MINERALOGY AND PETROLOGY OF THE SYSTEM Al$_2$O$_3$-SiO$_2$-H$_2$O IN SOME PYROPHYLLITE DEPOSITS OF NORTH CAROLINA

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Abstract

The mineral assemblages from seven pyrophyllite deposits in the Volcanic Slate belt of the North Carolina Piedmont were studied by *x*-ray and microscopic methods. These deposits are at Glendon, Robbins, Staley, Snow Camp, Hillsboro, Hager's Mountain, and Bowling's Mountain.

Six of the minerals found in these deposits belong to the ternary system Al$_2$O$_3$-SiO$_2$-H$_2$O: quartz, pyrophyllite, andalusite, kyanite, kaolinite, and diaspore. The following are 3-phase assemblages belonging to the ternary system: quartz-kaolinite-pyrophyllite; pyrophyllite-andalusite-quartz; and kaolinite-diaspore-pyrophyllite. All the observed relations, in detail, are consistent with the assumption of mutual equilibrium among the minerals. The occurrence of andalusite-kaolinite assemblage at Hillsboro but of pyrophyllite-diaspore at Staley suggest differences in physical conditions of metamorphism at these localities.

The prevalence of 3-phase assemblages indicates that H$_2$O behaved as a fixed chemical component during the formation of the pyrophyllite bodies. This conclusion is inconsistent with a hydrothermal-replacement origin for these bodies, as such a theory implies that H$_2$O belonged to an open system and thus was a mobile component. An alternative mode of origin, consistent with the mineralogical and geological data, starts with saprolite bodies on the weathered surfaces of the volcanic rocks. The saprolite was buried by later volcanic rocks and subsequently the entire sequence was metamorphosed; during recrystallization the saprolite bodies behaved as closed systems. Relative concentrations of Al$_2$O$_3$, SiO$_2$, and H$_2$O at different parts of each deposit account for the difference in mineral assemblages. The regional metamorphism was of low grade; nowhere was the almandite isograd reached.

Introduction

The pyrophyllite deposits of North Carolina are intimately related geologically to the Volcanic Slate belt of the Piedmont region. The general mode of occurrence of the pyrophyllite deposits and their possible origin, as well as the geology of the surrounding areas, have been discussed by Stuckey (1928) and by Broadhurst and Councill (1953).

The writer has recently studied the detailed mineralogy and petrography of seven of these deposits, as well as their wall rocks. Although the work is yet incomplete, enough has emerged to justify a report on the relations among those minerals that belong to the chemical system Al$_2$O$_3$-SiO$_2$-H$_2$O.

The seven deposits reported here are at Glendon (both the Womble and Phillips pits), and Robbins, both in the Deep River region in the northern part of Moore County; at Staley in Randolph County, at

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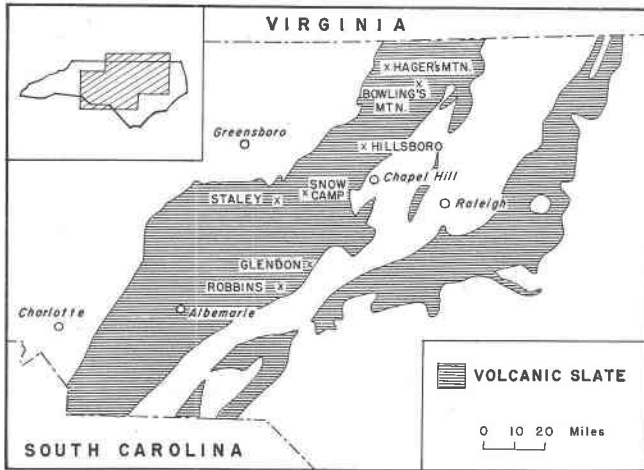
Fig. 1. Map showing location of the seven pyrophyllite deposits reported in this paper (crosses), and principal communities (circles). Inset relates the location of the map to the boundary of North Carolina.

Hillsboro in Orange County, at Hager's Mountain in Person County, at Bowling's Mountain in Granville County, and in several small pits near Snow Camp in Alamance County (Fig. 1; Stuckey, 1928; Broadhurst and Councill, 1953; Conley, 1958). The samples were studied both with the petrographic microscope and with a Norelco X-ray Diffractometer; wherever possible results using the two methods are correlated with each other.

