

## An occurrence of a modulated serpentine related to the greenalite-caryopilite series

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### ABSTRACT

Transmission electron microscope (TEM) and X-ray powder-diffraction studies indicate that material originally described as the Zn- and Mn-rich serpentine mineral baumite contains predominantly submicroscopic coherent intergrowths of 7-Å and 14-Å phases. The 7-Å phases include at least two polytypes (group A and either group B, C, or D) of lizardite and a modulated 1:1 layer silicate similar to those of the greenalite-caryopilite series. The 14-Å phase includes a dominant chlorite-*Ibb* structure. A chrysotile-like phase is present also, although it is rare. Semiquantitative chemical analyses indicate that all phases are Zn and Mn rich, but crystal-chemical arguments are used to suggest that the greenalite-caryopilite-like phase is relatively Al poor. The modulated 1:1 layer silicate differs structurally from greenalite and caryopilite by having island-like domains of about 30 Å (vs. 21.3–23.3 Å for greenalite and 16.7–17.2 Å for caryopilite). Accompanying veinlets appear to be lizardite-*IT* altering to chlorite-*Ibb* and chlorite-*Iba*, with these phases chemically distinct from those more directly associated with the modulated 1:1 layer-silicate phase.

### INTRODUCTION

Fron del and Ito (1975) described baumite, a new serpentine mineral, and “brunsvigite,” a variety of chlorite, from specimens found at the Buckwheat dump at Franklin, New Jersey. They also reported a “pennine” from a franklinite ore specimen. These minerals contain unusually large amounts of MnO (5.5 to 12.3 wt%) and ZnO (4.75 to 9.6 wt%). Baumite occurs as fine-grained, dense, black masses “up to a foot in diameter” and is brownish yellow in thin section. The “brunsvigite” occurs as greenish-black radial crystals in low-temperature hydrothermal veinlets crossing the baumite. The “brunsvigite” and “pennine” described by Fron del and Ito are more properly designated manganoan zincian chamosite and clinochlore, respectively, based on the reported chemical analyses. Both chlorites contain substantial amounts (13.1 to 14.0 wt%) of alumina, and baumite apparently contains lesser amounts (6.60 wt%). Bayliss (1981) argued that baumite should be redefined as a manganoan ferroan lizardite-*IT*, after he confirmed that the powder pattern as presented by Fron del and Ito could be indexed on a *IT* cell. This suggestion, however, was not approved by the IMA (E. H. Nickel, personal communication, 1988).

Unpublished work (P. Dunn, personal communication, 1988) indicated that a clinochlore does occur associated with baumite, but this material has not been studied. Dunn re-examined the original material and found baumite to occur as a breccia cement in a low-temperature cavity or vein filling. Although the original mass was

over a foot in length, baumite comprised no more than 25% by volume. The chamosite and baumite breccia hosts white willemite (crystallites 1 × 3 cm in size) and white granular calcite, along with franklinite, acmite (=aegirine), and stilpnomelane. The stilpnomelane is brown, probably Fe rich, and varies in texture from fine to coarse grained. Locally, stilpnomelane may be enclosed by friedelite, which occurs as late-stage crystals in fractures.

Baumite is of special interest because it is possibly a modulated structure as a result of its reported low Al content and its high tetrahedral Si and octahedral Fe + Mn + Mg + Zn. Samples studied (Harvard Museum no. 114072: type material labeled “baumite” and an unnumbered specimen labeled “brunsvigite” from J. L. Baum) did not contain any of the clinochlore crusts. The present paper concludes that both the baumite and the chamosite are submicroscopic, coherent intergrowths of 7-Å and 14-Å phases plus small amounts of other materials. It is noted, furthermore, that the material does contain a new mineral similar to those of the greenalite-caryopilite series. However, this mineral cannot be documented adequately to give it new species status because it is intimately mixed with other phases.

