CHANGES IN THE CONSTITUTION AND MICROSTRUCTURE OF ANDALUSITE, CYANITE, AND SILLIMANITE AT HIGH TEMPERATURES AND THEIR SIGNIFICANCE IN INDUSTRIAL PRACTICE*

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Abstract

Owing to their growing commercial importance in the manufacture of refractories and porcelain, the minerals of the sillimanite group (andalusite, cyanite, and sillimanite) were investigated as to their decomposition products and volume changes between cones 10 and 15.

Petrographic-microscopic examinations showed that andalusite breaks down at cone 13 into mullite and glass, while cyanite also breaks down into the same components but at cone 12. Sillimanite is not decomposed up to cone 15. The composition of the mullite was checked by chemical analysis.

Andalusite shows almost no volume change at dissociation; sillimanite shows a slight expansion up to cone 15; cyanite shows a great expansion and disintegration at dissociation.

The practical significance of the behavior of the minerals is discussed as well as their possibilities for use in ceramic ware. Andalusite could be used in the raw state; cyanite would require calcination before use, so that andalusite appears to be best suited for most bodies.

INTRODUCTION

As a result of heating at high temperatures or of fusion at atmospheric pressure, many aluminium silicate minerals, including andalusite, cyanite, topaz, dumortierite, kaolin, and others, invert or break down into other substances. One product of this change is a crystalline compound which, until very recently, has been interpreted as artificially produced sillimanite with the composition $Al_2O_3 \cdot SiO_2$. A knowledge of the conditions under which this alteration takes place is very important because of the use of some of these minerals in industrial processes. This is especially true of the trimorphous group of the minerals andalusite, cyanite, and sillimanite, with which this investigation is concerned.

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TRIMORPHISM OF $Al_2O_3 \cdot SiO_2$

The compound $Al_2O_3 \cdot SiO_2$ is trimorphous, forming a group of three minerals, andalusite, cyanite, and sillimanite, generally referred to in the literature as the sillimanite group. These minerals, while of the same empirical chemical formula, differ crystallographically Two of them, andalusite and sillimanite, are orthorhombic in crystallization, forming somewhat similar crystals which however, can be differentiated by the accurate measurement of their interfacial angles. The third mineral, cyanite, is triclinic, having a typical crystal form and certain very distinctive physical properties. The optical constants of these minerals, however, allow complete differentiation to be made.

GEOLOGICAL ASPECT OF THE TRIMORPHISM OF $Al_2O_3 \cdot SiO_2$

Inversion in dimorphous or trimorphous groups of minerals may bear an important relation to the conditions during the formation of the rocks in which they occur. In fact, inversion has sometimes been interpreted as indicating that rocks containing these minerals must have been formed below certain temperatures. This is true of the minerals of the sillimanite group. For example, Vernadsky[1] concludes, as a result of his experiments, that cyanite must have been formed at a temperature not exceeding 1330° C. However, great pressures are almost certain to accompany the rock-forming processes under which the minerals of the sillimanite group are produced. Furthermore, Vernadsky does not appear to have considered the probable effect of these pressures upon the modification of polymorphous minerals.

From the geogical standpoint, the type of rocks in which these minerals occur leaves no doubt that these minerals have been formed under different conditions and that they therefore might be expected to react differently when heated. For example, sillimanite is frequently found near the contact of igneous intrusions with clay rocks, while farther away from the contact and in the same rock andalusite is sometimes noted. In nature, sillimanite is apparently more stable than cyanite and andalusite toward heat. This has also been observed to be the case under the artificial conditions of the laboratory.

On the other hand there appears to be ample evidence that great pressure is an important factor in the formation of cyanite. Van Hise[2] believes that cyanite is formed in the zone of anamorphism, as a result of several possible reactions, such as the combination of corundum, diaspore, or gibbsite, with quartz. In every case there is a marked increase in specific gravity during the change. This is due in large measure to the great pressures exerted in the zone of anamorphism. The greater specific gravity of cyanite (3.6, the highest of the sillimanite group) also indicates that it has been formed under higher pressures than the other two members of the group. According to Van Hise, the mineral formed under greatest pressure should have the most closely packed molecules and hence the greatest amount of substance per unit volume, or the highest specific gravity.