<div align="center">MINERALOGY</div>

Introduction

Although many of the minerals in these deposits do not belong to the simple system Al_2O_3-SiO_2-H_2O, discussion of the other minerals will be omitted. The principal omitted minerals are chloritoid, clinozoisite, chlorite, muscovite, paragonite, hematite, rutile, and pyrite.

Pyrophyllite $Al_2Si_4O_{10} (OH)_2$

Pyrophyllite is one of the commonest and most abundant minerals in the deposits; it is also found in the country rock. It occurs rarely as radiating rosettes of clear pale blue-green crystals up to 2 mm. by 10 mm. in size, and as such has been found at Staley,† and at Bowling's Mountain. More commonly, pyrophyllite occurs as fine, felty aggregates. The indi-

† The thermochemical properties of the best sample from Staley are being measured by R. A. Robie of the Theoretical Geophysics Branch, U. S. Geological Survey.

vidual crystals are too small to be seen in a hand specimen but the mineral is easily detected by the soapy feel of the rocks containing it. Fine aggregates of pyrophyllite occur in nodules, and in massive as well as banded rocks.

Microscopically, pyrophyllite is easily distinguished from kaolinite by its much higher birefringence, but it can be distinguished from muscovite and paragonite only by x-ray diffraction. The series of diffraction lines due to the (00l) planes, with the basal spacing of about 9.2 Å, is diagnostic. The only possible mineral with which it might be confused, talc, has not been found in the pyrophyllite deposits.

Kaolinite, $Al_2Si_2O_5(OH)_4$

Kaolinite is a common mineral in all seven deposits. It occurs not only in clearly secondary, cross-cutting veins and joint-fractures, as at Hillsboro, but also occurs in the bulk of the deposits. In fact, few pyrophyllite-rich samples are free of kaolinite. Kaolinite also occurs in the country rock without pyrophyllite.

Microscopically, kaolinite occurs as small lath-shaped crystals of low birefringence, showing at most first-order grey interference color. Where intergrown with pyrophyllite, the sharp contrast in birefringence separates the two phases easily. Many of these intergrowths are on a microscopic scale, with both phases scattered throughout a thin section. There is no textural evidence in any of the samples studied to indicate that either mineral is an alteration product of the other.

The chief basis for the identification of kaolinite in a sample is by its x-ray diffraction pattern, with the strong 7 Å basal reflection and its higher harmonics. As the samples rarely contain chlorite, it causes little confusion in identification.

Diaspore AlOOH

Diaspore occurs in the Staley deposit (Broadhurst and Councill, 1953, p. 18). The writer has not found this mineral in the quarry; however, Dr. J. L. Stuckey kindly contributed a small sample from his collection. The sample is grey and shows crude blade-like crystal forms covered by scales of a white mica. Diaspore is identified by its x-ray diffraction pattern; the associated white mica is pyrophyllite with a trace of kaolinite. Due to the unavailability of more samples, no microscopic study has been made.

Andalusite Al_2SiO_5

Andalusite is found at Staley and at Hillsboro, and has been reported by Broadhurst and Councill (1953, p. 15) from Bowling's Mountain. The color is grey in some, but more commonly is light blue or turquoise.

Microscopically, andalusite is characterized by its optical properties (Winchell and Winchell, 1951, p. 521). Its relatively high refringence makes it stand out in strong relief. In most samples, it occurs as anhedral to subhedral masses, strongly poikilitic with inclusions of subhedral quartz, and a few crystals of pyrophyllite or kaolinite scattered both inside and around the andalusite. The andalusite crystals are up to 5 mm. across.

The x-ray pattern of andalusite is compared with that of a standard andalusite from Laws, California, in the Holden Collection of the Mineralogical Museum, Harvard University (no. 95769).

Kyanite Al_2SiO_5

In this study, kyanite has been found only at Hager's Mountain near Roxboro, Person County. Here it is found in two modes of occurrence: as large (up to 6 inches long) crystals in the bulk of the deposit, associated principally with quartz. Such kyanite forms large knobs on slightly weathered surfaces and is commonly pseudomorphed after by white mica. It also occurs as pale blue, clear, blade-like crystals in vein fillings in the rock, and is associated with pyrophyllite and quartz.