### EXPERIMENTAL METHODS AND INTERPRETATION

#### Baumite

**X-ray study.** Over 40 Debye-Scherrer patterns were obtained from different submillimeter-sized particles of baumite. Most particles were cut from thin sections so as

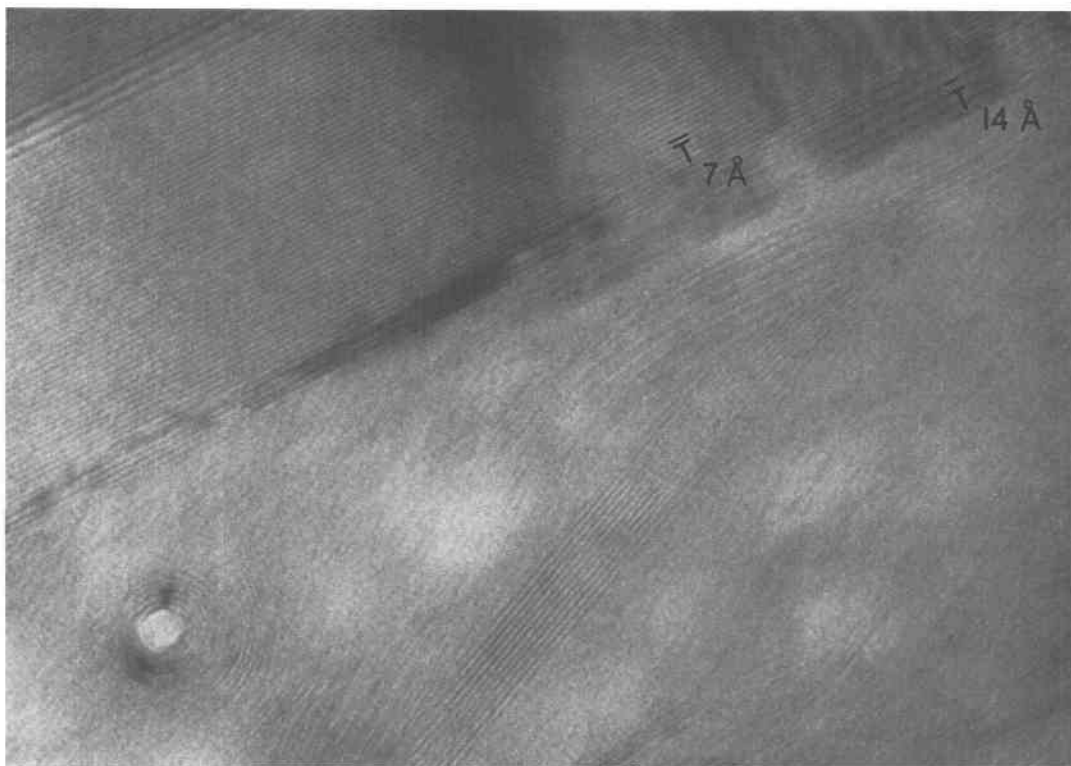


Fig. 1. Lattice fringes in optical (TEM) images show 7-Å and 14-Å phases commonly intergrown as aligned plates on the (001) plane. Chrysotile-like grains (note ring-like feature) were rare. The upper portion of this photograph, therefore, is more representative of the sample than the lower portion.

to include only microscopically homogeneous material. The particles were mounted on glass fibers, centered in 114.6-mm-diameter film cameras, and exposed to filtered  $\text{FeK}_\alpha$  X-radiation.

All patterns contain a strong 7-Å diffraction line and a medium-intensity 14-Å line. The ratio of the two intensities is approximately constant in patterns from most particles, although in some cases, the 7-Å line is enhanced. The non-00 $l$  lines show considerable similarities between diffraction patterns also, but with some differences in the weaker lines. Two patterns contained a line at about 9.5 Å that is interpreted as indicating the presence of a talc-like phase.

