30 min (or 5 min at >80° C.). Separate solid from liquid and wash solid with 5 ml water; shake solid for 5 min with 2 ml 0.5 M TBAB solution (adjusted to pH 5 to 6). Let solid settle out and measure pH of supernatant liquid. With zeolites the pH is 9 to 11, and with clays about 6.5 to 7.5.

The test described has been used with success by Dr. H. D. Curry on natural zeolites.

I am indebted to Dr. D. L. Peterson for his valuable assistance, and to Dr. E. A. Jenne for pointing out that certain nonzeolitic alumosilicates give positive reactions with tetraethylammonium bromide reagents.

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MAGNESIUM VERMICULITE FROM THE TWIN SISTERS MOUNTAINS, WASHINGTON

HENRI E. GAUDETTE, *Department of Geology, University of Illinois, Urbana, Illinois.*

INTRODUCTION

A micaceous mineral vein in close association with a massive chromite deposit in the Twin Sisters mountains of northwestern Washington, was found to be composed exclusively of vermiculite. This is one of a small number of occurrences of this mineral (Bennett, 1964) in the Twin Sisters range which has been formed from a relatively unaltered, coarse-grained dunite body. This vermiculite occurrence is also of interest due to its unusual mode of origin.

The general geology of the Twin Sisters area, in Whatcom and Skagit counties, Washington, and the petrology and emplacement mechanics of the Twin Sisters dunite body have been reported by Ragan (1963). The author previously has studied the compositional variations and the geochemistry of elemental distributions within the constituent mineral phases of the dunite mass (Gaudette, 1963). It was during this latter investigation that the field occurrence of the vermiculite vein was noted.

GEOLOGIC SETTING

The vermiculite is found as a thin, irregular vein, $\frac{1}{2}$ to 3 inches in width, in the coarse-grained dunite. In the vicinity of the vein, the dunite is composed of 91.0% olivine (Fo93), 8.5% orthopyroxene (En91), and 0.5% of opaque minerals visually identified as chromite. The dunite is, in general, granulated and exhibits recrystallization effects, notably in, or adjacent to shear or granulation zones. Translational lamellae are prominent in the olivine, principally along the (100) plane, and produce a well-defined twinning effect in the olivine which has been commonly described in studies of other ultramafic masses.

The vermiculite vein occurs as an extension approximately two to three feet long, into the dunite from a large lens of chromite. It is located on the Danny claim, in the northeastern portion of the dunite mass. The chromite lens strikes N5OW and dips steeply toward the south. The attitudes of both the chromite mass and the vermiculite vein are similar, and conform to the trends of veins of enstatite and chromium diopside which are found in that portion of the dunite body, as well as to the dominant jointing directions in the dunite.

The vermiculite occurs as closely packed cleavage fragments in the vein with the cleavage planes, in general, in random orientation within the vein. Field examination of the vein-country rock contacts show them to be relatively sharp, with little apparent interpenetration.

PHYSICAL PROPERTIES

The vermiculite has a characteristic light grey-green color with a distinctive bronze sheen. When handled, portions of the vein break up into small irregular flakes with a perfect basal cleavage. Many of these flakes appear to be slightly crinkled or crenulated.

The vermiculite flakes are non-elastic, and do not exfoliate upon sudden heating.

Microscopic examination of the mineral shows it to be a pale yellow in white transmitted light, and a blue-grey under crossed nicols. It is non-pleochroic. Optically, the vermiculite is biaxial negative, has a 2V of 5 to 10 degrees, with lath shaped fragments exhibiting parallel extinction. Indices measured in sodium light are: $\alpha = 1.518 \pm .002$, $\beta = \gamma = 1.528 \pm .002$.

Base exchange capacity of the vermiculite measured by a calcium versenate method was found to be 175.1 meq/100 grams. A calculated exchange capacity of 152 meq/100 grams was determined based upon the charge distribution per unit cell (Foster, 1963). Analysis by flame photometry showed the presence of magnesium and a minor amount of calcium as the exchangeable cations.

CHEMICAL DATA

The chemical analysis of the Twin Sisters vermiculite is shown in Table 1. It corresponds closely to those of vermiculite from other studies (Mathieson and Walker, 1954; Bradley and Serratosa, 1960). In Table 2 the ionic population of the Twin Sisters vermiculite is compared with the Llano vermiculite from the Texas Mines magnesite quarry (Clabaugh and Barnes, 1959). These are both based upon the assumptions that 14 cations occupy the 14 structural sites of the mineral lattice, that all excess cations are then considered to be interlayer occupants, and that the oxygen content per cell is expressed as 20 oxygens plus the ferric iron content of the ignited sample, with the amount of hydroxyls added to bring the total to 24. Any additional water is then considered to be molecular.