Both kyanite and andalusite have been reported from Bowling's Mountain (Broadhurst and Councill, 1953, p. 15). In the present study, however, neither was found.

Quartz SiO_2

Quartz is common in the specimens studied, although it is absent in some samples and is subordinate in many others. Quartz occurs both as fine, subhedral grains more or less uniformly disseminated in the rocks, and in veins.

PETROLOGY

Mineral Assemblages

The minerals found at the seven pyrophyllite localities are listed in Table I; for completeness the entire assemblages are given and those minerals belonging to the ternary system Al_2O_3-SiO_2-H_2O are set in italics. Each assemblage represents the minerals found in a single thin-section, or a single x-ray mount.

Phase Relationships

The observed phase relationships in the ternary system Al_2O_3-SiO_2-H_2O are depicted in Fig. 2. A few comments are necessary.

The first point concerns the anhydrous phase, andalusite. As remarked before, andalusite occurs as stout, poikilitic porphyroblasts in most of the specimens. In a hand specimen it may appear corroded, yet microscopi-

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TABLE I

I. *Assemblages with four phases in the ternary system*
   Pyrophyllite-kaolinite-andalusite-quartz (Hillsboro, Glendon?)
   Pyrophyllite-kaolinite-kyanite-quartz (Hager's Mountain)

II. *Assemblages with three phases in the ternary system*
   Pyrophyllite-kaolinite-quartz (Hillsboro; Glendon; Hager's Mountain; Staley?)

   Pyrophyllite-kaolinite-quartz-chloritoid (Glendon; Robbins)
   Pyrophyllite-kaolinite-quartz-hematite (Glendon)
   Pyrophyllite-kaolinite-quartz-muscovite-chlorite (?) (Robbins)
   Pyrophyllite-kaolinite (?)-*quartz*-chlorite (Hager's Mountain)
   Andalusite-pyrophyllite-quartz (Staley; Hillsboro)
   Andalusite-kaolinite (?)-*quartz* (Hillsboro)
   Pyrophyllite-diaspore-kaolinite (Staley)

III. *Assemblages with two phases in the ternary system*
   Kaolinite-quartz (Glendon)
   Kaolinite-quartz-muscovite (Hillsboro; Bowling's Mountain)

   Kaolinite-quartz-chloritoid-chlorite (?) (Glendon)
   Kaolinite (?)-*quartz*-muscovite-chlorite (?) (Snow Camp)
   Pyrophyllite-kaolinite (Glendon; Robbins; Staley)
   Pyrophyllite-kaolinite-muscovite (Glendon)
   Pyrophyllite-kaolinite-clinozoisite-chlorite (?) (Glendon)
   Pyrophyllite-kaolinite-chloritoid-muscovite (Glendon)
   Pyrophyllite-kaolinite-chlorite-chloritoid (Robbins)
   Pyrophyllite-kaolinite-chloritoid (Hillsboro; Staley)
   Andalusite-quartz (Hillsboro)
   Andalusite-kaolinite-muscovite (Staley)
   Pyrophyllite-quartz (Staley; Robbins; Snow Camp)
   Pyrophyllite-quartz-muscovite (Glendon)
   Pyrophyllite-quartz-chloritoid-hematite (Glendon; Staley; Robbins; Snow Camp)
   Pyrophyllite-quartz-chloritoid

   Pyrophyllite-quartz-chloritoid-chlorite-muscovite (?) (Glendon)
   Pyrophyllite-quartz-muscovite-chloritoid (Snow Camp)
   Kyanite-quartz-chloritoid (Hager's Mountain)

IV. *Assemblages with one phase in the ternary system*
   Pyrophyllite (Staley)
   Pyrophyllite-muscovite (Staley; Robbins)
   Pyrophyllite-chloritoid-chlorite-muscovite (Staley)
   Quartz-muscovite (Glendon; Bowling's Mountain; Snow Camp)

   Quartz-chloritoid (Glendon; Hager's Mountain)
   Quartz-chloritoid-hematite (Glendon; Staley; Snow Camp)
   Quartz-chloritoid-chlorite (Glendon; Staley)

TABLE I (continued)

Quartz-chloritoid-chlorite-muscovite	(Glendon)
Quartz-muscovite-paragonite	(Hager's Mountain)
Quartz-chlorite-muscovite	(Hager's Mountain)
Quartz-muscovite-chloritoid	(Staley; Snow Camp?)