The 14-Å line indicates that chlorite is a major constituent of baumite, but the structural type could not be identified because of the overlap with the patterns from one or more 7-Å phases. It was observed that the even orders of the 14-Å spacing (00 $l$ ,  $l = 2n$ ) are consistently stronger than the odd orders. Calculations show that no distribution of heavy and light atoms between the octahedral interlayer sheet and the octahedral sheet of the 2:1 layer of a chlorite structure can account for the observed intensity ratios. For example, increasing the heavy atom content of the interlayer decreases the 001 intensity relative to 002, but increases that of 003. The observed intensities require either an interstratified 7- and 14-Å

series or a physical mixture of 7 Å and 14 Å phases. Support for both interpretations can be found in the accompanying TEM study. A few diffraction patterns show even-order 00 $l$  reflections as doublets, apparently because of compositional differences between the 7-Å and 14-Å phases within some particles. Nearly all patterns also show diffraction lines of strong to medium intensity at 1.54 Å and 1.60 Å, which can be indexed as  $d_{060}$  of chlorite and  $d_{060}$  of a greenalite-caryopilite-like phase, respectively. Heating particles at 500 °C increases the intensity of the 14-Å line and decreases all other lines.

**Transmission electron microscopy (TEM) study.** Samples of baumite were prepared by standard ion-thinning techniques using Cu grid supports. Also, powder mounts were made by dispersing finely abraded material on holey C film supported on a nylon grid. Material was examined in a JEOL 100CX microscope with a Tracor Northern EDS attachment.

The ion-thinned grids showed the variable morphology and textures of the mineral assemblages of the samples. Although most of the grains have platy morphology, some sample areas exhibit chrysotile-like rolls (Fig. 1). Most platy grains are intergrowths of 7-Å and 14-Å phases aligned parallel to the (001) planes. In one case, a 21-Å repeat was observed in the diffraction pattern, suggesting a regularity in intergrowth at the unit-cell level. This phase,

however, was extremely rare. Unlike the X-ray study, no phase with a 9.5-Å spacing was noted by TEM.

Electron-diffraction patterns of grains showing a platy morphology and containing  $c^*$  characteristically show the superposition of two nets. One net could be attributed to a 14-Å chlorite and the other to a 7-Å greenalite-caryopilite-like serpentine. Like greenalite-caryopilite (cf. Guggenheim et al., 1982, Fig. 5C), this 7-Å phase has a modulation that produces satellite reflections adjacent to the reflections normally observed in serpentines of ideal 1:1 structure, thereby making identification definitive. In all cases where the  $00l$  diffraction patterns were composites, the 14-Å reflections either superimpose directly over the reflections of the 7-Å phase or fall exactly halfway between. Therefore, any differences in chemical composition between the 7-Å phase and the 14-Å phase are not observed by comparing  $c$ -axis spacings. Reflections on  $0kl$ -type nets with  $k \neq 3n$  are generally streaked along the row lines because of random layer-stacking sequences.

For one grain, however, the diffraction pattern showed sharp  $k \neq 3n$  reflections superimposed on the streaks. The modulated 7-Å phase is dominant in this grain, and it is apparent that the lateral dimensions of this phase are larger than those of the 14-Å phase. The 14-Å  $00l$  reflections could be removed from the pattern by tilting the sample stage, thereby allowing the identification of the polytype of the 7-Å modulated phase. The positions of the sharp  $k \neq 3n$  reflections require a one-layer  $c$  repeat with  $\beta = 90^\circ$ , and this uniquely identifies the 7-Å modulated phase as related to the  $1T$  polytype of group C. This is the structure on which the modulated greenalite superlattice is based (Guggenheim et al., 1982). The overlap of reflections prevented the accurate determination of lateral cell dimensions  $a^*$  and  $b^*$ , but such determinations were possible from the  $hk0$ -type patterns (see below).

A second set of superimposed nets containing  $00l$  reflections shows spacings similar to those described above and also contains lateral directions of both a 7-Å and 14-Å phase in fixed orientations. These diffraction patterns are either  $0kl$  type (containing  $Y^*$  or pseudo- $Y^*$  directions) or  $h0l$  type (containing  $X^*$  or pseudo- $X^*$  directions) superimposed nets with considerable reflection overlap. Because of these complexities, recognition of 7-Å and 14-Å intergrowths is based on the intensity ratios of  $00l$  reflections ( $l = 2n$  vs.  $l = 2n + 1$ , see above) and unit-cell geometry: a chlorite structure alone cannot account for these nets. In contrast to the superimposed nets that involved a greenalite-caryopilite-like phase, the 7-Å phase in these patterns does not show satellite reflections. Therefore, both lizardite and chlorite phases exist in these grains. Almost all of the  $h0l$  nets of these composite patterns are based on a lattice with  $\beta = 90^\circ$  for both the 14-Å and 7-Å phases (Fig. 2). This identifies the chlorite uniquely as the  $Ibb$  structural type in the revised terminology of Bailey (1988). Because of overlap of  $20l$  and  $40l$  reflections from the two phases, the serpentine can