TABLE 1. CHEMICAL ANALYSIS OF THE TWIN SISTERS VERMICULITE

	Wgt %
SiO_2	41.50
Al_2O_3	14.41
Fe_2O_3	2.69[1]
MgO	29.13
CaO	0.20
NiO	0.30
TiO_2	0.62
H_2O^+	11.14
	99.99

Analyst: J. Witters, Illinois State Geological Survey.

[1] Total iron expressed as Fe_2O_3.

On these bases, the structural formulae for one half cells of the Twin Sisters and Llano vermiculite are:

Twin Sisters

$$\Big[\underbrace{\overset{+.32}{(Al_{0.12}Ti_{0.03}Fe^{3+}_{0.14}Mg_{2.69}Ni_{0.02})}}_{3.00}\overset{-1.08}{(Si_{2.92}Al_{1.08})}\overset{-.76}{O_{10}(OH)_2}\Big]\overset{+.76}{(Ca_{0.02}Mg_{0.36})}_{.38}$$

Llano

$$\Big[\underbrace{\overset{+.16}{(Al_{0.13}Ti_{0.01}Fe^{2+}_{0.02}Mg_{2.84}Mn_{0.0})}}_{3.00}\overset{-1.16}{(Si_{2.84}Al_{1.16})}\overset{-1.00}{O_{10}(OH)_2}\Big]\overset{+.99}{(Ca_{0.03}Na_{0.01}K_{0.01}Mg_{0.45})}_{.50}$$

Comparison of the two structural formulae shows that only slight differences exist between the two samples. The Twin Sisters vermiculite appears to be more siliceous in the tetrahedral portion of the layer structure than the Llano sample, but compares favorably to the "average" vermiculite shown by Gruner (1934). Sufficient aluminum is present to be allocated to both tetrahedral and octahedral positions. The remaining octahedral positions are occupied primarily by magnesium, along with minor amounts of ferric iron, titanium and nickel. The interlayer positions are occupied by magnesium plus a minor amount of calcium confirming previous determinations by flame photometric analysis. Other points of comparison are the increase in the iron content in the octahedral positions of the silicate portion of the structure, as well as the deficiency of magnesium in the interlayer sites as compared to the Llano sample.

Table 2. Ion Populations

Ion	Llano vermiculite	Twin Sisters vermiculite
Si	5.68	5.84
Al_T	2.32	2.16
Al_O	0.25	0.24
Fe^{2+}	0.03	—
Fe^{3+}	—	0.28
Ti	0.03	0.06
Mg	5.69	5.38
Mg^{2+}	0.90	0.73
Other 2+ bases	0.08	0.03
Ni	—	0.03
O	20.00	20.28
OH	4.00	3.72
H_2O	9.45	10.00

Differential Thermal Analysis

The effects of heating on vermiculite have been summarized in previous reports notably by Barshad (1948) and Grim (1953). The differential thermal curve for the Twin Sisters vermiculite as shown in Fig. 1 is characterized by endothermic peaks in the 100° to 300° C. region, and a third endothermic reaction at approximately 800° C. This third endothermic reaction is followed immediately by a small exothermic peak.

The initial endothermic reaction results from loss of adsorbed or "unbound" water and occurs at approximately 150° C. The distinct and separate endothermic peak at 250° C. is produced by the loss of water which is organized as hydration envelopes of the interlayer cat-