V. *Assemblages with no phase in the ternary system*
   Muscovite   (Hillsboro; Glendon; Snow Camp)

   Fluorite   (Glendon)

VI. *Assemblages with phase questionably in the ternary system*
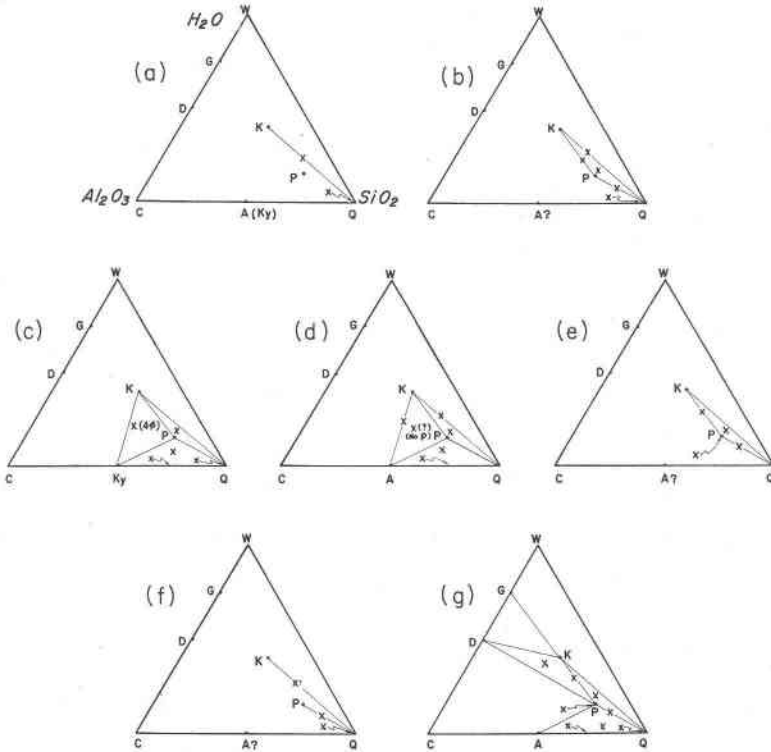   Montmorillonite (?)   (Glendon)

FIG. 2. Observed mineral assemblages (crosses) in the ternary system Al_2O_3-SiO_2-H_2O. (*a*), Bowling's Mountain; (*b*), Glendon; (*c*), Hager's Mountain; (*d*), Hillsboro; (*e*), Robbins; (*f*), pits near Snow Camp; (*g*), Staley. Key to mineral phases: W, a H_2O phase (vapour or liquid); G, gibbsite; D, diaspore; C, corundum; A, andalusite; Ky, kyanite; K, kaolinite; P, pyrophyllite; and Q, quartz. Symbol ϕ stands for "phase."

cally there is no evidence of its conversion to other minerals. Its grain contact is mostly with quartz, but even where it is in contact with pyrophyllite and, more rarely, kaolinite, the contact is clean and the crystals are well-developed. Andalusite therefore is presumably in chemical equilibrium with the surrounding minerals.

The occurrence of the four-phase assemblage, andalusite-kaolinite-pyrophyllite-quartz, at Hillsboro, may therefore seem anomalous, inasmuch as according to Goldschmidt's Phase Rule (Goldschmidt, 1911, p. 123), in general no more than three solids may be expected in a ternary system. Microscopic examination shows, however, that no more than three of these solids occur in direct contact with one another. One of the specimens from Hillsboro showing the four-phase assemblage on the x-ray chart consists of these sub-assemblages, when the mutual contacts are noted: pyrophyllite-andalusite-quartz, kaolinite-andalusite, pyrophyllite-quartz, andalusite-quartz. Thus even though the specimen, on the scale of a thin section, may be out of chemical equilibrium, yet locally such equilibrium prevails, and all the phases present, including andalusite, may be interpreted as stable with their surroundings. The large number of sub-assemblages even in a thin section must then be explained by the immobility of the chemical components during recrystallization. The 3-phase assemblage from Hillsboro, with andalusite-kaolinite-quartz, appears to contradict the phase diagram drawn on the basis of the above discussion; however in this particular sample the identification of kaolinite is questionable and the rock is predominately an andalusite-quartz rock.