Moreover, the type of rocks with which it is usually associated is another indication that cyanite is formed under greater pressures than sillimanite or andalusite. Cyanite is usually associated with mica or quartz-mica schists which represent some of the most intensely metamorphosed, folded, or compressed rocks.

On the other hand, if the results of laboratory experiments are accepted, cyanite is the least stable toward heat and was formed at the lowest temperature of any of these minerals. This, however, would be a rather bold statement to make without qualifications, especially in view of the meager state of our experimental knowledge of the effect of high pressure upon the formation of minerals.

INDUSTRIAL ASPECT OF THE INVESTIGATION

A crystalline constituent having optical properties very similar to sillimanite has been observed as one of the components of many ceramic wares for a long time. This constituent has usually been referred to as "artificial sillimanite." It was also a commonly known fact that the good qualities of many porcelains were due, at least in part, to the formation of this compound. Accordingly, the development of any method or the use of any material which increases the amount of this compound in the ware necessarily becomes of great value in industrial practice.

For some years, therefore, the manufacture of special types of porcelain has tended toward the formation, during burning, of an increasingly higher content of "artificial sillimanite." Bowen and Greig[3] have recently shown, however, that its composition is not the same as natural sillimanite ($Al_2O_3 \cdot SiO_2$), as previously supposed, but rather, is $3Al_2O_3 \cdot 2SiO_2$. Their work showed that the two compounds are not only similar chemically but also strikingly similar optically.

"Artificial sillimanite" as produced in ceramic ware usually results from molecular changes taking place in clay under the influence of heat and various fluxes. The highest content of "sillimanite" has been developed by introducing into the unfired body artificially prepared "sillimanite" in the form of the product of direct fusion or of a calcine—a mixture of clay, alumina and fluxes heated to a temperature of about 1500°C. Although this method has been in use for several years in the manufacture of spark plug porcelains, it was, of course, an expensive way to obtain the desired end.

In order to eliminate the necessity of making an "artificial sillimanite" to be introduced into the body, the logical procedure was to attempt to employ one of the natural Al_2SiO_5 compounds; namely, andalusite, cyanite, or sillimanite. However, the difficulty of obtaining any of these minerals in sufficiently large quantities and in a pure state was not overcome until recently when a large deposit of andalusite was located in California. It was then possible to substitute the natural material for the "artificial sillimanite." Undoubtedly, andalusite will be used in the future for other purposes as well.

As a result of the discovery of this new deposit, a knowledge of the temperatures or points at which the different members of the sillimanite group break down is important from the industrial standpoint in three ways.

First, it is desirable to know in each instance, what products are formed as a result of the breakdown of these minerals. This must be known in order to approach other problems more intelligently.

Second, it is also important to know (a) at what temperature decomposition is complete; (b) whether this point is reasonably stationary and the breakdown sharp; (c) whether the breakdown is slow and persists over a range of temperature.

Third, because of accompanying volume changes in the material at its decomposition point, these changes as well as the actual point of breakdown are important. In order that volume changes may be fully stabilized it is necessary to carry the firing of the ware well beyond the decomposition point, especially if the volume change is large and takes place slowly.

PURPOSE OF THE INVESTIGATION

The purpose of the present investigation is not to establish the exact temperatures at which andalusite, cyanite, and sillimanite undergo change but rather to establish, first, the nature of the resulting product; second, the points at which decomposition takes place, and whether this decomposition is a sharp change or covers a range of temperature; third, the character of the accompanying volume changes. Any of these changes, when produced under industrial conditions, may take place at quite different temperatures than under the more exactly controlled conditions of the laboratory devoted to pure science.

HISTORICAL

A review of the literature reveals the fact that the investigations of the effect of heat upon minerals of the sillimanite group range from simple descriptions of the loss of color of the minerals when heated in the blowpipe flame, to various attempts to form the minerals synthetically. The most recent work of this kind is that of Bowen and Greig upon the revision of the system $Al_2O_3 \cdot SiO_2$ and the true nature of the compounds formed in the breakdown of sillimanite.