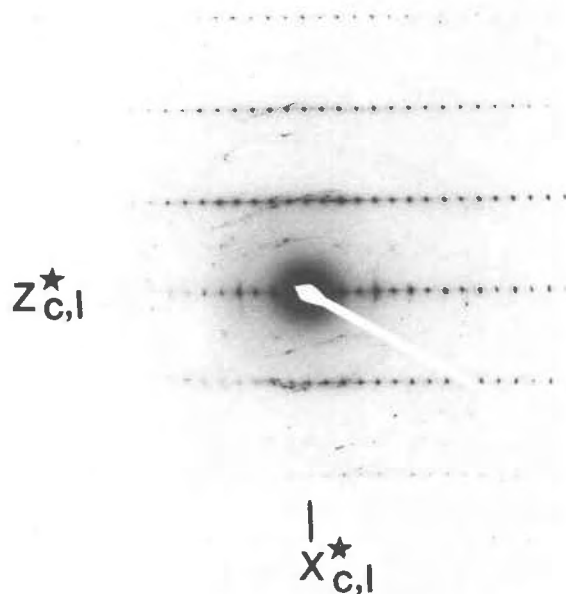


Fig. 2. Electron-diffraction pattern showing the superposition of two  $h0l$ -type nets, one 7-Å (lizardite of group B, C, or D) and one 14-Å (chlorite- $Ibb$ ) phase. Both phases have  $\beta = 90^\circ$ ;  $c$  = chlorite,  $l$  = lizardite.

only be characterized as a member of groups B, C, or D (Bailey, 1988), with group A serpentine eliminated as a possibility.

One observed  $h0l$  pattern is an exception in that the chlorite can be indexed on a lattice with  $\beta = 97^\circ$  and not on a lattice with  $\beta = 90^\circ$ . Overlap on this pattern with reflections from the intergrown 7-Å phase prohibits the use of the  $h0l$  intensities to characterize the chlorite further. The 7-Å phase can be identified from the lattice geometry as a group A ( $1M$ ,  $2M_1$ , or  $3T$ ) serpentine.

Finely divided material examined on holey C films commonly showed  $hk0$  diffraction patterns that could be attributed to a greenalite-caryopilite-like phase with a pattern typical of a modulated structure (cf. Fig. 3 to Guggenheim et al., 1982, Fig. 6) and to normal (non-modulated) structures with a simple hexagonal array. Patterns of the latter type can be produced by chlorite, lizardite, or any similar normal layer silicate, such as a 9.5-Å talc-like phase. All patterns were compatible with a  $d_{060}$  equal to 1.54 Å ( $b = 9.24$  Å) of a chlorite or a lizardite and 1.60 Å ( $b_0 = 9.60$  Å) of a greenalite-caryopilite-like phase, indicating significant chemical differences between the two types of phases. The satellite separation,  $S$ , from the central subcell ( $k = 3n$ ) reflections on the  $hk0$  net of the greenalite-caryopilite-like phase is equal to approximately 30 Å. As is sometimes observed for poorly crystallized greenalite and caryopilite, satellites form rings around the subcell reflections ( $k = 3n$ ), indicating a rotational disorder of the portions of the structure producing the satellites (see Fig. 3).