The detailed textural relation of kyanite to its associated minerals from Hager's Mountain is as yet unknown. Kyanite and andalusite have not been found together by the writer. This may be due to imperfect sampling, however; for Broadhurst and Councill (1953, p. 13, 16) report both kyanite and andalusite from the Bowling's Mountain deposit.

The second point of interest is that, as far as the ternary system is concerned, the mineralogical assemblages at each locality are mutually compatible; the ternary diagrams (Fig. 2) relating these phases, drawn on the basis of mineralogical data, make sense. None of the other phases listed with these assemblages, moreover, count in this system, since for all such phases other distinct chemical components must be reckoned with. Thus for muscovite, we have K_2O; for paragonite, Na_2O; clinozoisite, CaO; chloritoid and/or chlorite, FeO and MgO; hematite, Fe_2O_3;* and

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* If oxygen should turn out to be a mobile component (Korzhinskii, 1950) during the metamorphism, Fe_2O_3 would not count as a distinct component in addition to FeO (Thompson, 1957; Zen, 1960). However, of the three phases, hematite, chlorite, and chloritoid, only two have been found in a given sample.

fluorite, F.* Other phases and their corresponding components are: lazulite, P_2O_5 (Staley, Glendon; Conley, 1958, p. 60, 62); ilmenite, TiO_2 (Glendon, Robbins; Conley, 1958, p. 60); malachite, CuO (Bowling's Mountain; Conley, 1958, p. 32); pyrite, S (all deposits; the writer's own observations). Unfortunately, in the literature the specific mineral associations are not always cited.

The third feature of petrologic interest is the nature and occurrence of some 3-phase assemblages. The assemblage pyrophyllite-kaolinite-quartz is common and occurs at all places except Bowling's Mountain and the pits near Snow Camp. The assemblage diaspore-kaolinite-pyrophyllite is found only at Staley by the writer, whereas andalusite-pyrophyllite-quartz is found both at Hillsboro and at Staley. Textural evidence is consistent with the interpretation that these 3-phase assemblages represent equilibrium assemblages. Kaolinite and pyrophyllite generally are intermixed; more rarely pyrophyllite occurs as clusters in a matrix of kaolinite. Prevalence of such phase assemblages in a finite volume, in a system with H_2O as one of the components, if in internal equilibrium, implies that H_2O behaved as a fixed component (Thompson, 1955, p. 80) during metamorphism. The significance of this point is discussed in the next section.

A final point of petrologic interest is the existence, at Staley, of the assemblage pyrophyllite-diaspore-kaolinite (trace). Diaspore is also reported by Broadhurst and Councill (1953, p. 20) from Holman's Mill, Snow Camp, presumably with pyrophyllite. This mineral pair is incompatible with the pair andalusite-kaolinite (Fig. 2g), which is found at Hillsboro. This fact indicates a crossing of 2-phase tie lines; for even if it be assumed that andalusite is a metastable relict, still if pyrophyllite and diaspore are stable together, hydration of andalusite should result in the formation of this pair before any kaolinite could appear. Since all four phases, kaolinite, pyrophyllite, andalusite, and diaspore, belong, as far as we know, strictly to the ternary system Al_2O_3-SiO_2-H_2O, the fact that andalusite-kaolinite and andalusite-kaolinite-pyrophyllite assemblages prevail at Hillsboro and the alternative, pyrophyllite and diaspore, occur at Staley (and possibly Holman's Mill also) suggests therefore that real differences in the *physical* environment (temperature and total pressure) of metamorphism existed between Staley (and Snow Camp) and Hillsboro.