Apparently, no attempt has been made to correlate the changes involved with practical ceramics except in the work of Bowen and Greig. This is no doubt due to the fact that only quite recently have any of the minerals of the sillimanite group been used in the manufacture of ceramic ware To be sure, the presence in ceramic bodies of what has been called sillimanite has been known for a long time, but this substance has developed as a by-product of the molecular decomposition of clay and has recently been shown by Bowen to be not "sillimanite" but actually a compound of the composition $3Al_2O_3 \cdot 2SiO_2$. For some years so-called "artificial sillimanite" has been manufactured from its oxides or from clay for subsequent use in ceramic ware[4] This "sillimanite," however, is a synthetic product which should not be confused with the natural minerals.

METHODS USED AND THE CHANGES INVOLVED

In the study of the effect of heat upon minerals of the sillimanite group, three general methods of attack appear to have been used. These methods may be designated as physical, physical-optical, and physical-chemical-optical. A fourth method (chemical-optical) does not appear to have been used in investigations of changes in the natural minerals although it has been used extensively in the study of artificially formed "sillimanite." Vernadsky[1] summarizes excellently the various attempts of investigators up to 1889.

PHYSICAL METHOD—This represents the earliest type of study and consists largely in simply recording observations of the loss of color and of the whitening effect of minerals when subjected to the blowpipe flame. This, of course, represents a very crude method of determining what changes had taken place; in fact, there seems to be no evidence that there was any serious effort among the earliest observers to follow the matter further.

According to Vernadsky, Saussure,[5] who first found and described cyanite, observed that needles of cyanite, "losing to fire their color, whatever it may be, change to a dull white. They show a granular texture which renders them somewhat fragile." Many others make practically the same statement. Some ascribed the change to the decomposition of pigments and minerals included in the cyanite. Laugier[6] and Erdmann[7] reported losses in weight, sometimes as high as 0.61 per cent. Vernadsky confirmed this and interpreted the loss in weight as possibly indicating that the change may be due, in part, to the loss of some volatile constituent.

Many mineralogists record that andalusite does not lose its original compactness but simply whitens. The same is true of sillimanite.

PHYSICAL-OPTICAL METHOD—This method makes use of alterations taking place in the physical properties, such as hardness and specific gravity, under the influence of heat. These alterations are further supplemented by changes in optical properties.

Vernadsky used a method of this character in his work on cyanite. He found, first, that the average hardness of the mineral increased slightly; second, the specific gravity diminished markedly; third, the fragments showed distinct changes in optical properties. Curiously enough he does not appear to have observed the optical property which is generally considered most important of all: namely, the index of refraction. As a result of this work Vernadsky was able to make the statement that "heated to a determined temperature (about 1200-1330°C), cyanite changes to another mineral which is probably sillimanite." Apparently he had no way of accurately controlling the temperature in these experiments; hence the wide range of temperature mentioned. He also states that sillimanite, and probably also andalusite, is stable at this temperature.

PHYSICAL-CHEMICAL-OPTICAL METHOD—Much credit for the development of this method as a means of investigation belongs to the staff of the Geophysical Laboratory of the Carnegie Institution. The method is essentially synthetic. It involves building up the various binary and ternary compounds from their oxides, and determining all important optical and physical properties, such as melting points of compounds and eutectics, dissociation points, inversion points, and so forth. Thus, the effects of variation in temperature and chemical composition are not only very accurately controlled but they are also supplemented by petrographic-microscopic examination.

Although this method was originally designed as a basis for further detailed study of petrologic problems from the standpoint of pure science, experience has shown that many of the methods developed and the results obtained by the above investigators can be applied to industrial, especially ceramic, problems either in explanation of existing conditions or as aids in research. Their work on the system Al_2O_3-SiO_2 has an important bearing in this connection.

One of the earliest investigations using the physical-chemical-optical method was conducted on the system Al_2O_3-SiO_2.[8] The results of this work seemed to indicate that there was only one compound of Al_2O_3 and SiO_2; namely, $Al_2O_3 \cdot SiO_2$, corresponding in most of its optical properties to the natural mineral sillimanite. Certain minor discrepencies somewhat difficult of explanation were observed. Thus, it was never possible to obtain the compound in a perfectly pure state, small amounts of glass always being present. Also, the refractive indices of the artificial crystals were distinctly lower than those of the natural mineral. Owing to the fact that chemically pure oxides were used, the observed optical properties were probably assumed to represent the true constants of the synthetic compound $Al_2O_3 \cdot SiO_2$, although they were quite different in some respects from those of natural sillimanite. Variations in the natural mineral were thought to be due to impurities. The presence of glass was explained by the high melting point of the compound, since, because of the high temperature at which it began to crystallize and on account of the apparently rapid rate of crystallization, some glass might easily be included between the fibrous crystals.