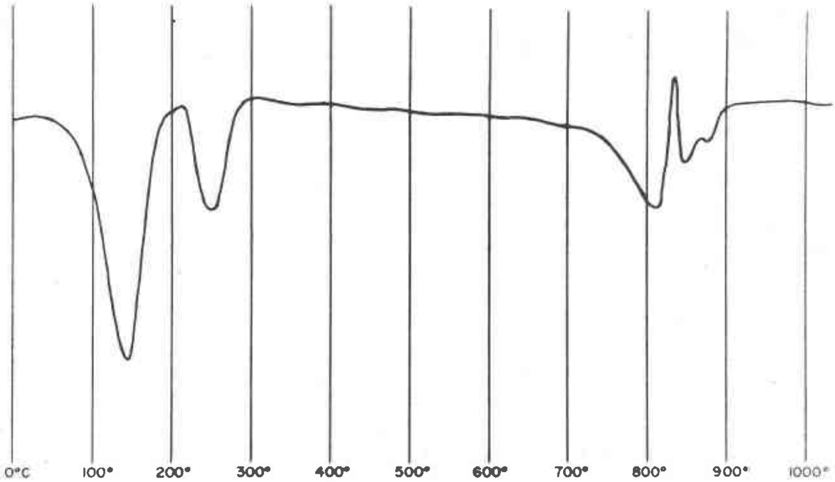


FIG. 1. Differential thermal analysis of the Twin Sisters vermiculite.

ions. The clearcut separation of these two endothermic reactions points out the differing levels and organization states of the molecular water present in the inter-layer space.

A slight endothermic slope in the DTA curve between 350° and 700° C. is interpreted to be the result of a gradual loss of hydroxyls from the silicate portion of the vermiculite structure. This loss is culminated at about 800° C. with the final loss of hydroxyls as reflected by the third endothermic peak.

Formation of a high-temperature phase at approximately 840° C. is shown by the sharp exothermic reaction. This high-temperature phase has been qualitatively identified as enstatite by *x*-ray diffraction techniques.

X-RAY DIFFRACTION ANALYSIS

A number of small cleavage flakes from the Twin Sisters vermiculite were separated, washed, and allowed to air dry before *x*-ray analysis. A Norelco Wide Range Goniometer, with nickel-filtered copper radiation, and pulse height analyzer were utilized in the *x*-ray examination of these flakes.

Seventeen basal reflections were obtained from the vermiculite cleavage flakes with the initial reflection corresponding to a basal spacing of 14.35 Angstroms; the interlayer distance generally considered to be that of the fully hydrated mineral. The succeeding reflections may all be attributed to vermiculite, with no contamination from mixedlayer material or hydrobiotite. Examination of the finely-ground powdered sample gave an (060) spacing of 1.537 Angstroms confirming the trioctahedral character of the mineral.

The availability of the 17 basal reflections from the cleavage flakes allowed structural analysis by one-dimensional Fourier summation. The calculated structure factors for one-dimensional analysis were based upon the structural model of magnesium vermiculite reported by Mathieson and Walker (1954), and were calculated from the atomic populations disclosed by chemical analysis.

Well defined electron density maxima corresponding to the silicate portion of the structure and the interlayer occupants were obtained. Agreement between the calculated and observed structure factors is 4.6% for the 17 reflections utilized. Thus, it is felt that the 001 projection (Fig. 2) is valid semi-quantitatively, and allows confirmation of certain assumptions which were made concerning the atomic populations.

A one-dimensional structural projection of the Llano vermiculite has been reported by Bradley and Serratosa (1960). Diffraction analysis of cleavage flakes of the Llano material received from Professor Bradley resulted in the one-dimensional projection shown in Fig. 2. The calculated structure factors for the Llano vermiculite were derived from the ion populations of Table 2. The agreement index between the calculated and observed structure amplitudes for 17 basal reflections is 3.1%.

In Fig. 2, the electron density maxima for the Llano structure are well-defined, and offer a comparison to the 001 projection of the Twin Sisters vermiculite. Agreement is apparent between the two one-dimensional projections in all portions of the structure with slightly greater maxima at the octahedral and tetrahedral portions of the Twin Sisters structural projection—the result of slight differences in atomic populations. For example, the differing amounts of silicon and aluminum in the tetrahedral portion of the silicate structures as indicated by their structural formulas, are reflected in the differences in the tetrahedral electron density maxima in the one-dimensional projections. The interlayer portions of the structures are similar, however, the differing amounts of magnesium as interlayer occupants are distinguishable. The hydration characteristics of the interlayer occupants of both specimens are clearly defined.