* Topaz has been reported from Bowling's Mountain, Hillsboro and Staley (Broadhurst and Councill, 1953, p. 15, 17, 19). The three phases, topaz, fluorite, and clinozoisite, share the two components, Ca and F, in the enumeration of number of components and phases when we apply the Gibbs Phase Rule. However, no more than two of these are known to occur in any deposit.
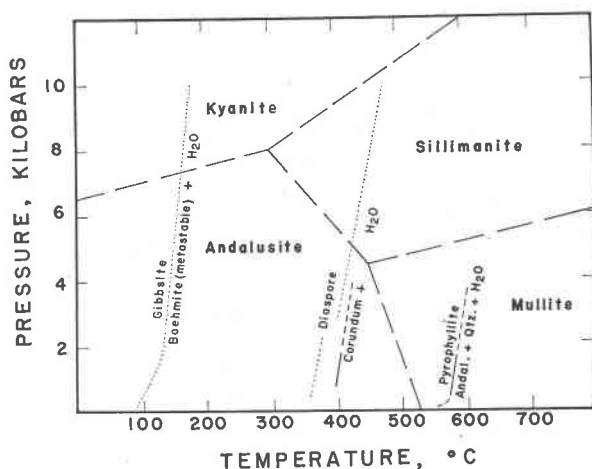
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F<small>IG</small>. 3. Experimental data on the system Al_2O_3-SiO_2-H_2O. Long dashed lines: the extrapolated univariant curves for the dry system, according to Clark, Robertson and Birch (1957). Solid lines and short dashed lines: determined and extrapolated breakdown curves due to Roy and Osborn (1954). Dotted lines: curves due to Kennedy (1959). The discontinuous high-pressure and low-pressure portions of the diaspore breakdown curve due to Kennedy are from his Figs. 1 and 2, respectively, obtained by different experimental techniques. All breakdown curves for hydrous phases are for equilibrium with pure H_2O.

P, T Conditions of Formation of Pyrophyllite Deposits

The mineral assemblage data from the several pyrophyllite deposits afford an estimate on the temperature and total pressure of formation of these deposits.

The high temperature-high pressure portion of the equilibrium diagram for the system Al_2SiO_5 was studied by Clark, Robertson and Birch (1957). These authors determined the kyanite-sillimanite univariant transition curve at $T > 900°$ C. and $P > 17$ kilobars. Using this curve and also available thermochemical data on these phases, the authors extrapolated their results to lower temperatures and total pressures, to include the probable phase region for andalusite. The position of the andalusite field is drawn on the basis that it is probably the relatively low-temperature, low-pressure phase. The lines thus obtained are consistent with the experimental work of Roy (1954) and Aramaki and Roy (1958), and with known geological occurrences.[*]

The extrapolated diagram of Clark, Robertson and Birch is shown in Fig. 3. It suggests the approximate conditions of formation of the Hills-

[*] It should be pointed out, however, that Aramaki and Roy (1959) now refer to the phase they obtained as a "disordered" phase with andalusite structure but rather different unit cell dimensions.

boro, Staley (both with andalusite), and Hager's Mountain (kyanite) deposits. Bowling's Mountain deposit, with reported kyanite *and* andalusite, may have formed near the univariant transition. Holman's Mill at Snow Camp is reported to yield andalusite (Broadhurst and Councill, 1953, p. 20); although this mineral is not found in the pits near Snow Camp, here reported, the proximity of these pits to Holman's Mill suggests that they, too, formed under conditions in which andalusite was stable.

The breakdown curves of Roy and Osborn (1953, p. 876) for pyrophyllite, forming andalusite, quartz, and vapour, and for diaspore, forming corundum plus vapour, are given Fig. 3 as dashed lines. These curves apply when the fluid phase is pure H_2O. Kennedy (1959, p. 565, 568) presents a breakdown curve for diaspore, forming corundum and vapour, which is slightly lower in temperature than the curve of Roy and Osborn; it is shown as dotted line. The discrepancy between the two sets of data is negligible for our purpose.

Kennedy (1959, p. 565, 568) also gives a breakdown curve for gibbsite, forming vapour plus diaspore (stable) or boehmite (metastable). The stable extension of this curve of course should extrapolate to the left (lower temperature) side of his gibbsite-boehmite curve, thus enlarging the diaspore stability field. The amount of this enlargement is unknown.

Roy and Osborn (1954, p. 876) also give a curve for the breakdown of kaolinite; however, the reaction product is hydralsite, which is metastable (Aramaki and Roy, 1958, p. 1530). Whereas at first sight the curve might seem to give a ceiling to the stability of kaolinite (as the product is a metastable phase), kaolinite is not compositionally equivalent to vapour plus hydralsite (using the probable composition of Roy and Osborn), and the effect of the as yet undetermined additional phase or phases participating in the reaction cannot be evaluated.