At the same time these investigators verified Vernadsky's statement that at high temperatures both andalusite and cyanite undergo changes to another form, probably to sillimanite. The exact temperatures of the changes were not definitely determined, except that they are somewhere between 1150° and 1500°C. Various fluxes apparently decomposed the minerals before the change took place. They were not, however, able to verify the statement that when andalusite undergoes this change an evolution of heat occurs.

The work on the system Al_2O_3-SiO_2 was quite generally accepted until recently when Bowen and Greig, in a revision of this system, showed that the former conception was inaccurate, and that although there was but one compound formed between Al_2O_3 and SiO_2, it is not $Al_2O_3 \cdot SiO_2$, but rather $3Al_2O_3 \cdot 2SiO_2$. From the melt of mixtures of the two oxides in these proportions only one component results, which is entirely crystalline and possesses the optical constants previously assigned to the "sillimanite" of the earlier work on the same system. The establishment of this fact immediately explained the discrepancies in the earlier study, such as the lower refractive indices of the so-called artificial sillimanite and the presence of excess glass in the melt of the 1:1 mixture.

Furthermore, Bowen and Greig showed that at 1545°C. natural sillimanite melts incongruently and breaks down into $3Al_2O_3 \cdot 2SiO_2$ and excess siliceous glass. At the same time they examined the "sillimanite" which had been produced in ceramic ware of various kinds and found that in each case it was not $Al_2O_3 \cdot SiO_2$ but the new compound $3Al_2O_3 \cdot 2SiO_2$. Subsequently, this new compound was also found to exist in certain fused argillaceous rocks and was given the name mullite.[9] Thus, although the compound $Al_2O_3 \cdot SiO_2$ exists in nature in three different crystalline forms, none of them have yet been produced in the laboratory.

SILLIMANITE AND MULLITE IN CERAMIC WARE

As already pointed out, the presence of a crystalline compound, having properties very similar to those of sillimanite, has been recorded in ceramic literature for about fifty years. Since its presence was first noted the occurrence of this compound in ceramic bodies has been studied from many angles. Its importance in lending valuable properties to the ware has become recognized more and more until recently a microscopic description of a ceramic body was not considered complete without some reference to the so-called sillimanite.

Behrens[10] was apparently the first to make a microscopic study of porcelain, the results of which were published in 1873. He stated that the groundmass of molten feldspar undergoes devitrification, and that the material which separated from the groundmass dissolved in hydrofluoric acid less readily than the quartz and glass present. He did not identify the crystals, but his description of their insolubility suggests crystals of "sillimanite."

In a microscopic study of porcelain, Hussak, in 1889,[11] described the presence of needle-like crystals, very minute and weakly, doubly refracting, resembling sillimanite. Mellor,[12] in 1907, reported "sillimanite" in Chinese and Berlin porcelains.

Plenske,[13] in an elaborate study of porcelains published in 1908, noted that porcelains could be divided into groups according to the presence or absence of crystalline products in the groundmass. Furthermore, he observed that "sillimanite" might also be present in masses of exceedingly minute grains which were apparently amorphous. Plenske also believed that the crystalline "sillimanite" was formed by devitrification of the glassy groundmass.

Zoellner,[14] also in 1908, identified optically the occurrence of "sillimanite" in porcelain, and also separated the crystals by hydrofluoric acid. He found that the ratio of Al_2O_3:SiO_2 was 1:1. He believed that the "sillimanite" was formed by a molecular change in the clay in the body and not through devitrification.

More recently, in 1916, Klein[15] made a detailed study of various types of porcelain and the relation of the development of "sillimanite" in them to the temperature of burning. Riddle,[16] in 1919, also described the presence of "sillimanite," and its relation to various fluxes and fine grinding. Of recent years reports of the development of "sillimanite" in porcelains have become very numerous.