The close comparison of the Twin Sisters material with the Llano vermiculate is of particular interest in view of the contrast in the initial materials. The Llano material from the Texas mines magnesite quarry is believed to be of secondary origin, formed by sub-aerial weathering of phlogopite within 40 feet of the ground surface (Clabaugh and Barnes, 1959). Although the Twin Sisters vermiculite is also believed to be of a

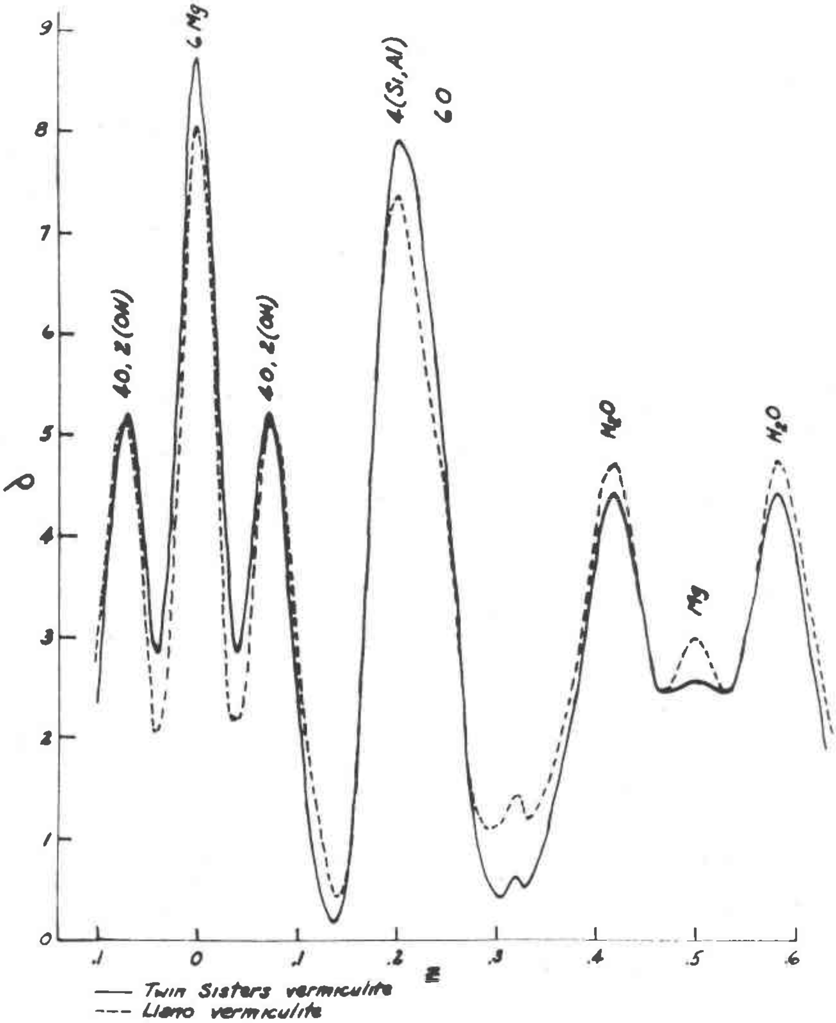


FIG. 2. One-dimensional structural projections of the Twin Sisters and Llano vermiculites.

secondary origin, the initial material in this case is thought to be chlorite, and/or serpentine. The processes involved in the development of this vermiculite are discussed more fully in the following section.

PROPOSED GENESIS OF THE TWIN SISTERS VERMICULITE

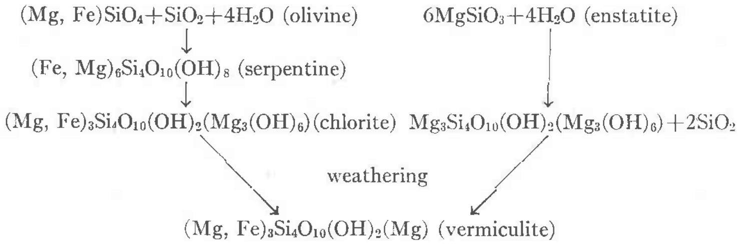
Occurrences of vermiculite in ultramafic bodies have been summarized by Bassett (1961). Almost exclusively, these occurrences have been shown to be in close association with pegmatites, or if in fractures away from the pegmatites, apparently genetically related to pegmatitic activity. Such is not the case in the Twin Sisters vermiculite, where no evidence of pegmatitic activity is to be found throughout the entire ultramafic mass.

Due to the close association of the vermiculite occurrences with the above mentioned pegmatitic activity in many ultramafic bodies, vermiculite had been thought to be of hydrothermal origin. However, as Bassett indicates, evidence is such that a supergene alteration from biotite or phlogopite now appears to be the most feasible explanation of its genesis.