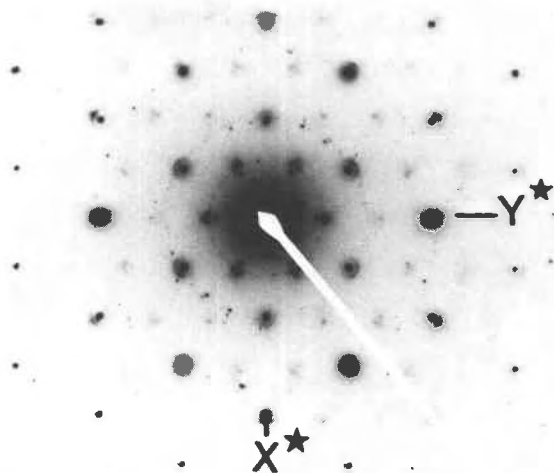


Fig. 3. Electron-diffraction  $hk0$  net of the greenalite-caryopilite-like phase showing satellite reflections around orthohexagonal  $k = 3n$  reflections. The satellite reflections form rings around the subcell ( $k = 3n$ ) reflections, suggesting considerable positional (rotational) disorder of the tetrahedral islands (see Guggenheim et al., 1982, for details on a structural model).

Semiquantitative chemical analysis of grains supported by the nylon-grid were made by EDS. Each grain was identified by the nature of its  $hk0$  pattern on the basis of either modulated or nonmodulated nets. Initial spectra collected from empty grids to establish base-line data indicated considerable Cu contamination caused by the sample holder and microscope column, but no Zn contamination. Zn appears to be present in all grains examined, but considerable overlap with the Cu spectrum makes Zn identification difficult. Spectra (not illustrated) showed high background, but all analyses indicated the presence of considerable amounts of Si, Fe, Mn, and Mg and lesser amounts of Zn and Al. Spectra varied considerably between grains and from point locations within the boundaries of individual grains. Because of the variations in grain thicknesses, high background, and considerable Cu contamination, phases could not be distinguished from these analyses alone.

### Chamosite

**X-ray study.** The ubiquitous presence of Mn- and Zn-rich chlorite intergrown with a modulated 7-Å phase in the original baumite mass may suggest that this chlorite is identical to the Mn- and Zn-rich chamosite in the low-temperature hydrothermal veinlets that cross through the baumite mass. Although the chamosite crystals measure up to 2 mm in size, they are very poorly crystallized and appear to be pseudomorphs. Precession photographs approximating a single-crystal pattern could be obtained only from very small fragments of the macroscopic crystals. Larger fragments produce powder patterns only.

Although the precession patterns are poor, they do show  $20l$  and  $40l$  row lines in which two nearly aligned patterns

are superimposed. The patterns were not sufficiently defined to permit detailed interpretation. The overlap of row lines is not due to twinning, as Gandolfi patterns of the same fragments show powder lines that require indexing on two differently shaped unit cells, one with  $\beta = 90^\circ$  and one with  $\beta = 97^\circ$  (or  $104^\circ$  for a 7-Å phase). Gandolfi patterns of 20 different particles are fairly consistent. The observed  $00l$  intensities of the chamosite can only be reproduced by having a mixture of 7-Å and 14-Å phases, similar to baumite. The evidence from the precession patterns is that the two phases are in an oriented intergrowth, at least within the small volumes of the crystal that were studied.

A 7-Å serpentine with  $\beta = 104^\circ$  (1M polytype) gives  $20l$  powder lines at  $d$  values similar to those of  $20l$ ,  $l = 2n$  lines of a chlorite with  $\beta = 97^\circ$ . Likewise, a 1T serpentine polytype has the same relationship compared to a chlorite with  $\beta = 90^\circ$ . This complicates the identification of the polytypes present. The phases with  $\beta = 90^\circ$  are dominant, however, and this suggests that an original 1T lizardite ( $\beta = 90^\circ$ ) has been partly transformed to chlorite, primarily a 1bb chlorite with  $\beta = 90^\circ$ . A powder line at  $d = 2.45$  Å, however, can only be indexed as  $203$  of a chlorite with  $\beta = 97^\circ$  (most likely chlorite type 1ba). The 1bb and 1ba chlorites are commonly intermixed in natural occurrences (Bailey and Brown, 1962, p. 848).