"Sillimanite" has also been reported in other ceramic bodies besides porcelain. In 1890 Vernadsky[17] called attention to its formation from the heating of clay. In 1919 Cox[18] claimed to have found it in fire clay exposed to a high temperature for a long period, although the chemical analysis which he gave did not indicate a ratio of 1:1 for the constituent oxides but was more nearly 3:2; namely, that of mullite. At various times Mellor[19] has reported its formation in fire brick. Many references might also be given in which its presence in glass is reported. In these cases its formation is believed to be due to the decomposition of clay from the tank or pot walls by the glass.

However, as already mentioned, it remained for Bowen and Greig to point out that the "sillimanite" in all the bodies examined by them was not of the composition $Al_2O_3 \cdot SiO_2$, but $3Al_2O_3 \cdot 2SiO_2$, now called artificial mullite. They were also fortunate in obtaining from an outside source some well crystallized $3Al_2O_3 \cdot 2SiO_2$, which was used to measure accurately both the crystallographic and optical constants and to show its very close similarity to natural sillimanite.

METHOD USED IN THE PRESENT INVESTIGATION

Owing to the accurate and detailed information available on the compounds developed in the system Al_2O_3-SiO_2 as worked out at the Geophysical Laboratory, the method used for the preparation of the samples and later identification of the resulting products was comparatively simple, involving four steps as follow:

1. Powdered samples of the raw materials were first fired to predetermined temperatures in open crucibles.
2. A careful petrographic-microscopic examination of each of these burns was made, using the method of immersed grains.
3. The crystalline products formed from andalusite and cyanite were analyzed chemically, affording evidence in addition to the work of Bowen and Greig on sillimanite.
4. Determinations were made of the changes in specific gravity between the unfired and fired minerals.

METHOD OF FIRING

The kiln in which the minerals were burned is a large laboratory kiln designed by the Champion Porcelain Company for research work and for the accurate reproduction of conditions in full sized kilns. It is of the down-draft type.

In overall size it is 8 feet high, 6 feet wide, and 4 feet 6 inches deep. The chamber is 3 feet 6 inches high, 3 feet 6 inches wide, and 1 foot 6 1/2 inches deep, and has a capacity of seven 15-inch by 5-inch saggers. Thermoelement pyrometer control is provided through several openings. Cone 32 may be fused in this kiln (about 1705°C.).

The minerals were fired in small open crucibles, each containing about five grams of material. Two series of firings were made, after the manner of draw trials. The first series of drawings was started at cone 8 and continued every two cones thereafter, inclusive of cone 16.

Orton cones were used and a definite rate of heating was followed in firing the samples. It should be stated here that standard pyrometric cones do not always indicate a definite temperature as does a thermocouple. According to conditions under which the heating takes place, they may register higher or lower than the actual temperature. They are useful, however, in indicating approximately the temperature reached. For example, cone 10 may bend over until its tip touches the base upon which it rests or be "down" at an actual indicated temperature of 1340°C., whereas the temperature at which it should come down theoretically is 1330°C. Likewise, other cones may not register the true temperature.

These anomolous conditions result from the fact that the fusion of a standard pyrometric cone involves viscosity and other factors as well as temperature, and therefore indicates heat-work. On this account the ceramist prefers the cone to the thermo-element in actual practice, since the cones show that a certain amount of work has been done. Therefore, since the purpose of this investigation is to obtain the reaction temperatures under working conditions, all temperatures will be expressed in cones. The ceramist uses the thermo-element mainly to indicate whether the temperature is rising, falling, or remaining stationary.

According to the standard scale, cone 1 has a fusion point of 1150°C. and each succeeding cone is 20°C. higher. The following table indicates the theoretical fusion temperatures from cones 10 to 15.

Cone 10	1330°C
11	1350
12	1370
13	1390
14	1410
15	1430

The microscopic examination of the firings showed that no changes were to be observed in the minerals below cone 11, and, further, that in andalusite and cyanite the changes were completed between cones 12 and 14. Sillimanite, however, showed no decomposition even at the highest temperature.

Having thus established the upper and lower limits of the changes in andalusite and cyanite, a second series of draw-trials was made from cones 10 to 15 inclusive, with samples taken at every cone. It was on these samples that the petrographic-microscopic examinations described later were carried out.

