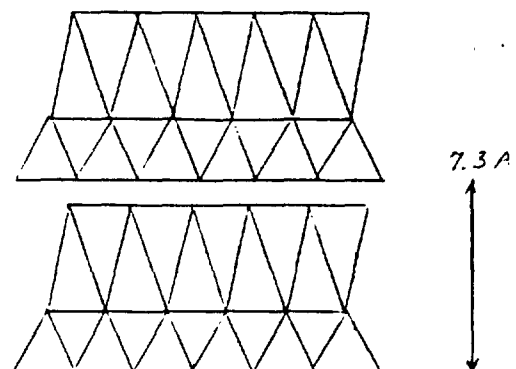
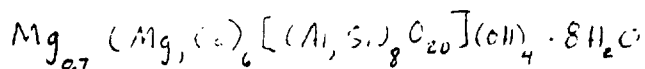
Phlogopite



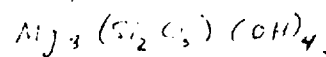
Magnesium Chlorite



Vermiculite



Chlorite



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