The 060 reflections of the two phases in chamosite are coincident in a very intense powder line at  $d = 1.56$  Å. This line is not present in any of the baumite patterns, in which  $d_{060} = 1.54$  Å for the chlorite phase. Likewise, the 060 reflection of the modulated 7-Å phase of baumite at  $d = 1.60$  Å is not present in any of the chamosite patterns. Therefore, the chlorites within baumite and chamosite are different, as are the 7-Å phases. Although TEM study of the 7-Å phase in chamosite has not been made, it is anticipated that it is a Fe-, Mn-, and Zn-rich lizardite without structural modulation.

### DISCUSSION

Baumite was described originally as a simple serpentine. Results here show that the material called baumite contains a modulated serpentine (1:1 layer silicate) structurally similar to the greenalite-caryopilite series. Although the diffraction patterns of these three minerals (greenalite, caryopilite, and the phase described here) are nearly identical in configuration, the phase described here differs in the measured satellite separation,  $S$ , of 30 Å. This contrasts sharply with the measured separation of greenalite (21.3–23.3 Å) and caryopilite (16.7–17.2 Å) as given by Guggenheim et al. (1982). These values represent a measure of the lateral extent to which congruence between misfit sheets of tetrahedra and octahedra can be maintained before strain must be relieved by a structural perturbation.

The relatively large  $S$  value indicates that misfit between the sheets of tetrahedra and octahedra is not as great as in the more Fe-rich (radius  $r = 0.78$  Å) or Mn-rich ( $r = 0.83$  Å) samples of the study by Guggenheim et

al. (1982), presumably because of the Zn ( $r = 0.74 \text{ \AA}$ ) and Mg ( $r = 0.72 \text{ \AA}$ ) content of this phase. This additional data point breaks the linear trend on a plot of  $S$  vs.  $b$  parameter (cf. Guggenheim et al., 1982, Fig. 7) and gives more credibility to the possibility that the variation in  $S$  is step-like.

The diffraction data ( $b_0 = 9.60 \text{ \AA}$  for the modulated serpentine vs.  $b = 9.24 \text{ \AA}$  for chlorite) imply a partitioning of the large (Mn, Fe) cations to the modulated serpentine structure. The qualitative chemical analysis suggests a significant Zn content in the modulated 1:1 layer silicate, in accord with the original bulk analysis. It seems unlikely, however, that the Al content in the modulated serpentine is as high as reported originally, presumably because the incorporation of Al would minimize the misfit between component sheets and that would lead to a nonmodulated phase. Likewise, partitioning Al to the chlorite phase would account for its more ideal (non-modulated) structure.

### CONCLUSIONS

Bulk material called baumite from Franklin, New Jersey, consists of a mixture of a chlorite with a modulated 7- $\text{\AA}$  phase that is similar to the modulated greenalite-caryopilite series but is different in composition and in scale of the modulation. In some places the two phases are intergrown coherently. Curled asbestiform particles are present, as well as a lizardite and a talc-like phase.

Chamosite ("brunsvigite") crystals in veinlets cutting the bulk material appear to be pseudomorphs of lizardite. As both lizardite and chamosite are present, transfor-

mation to chlorite is incomplete. The chlorite intergrown with the modulated serpentine is different from the chlorite described here as chamosite.

### ACKNOWLEDGMENTS

We thank C. Frondel and C. Francis for providing sample no. 114072 from the Harvard Mineralogical Museum. We thank P. Dunn of the Smithsonian Institution for unpublished data and for assistance in locating "brunsvigite" through J. L. Baum, who kindly permitted us to use material from his private collection. We thank also G. Harris, Department of Geological Sciences, University of Illinois at Chicago, for help with the semiquantitative chemical analysis and the Research Resources Center of the University of Illinois at Chicago for use of its electron-microscope facility. We thank F. Wicks, Royal Ontario Museum, for reviewing the manuscript. We gratefully acknowledge the support of the Petroleum Research Fund of the American Chemical Society through grants 17263-AC2 and 17966-AC2-C and the National Science Foundation under grants EAR87-04681 and EAR86-14868.

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MANUSCRIPT RECEIVED JUNE 27, 1988

MANUSCRIPT ACCEPTED JANUARY 20, 1989