OBSERVATIONS ON THE MATERIAL USED

A. ANDALUSITE

The andalusite which was used in these firings came from the mine owned by the Champion Porcelain Company and located on White Mountain, of the Inyo Range, Mono County, California. A complete description of the crystallography and mineralogy of this andalusite has been given elsewhere.[20]

Since the andalusite, as received from the mine, is in the form of large fragments, it was necessary to crush it and then to grind the coarse granules without water to a fine powder in a pebble mill. As it was not desired to use the material in a body, and as grains of any size could be studied on the microscope slide, no attempt was made to screen and size it. The powder consisted of about 80 per cent andalusite with minor amounts of pyrophyllite, mica, corundum, and rutile.

The Effect of Firing

The above powder, after being fired as previously indicated, was subjected to a careful petrographic-microscopic examination with results which follow.

At cone 10 the only apparent outward change is a slight consolidation of the powder into a firm but quite brittle mass. The microscopical examination shows no change in the andalusite grains. They still remain clear and retain all their original optical properties.

The plates of mica have decomposed into masses of exceedingly minute rounded grains embedded in a glassy matrix, and are quite similar in appearance to the products of the breakdown as it first occurs in kaolin upon hard firing. These granular masses show no double refraction and both constituents are too fine grained to identify.

At cones 11 and 12 there still is no outward change in the appearance of the firings, nor is there any change in the optical properties of the andalusite grains. Due to the higher temperature of firing, the plates of mica show the grains resulting from the breakdown to be somewhat enlarged. Some of these grains are slightly elongated, the long direction being perpendicular to the original cleavage of the mica. Although they are still too minute for complete identification, their optical elongation can be determined as negative. (Figures 1 and 2).

With an increase to cone 13, the mass in the crucible is a distinctly firmer body than in previous burns, a slight amount of sintering having taken place.

Microscopically, the andalusite also is noticeably altered, about half the grains showing the changed character. As is to be expected, most of the smaller grains are decidedly altered while the larger ones may be only partially affected and even in some cases entirely unaffected. The change in the andalusite fragments is apparently due to a breakdown into two components. One of these is crystalline and more abundant, while the other is a glass and minor in amount.

The crystalline component occurs as elongated crystals parallel to each other throughout the whole grain where it is completely decomposed, so that extinction between crossed nicols is complete over the whole grain at the same time. Optically, the indices of refraction are, $\gamma = 1.657$ and $\alpha = 1.643$. The elongation is positive On account of the small size of the crystals, other optical properties could not be determined. These facts indicate that the crystalline compound formed is artificial mullite, $3Al_2O_3 \cdot 2SiO_2$, described by Bowen and Greig, and which they determined to be the decomposition product resulting from the heating of natural sillimanite above 1545°C. As already indicated, this compound, heretofore supposed to be artificial sillimanite, was also found by them in ceramic ware. (Figures 3 and 4).

The second component is isotropic in character and non-crystalline as far as can be determined. It is apparently a glass. Its refractive index is slightly variable, depending probably upon the character of the impurities present, which have been taken into solution. In general, the index is near 1.54. As pointed out by Bowen and Greig, this glass is probably very siliceous in composition.

As previously mentioned, not all of the grains are decomposed to this mixture of crystals and glass. The change can sometimes be observed at an intermediate stage where grains show a fringe of parallel crystals around the outer edges with an unchanged center. The crystals in the fragment are not formed as radiating crystals but they are parallel throughout, without regard to the part of the grain in which they occur. The border consisting of crystals and glass does not have a definite boundary but passes irregularly and imperceptibly into unaltered andalusite at the center. Of interest also is the fact that the crystals which have formed in the andalusite grain are of opposite optical orientation from the original grain. (Figures 5 and 6).

Heated to cone 14 the powdered mass shows an increased firmness but is still not solid. The microscopic examination indicates that the decomposition is complete in all of the smaller grains of andalusite and in most of the larger ones. The smaller grains show crystals of mullite which are slightly larger than those formed at cone 13. A few of the largest grains still possess unchanged centers with crystal borders, but these are uncommon. (Figure 7).

At cone 15 it is apparent that every grain is decomposed, even the largest and coarsest.

B. CYANITE

The cyanite used in these firings was obtained from Charlotte Court House, Virginia. Although the material is composed largely of cyanite, considerable amounts of quartz and a little muscovite mica are present as admixtures. Before being used commercially the crude material would probably require treatment to eliminate most of the quartz and mica, but for the purposes of the present work this was unnecessary.