The *P-T* region between the gibbsite breakdown curve (between 100° C. and 200° C.) and the diaspore breakdown curve (around 400° C.) gives the stability field for diaspore (found at Staley and Holman's Mill, Snow Camp) for equilibrium with pure H_2O.* For the other deposits, the breakdown curve for pyrophyllite would give the upper limit. A more realistic reaction to consider, however, is

$$\text{kaolinite} + \text{quartz} = \text{pyrophyllite} + H_2O$$
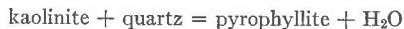
This reaction curve would occur to the low-temperature side of the breakdown curve for kaolinite alone and thus should impose a lower ceiling on

* The reaction

$$\text{Diaspore} + \text{pyrophyllite} = \text{andalusite} + H_2O$$

is more realistic than the breakdown of either pyrophyllite or of diaspore alone; this curve must be located to the left of the breakdown curve for diaspore alone.

the temperature of formation of the pyrophyllite deposits carrying kaolinite.

The metamorphism of the pyrophyllite deposits probably did not occur in equilibrium with pure H_2O, owing to the fact that many of these deposits contain three-solid-phase assemblages in the system Al_2O_3-SiO_2-H_2O, apparently in internal equilibrium. This fact precludes a free H_2O phase. Even though addition of other components in the fluid phase could result in its coexistence with the three solids, the value of the chemical activity of H_2O in such a solution is necessarily lower than that of a fluid phase composed of pure H_2O. The temperatures of formation of the pyrophyllite deposits therefore were likely lower than the maximum predictable from the curves in Fig. 3, although by an unknown amount.

This last conclusion is consistent with the coexistence of andalusite and pyrophyllite in the deposits. The diagram of Clark, Robertson and Birch, and of Roy and Osborn indicate (see Fig. 3) that sillimanite or mullite, rather than andalusite, should be the anhydrous aluminum silicate stable with pyrophyllite, for equilibrium with pure H_2O, except at extremely low pressures where the pyrophyllite breakdown curve begins to curve sharply to the left. With dilution of the fluid phase, however, the breakdown curves for the hydrous phases shift progressively to lower temperatures (Thompson, 1955) and thus the breakdown curve for pyrophyllite should eventually enter the stability field of andalusite, resulting in the observed association of andalusite and pyrophyllite.

ORIGIN OF THE PYROPHYLLITE DEPOSITS

Stuckey, after a field and microscopic study of many of the North Carolina pyrophyllite deposits, concludes that these deposits originated from hydrothermal replacement of preëxisting volcanic tuffs and breccias of dacitic and rhyolitic composition (1928, p. 35). The deposits are thought to be located along zones of structural weakness; where no pre-pyrophyllite faults are found, the zones of weakness are attributed to drag folding and shearing along the limbs of folds (1928, p. 41) since some of the deposits are found to occur in such positions (1928, p. 40). Broadhurst and Councill (1953, p. 12) agree with Stuckey's conclusions, without stating supporting evidence.

The present data on mineral assemblages bear upon the possible origin of the deposits. The fundamental assumption is that, unless evidence points to the contrary, the minerals in each assemblage are in mutual equilibrium.

The existence of three-phase assemblages, diaspore-pyrophyllite-kaolinite, andalusite-quartz-pyrophyllite, and pyrophyllite-kaolinite-quartz, excludes the possible existence, during the formation of the

deposits, of a free solution phase which a "hydrothermal solution" implies. Even though the coexistence of four phases (3 solids plus a solution) in a ternary system is permitted by Gibbs' Phase Rule, such an assemblage implies univariant equilibrium and specific combinations of temperature and total pressure. Such combinations are not expected in general to be of geologic importance (Goldschmidt, 1911, p. 123).

One may argue that hydrothermal solutions are probably not pure H_2O but contain other dissolved components; an assemblage like pyrophyllite-kaolinite-quartz-solution therefore is not ternary and more than three phases may be expected in general. However, a hydrothermal solution implies that H_2O behaved as a "mobile" component whose amount is not determined by the initial composition of the local system (Thompson, 1955). Similarly, a hypothetical component whose sole function is to allow an additional solution phase, but which does not manifest itself in the mineralogy of the product, must also have moved in and out of the system and therefore is mobile in the same thermodynamic sense. Thompson (1955) and Korzhinskii (1950) have independently shown that for a system which is thermodynamically open, at arbitrary values of T and P_{total} the maximum number of phases, $\phi_{maximum}$, is related to the total number of distinct chemical components, c, and the number of distinct mobile components, c', by the equation $\phi_{maximum} = c - c'$. The mobile components therefore cannot contribute to the number of solid phases present. If a hydrothermal solution existed, in fact, in the ternary system Al_2O_3-SiO_2-H_2O, in general only two solid phases should be found, since $c = 3$ and $c' = 1$ (H_2O). These 2-phase assemblages should be spatially so distributed that they reflect the existence of chemical potential gradients of the mobile components during recrystallization. At Glendon, the sample collection was arranged with this possibility in mind. No systematic mineralogical variation of this sort was found.