The Twin Sisters vermiculite occurs in coarse-grained dunite which is fresh and completely unaltered except for serpentinization along occasional joints and fractures. Conversion of olivine and/or pyroxenes to serpentine along fractures in the dunite is common. Serpentinization of olivine has been shown experimentally to occur at temperatures below 500° C., and a proposed mechanism causing the serpentinization of the Twin Sisters ultramafic body by adsorption of water or water vapor from the sedimentary and meta-sedimentary country rocks during emplacement of the dunite has also been suggested (Ragan, 1963). The conversion of olivine or pyroxenes to serpentine by the addition of silica and water along fractures in the fresh dunite is considered to be the primary step in the genesis of the Twin Sisters vermiculite.

The vermiculite has apparently formed as a result of secondary alteration of chlorite or serpentine by sub-aerial weathering processes. The presence of the chlorite may be explained by re-organization of serpentine formed in through-going fractures in the fresh dunite by the action of silica rich adsorbed water or water vapors, or by the reaction of silica deficient water or water vapor with pyroxenes present as veins and fracture fillings. Field conditions, and the prevalence of serpentinized fractures which appear to be the result of the reaction of forsterite with silica rich water or water vapor, as well as the abundance of high silica country rocks which could serve as a ready supply for this silica-laden water or water vapor phase, indicate the former condition to be the most important consideration. The conversion of the serpentine to chlorite through reorganization may be accomplished by only a slight increase in the activation energy of the serpentine. This could result from slight temperature increases, small changes in the pressure of the environment, or merely from the extended duration of geologic time during which such re-organization might be accomplished.

Consideration of the genesis of the Twin Sisters vermiculite in terms of idealized reactions is outlined as follows:



CONCLUSIONS

Magnesium vermiculite is found as a small thin vein which appears as an extension of a large massive chromite deposit in the Twin Sisters mountains of northwestern Washington. The association of the vermiculite vein with the chromite deposit is considered to be completely fortuitous, however. Analyses show the mineral to be a trioctahedral vermiculite, with magnesium present as the hydrated cation in interlayer positions.

The Twin Sisters vermiculite compares closely to the magnesium Llano vermiculite of Bradley and Serratosa (1960). One-dimensional structural projections along the "c" axis of the minerals point out this similarity, and confirm allocation of the various ions to their proper structural positions.

Formation of the Twin Sisters material has apparently occurred by the secondary alteration of chlorite by sub-aerial weathering processes. The chlorite has most probably formed by re-organization of serpentine which previously formed along through-going fractures in the fresh dunite by reaction with silica rich water or water vapor phases, or by reaction of of silica deficient water or water vapors with pyroxene that was present as vein or fracture fillings. Neither a hydrothermal origin (in the strict sense) for the vermiculite nor the formation of vermiculite from the weathering of biotite or phlogopite are considered appropriate in this case. The sequence olivine—serpentine—chlorite—vermiculite appears most feasible for the development of this material.

ACKNOWLEDGMENTS

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SOME PROPERTIES OF ALUNOGEN FROM NEW SOUTH WALES

P. BAYLISS, *School of Applied Geology, University of New South Wales.*

Deposits of evaporite, consisting essentially of alunogen as first described by Bayliss (1963), are located near Joadja, 65 miles south-west of Sydney, N.S.W. The deposits occur beneath a calcareous sandstone within the Permian Shoalhaven series, as white, fibrous lenses, which measure up to 9 feet in diameter and 9 inches in depth. Each deposit consists of a sequence of horizontal layers of vertically stacked alunogen fibres with a maximum length of about 5 mm and a thickness of several microns. Small irregular-shaped quartz grains and iron oxide film coatings are also present.

The individual fibers have been identified either as alunogen ($Al_2(SO_4)_3 \cdot 16H_2O$; frequently referred to as alunogenite), or as pickeringite ($MgAl_2(SO_4) \cdot 22H_2O$), by means of *x*-ray diffraction. Confirmation of this identification was first obtained by means of both DTA and thermogravimetric analysis utilizing apparatus described by Warne and Bayliss (1962), and subsequently by both chemical and spectrographic analysis.

The *x*-ray diffraction data for alunogen recorded by Hanawalt *et al.* (1938) and Bassett and Goodwin (1949) lack the detail that has been obtained by means of copper radiation from a diffractometer with a 114.4 mm radius goniometer. Because of this the appropriate data are recorded in Table 1.