Before firing, the material was ground to a powder but was not screened to any definite size, following the same procedure as with andalusite. This, however, did not affect the results as grains of the same size were considered in each case.

The Effect of Firing

Since all three members of the group were fired together, the conditions were the same for cyanite as those described for andalusite.

At cone 10 the powder retains its slightly bluish green color. The cleavage surfaces of the larger grains can still be seen to be smooth and bright. The mass shows a very slight cohesion such as was noted in the corresponding burn of andalusite.

When examined microscopically no change in the optical properties of the fragments can be detected. They are still the same flat, straight-edged fragments, sometimes showing step-like terminations and cleavage cracks as in the unburned material. (Figures 8 and 9). The small amounts of mica present appear the same as in the andalusite burn at cone 10.

When heated to cone 11 there is still no outward change in the powder. Cleavage surfaces are bright and smooth for the most part, and the faint bluish color is present.

Slight changes in microstructure appear to have commenced. Some fragments show the development of a few scattered fibrous crystals. These are similar in appearance to those formed in andalusite but are too far underdeveloped to make identification certain. Cleavage cracks in the fragments are somewhat more numerous, especially those perpendicular to the length of the grain. These are no doubt due to the expansion of the fragments under the influence of increasing temperature. The above evidence, though slight, suggests that a point is being approached where marked changes will take place.

When fired to cone 12, the powder loses some of its color and assumes an external appearance slightly different from that of the preceding burn. Smooth, glistening cleavage surfaces are also less common.

The microscopic decomposition is far more pronounced than would be suspected from the appearance of the powder alone. The fragments have broken up into irregular areas of crystals showing double refraction but these areas do not extinguish together. Only the largest grains show unchanged centers with altered borders. The small fragments show fibrous areas of elongated crystals, these areas being oriented in all directions and forming interlocking aggregates of needles; hence, the fragments have a peculiar mottled appearance between crossed nicols. This is in distinct contrast to the marked parallelism of the crystals developed from andalusite. The crystals formed from cyanite have between them, as in andalusite, an amorphous, glass-like substance. The refractive indices of the crystals are: $\gamma = 1.655$ and $\alpha = 1.642$. The glass has an index of 1.54. The elongation of the crystals is positive. As in the case of andalusite, other optical properties are not obtainable because of the small size of the crystals. Thus, from all indications optically, both the crystals and the glass are the same components as are formed during the breakdown of andalusite. (Figures 10 and 11).

At cone 13 there is a very pronounced external change in the powder. It becomes dull white in color and loses much of the slight cohesion it previously had. A large fragment burned along with the powder became dull white in color and very brittle, breaking down into many fragments during burning. These fragments when touched lightly, in turn crumble to a fine powder. This is due as pointed out by Vernadsky[1] to a pronounced expansion in volume and a decrease in specific gravity accompanying the change in constitution.

The microscopic examination reveals that the breakdown, which was well started at cone 12, has been entirely completed on the largest fragments. It shows, however, a more complete and definite development of variously oriented areas of mullite crystals and glass, and also that in many instances the firing to the higher temperature has served to increase the size of the crystals.

No further marked change from cone 13 is apparent either externally or microscopically, at cones 14 or 15. In each case there is a tendency toward further growth in the size of the mullite crystals formed.

C. SILLIMANITE

The sillimanite used in firings covering the same range as those of andalusite and cyanite was obtained from a recently reported Indian deposit, presumably from the Khasia Hills of Assam.[21]

It was used in the form of a fairly coarse powder with a grain size somewhat greater than the cyanite. The material was rather pure, consisting of irregular grains with an internal fibrous structure. Only a small amount of muscovite mica, quartz, and iron oxides were present as impurities.

The Effect of Firing

The firing was carried out in the same manner as for the other two members of the group.

As Bowen and Greig have pointed out, sillimanite does not decompose until a temperature of 1545°C has been reached, and since the maximum cone of the present series was only cone 15, no changes in structure were anticipated but the mineral was included mainly for the purpose of completeness.

At all cones including cone 15 the material remained a loose, incoherent sand, no hint of sintering being observed. There was no external change in the grains.

Upon microscopic examination no decomposition could be detected even at cone 15, the grains at all times retaining the optical properties of sillimanite, losing none of their original structure, and showing no signs of a breakdown similar to the other two members of the group.