The prevalence of the 3-phase assemblages in the ternary system, in fact, indicates strongly that H_2O behaved as a fixed component during the formation of the pyrophyllite deposits, contrary to the general situation in regional metamorphism (Thompson, 1957; Zen, 1960).

An alternative origin, consistent with the mineral assemblage data, and, as far as the writer is aware of, the geologic information, is as follows.

The protolith for the pyrophyllite deposits studied in this report were bodies of saprolite which resulted from the deep weathering of the rhyolitic or dacitic country rock. The residual material would be high in silica, alumina, and ferric oxide. Most of the other components tend to be leached out; among the alkali and alkaline earth oxides, K_2O would be the most stable and lag behind (Goldich, 1938, p. 54). The resulting rock would have the general chemical composition of the pyrophyllite de-

posits. The envisioned condition of weathering is much like the present one in North Carolina.

This picture of surface weathering of volcanic rocks implies disconformities or unconformities in the Volcanic Slate sequence. Recent mapping (Conley, 1959; Stromquist and Conley, 1959) in the Albemarle and Denton quadrangles in south-central North Carolina has revealed at least one major unconformity in the Volcanic Slate sequence; it would be interesting to see if the same, or a similar, stratigraphic break occurs at the zone of pyrophyllite deposits.

The saprolitic deposits, scattered on the disconformity surface, were buried by later, additional volcanic eruptions. At a later date, the entire rock sequence was deformed and metamorphosed. In the saprolitic bodies, the alumina:silica ratio varied from one place to another, and the H_2O concentration also varied. For some reason, the component H_2O remained fixed during metamorphism; there was little redistribution of this component even on a very small scale, and certainly none on the scale of the individual deposits. Depending on the relative proportions of the three components, therefore, different mineral assemblages resulted—for instance, andalusite and quartz if the system were free of H_2O, but kaolinite-quartz if the system were very hydrous. A few portions of the bodies were low in silica relative to alumina (approaching a true laterite), and now contain diaspore; by and large however quartz is present.

The metamorphic grade of the rock sequence as a whole was such that, in the country rock, such mineral assemblages as muscovite-pyrophyllite chlorite-chloritoid-quartz, and pyrophyllite-clinozoisite-muscovite-quartz resulted. Hematite, rather than magnetite, was the predominant iron oxide phase. These are mineral assemblages typical of metamorphism near or just below the almandite isograd; in west-central Vermont (Zen, 1960), similar mineral assemblages characterize phyllites and slates. The country rock of the pyrophyllite deposits is also slate and phyllite (Stuckey, 1928); similarly almandite has not been found in these rocks to date.

It should be stressed that to say H_2O behaved as a fixed component during metamorphism, in no way implies the presence or absence of a free solution phase. The chemical activity of H_2O, for example, might be controlled by the buffering assemblage kaolinite-pyrophyllite-quartz, which being bivariant in the ternary system, possesses a unique value of the chemical activity of H_2O at given temperatures and pressures. On the other hand, if H_2O and also other components in the fluid phase behaved as fixed components, then, according to Gibbs' Phase Rule, a solution phase *could* have been present, although it certainly did not circulate freely through the system to destroy the buffering mineral assemblages.

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* Note added in press: Since the manuscript went to press, two pertinent papers have appeared to which the reader's attention is drawn. (1) Carr, R. M., and Fyfe, W. S., 1960, Synthesis fields of some aluminium silicates, *Geoch. et Cosmoch. Acta* **21,** p. 99–109; (2) Espenshade, G. H., and Potter, D. B., 1960, Kyanite, sillimanite, and andalusite deposits of the southeastern states. *U. S. Geol. Survey Prof. Paper* **336,** 121 p. (see esp. p. 8–16, 109–110.