CHEMICAL COMPOSITION OF ARTIFICIAL MULLITE

Although Bowen and Greig did not analyze the artificial mullite crystals which were developed by heating natural sillimanite, they did show that these crystals had the same optical properties as pure artificial mullite. They also separated and analyzed crystals produced in the burning of various types of ceramic ware, and showed that these, too, were the same as mullite except that small amounts of Fe_2O_3 and TiO_2 which had been taken into solid solution increased the indices of refraction of the crystals noticeably and also produced a violet or pink pleochroism.

Since the optical properties of the crystals formed by the dissociation of andalusite and cyanite are very similar to those of mullite, chemical analyses of them were made. The chief obstacle encountered in determining the composition of these crystals was due to their very minute size. This not only renders it difficult to free them from the admixed silica glass but appears to make the crystals themselves very susceptible to decomposition in cold hydrofluoric acid.

In the preliminary examination the crystals were exposed to cold hydrofluoric acid for one week, the fired material having been previously ground to a very fine powder. This treatment resulted in the complete decomposition of the crystals as well as the silica glass. Finally, the method used by Vernadsky and adapted by Bowen[9] was followed, allowing the powder to stand in 25 per cent hydrofluoric acid over night at room temperature. After the crystals were freed from excess acid by repeated decantations, they were finally filtered off. Treated in this manner both the andalusite and cyanite burns gave fairly pure residues of mullite crystals. The former contained appreciable amounts of corundum, some undissociated andalusite, rutile, and a little glass, while the latter showed a slight decomposition of the crystals and a very little corundum.

The results of the chemical analyses given in the table below confirm the optical evidence.

COMPOSITION OF MULLITE CRYSTALS FORMED FROM

	Andalusite	Cyanite	Theoretical for $3Al_2O_3 \cdot 2SiO_2$
SiO_2 (corrected)	31.98	27.37	28.2
Al_2O_3 "	68.02	72.63	71.8
Corundum	1.50	1.39	
Rutile	1.77		

Thus, it is quite apparent that the agreement between the analyses and the theoretical composition is sufficiently close to warrant the composition of the crystals being placed at $3Al_2O_3{:}2SiO_2$. The more siliceous character of those obtained from the andalusite burn is mainly due to the presence of some andalusite which was not entirely decomposed during burning. There does not appear to be any method at present to determine andalusite separately, as can be done for corundum and rutile. The low SiO_2 in those from the cyanite burn is probably due to slight decomposition previous to analysis.

Attention is called particularly to the fact that TiO_2 is present as rutile and is not in solid solution in the mullite. This accounts for the fact that the indices of refraction of the mullite crystals do not vary appreciably from those of pure synthetic mullite, nor do these crystals exhibit the characteristic pleochroism of mullite containing TiO_2.

CHANGES IN SPECIFIC GRAVITY AS A RESULT OF FIRING

While very little change in volume was observed in the andalusite powder at its dissociation point, that which accompanied the dissociation of cyanite was very pronounced. This was more apparent when a comparison of the unfired and fired powders was made, as shown in the following table. The standard pycnometer method was used.

	Specific Gravity	
	Unfired	Fired to cone 15
Andalusite	3.29	3.20
Cyanite	3.59	3.09
Sillimanite	3.15	2.92

It is quite apparent that cyanite is most affected as a result of heating, while sillimanite is affected much less and andalusite least of all.

The decrease in specific gravity in andalusite and cyanite is attributable directly to the dissociation. In sillimanite, however, no dissociation is apparent microscopically. The change, therefore, would seem to be due to the production of fine microscopic or submicroscopic cracks caused by the natural thermal expansion with increasing temperature or, perhaps more likely still, to volume changes in the associated minerals which were present in small amounts.

SUMMARY OF CHANGES DURING FIRING

The results of the changes in constitution, microstructure, and volume of the members of the sillimanite group when fired up to cone 15 may be briefly summarized as follows.

ANDALUSITE—From the evidence furnished by the petrographic-microscopic examination of the various burns it is certain that, under the conditions detailed, andalusite breaks down rather abruptly at cone 13, yielding a mixture of mullite and a siliceous glass. The resulting structure is one of parallel crystals extending throughout the whole area of a grain of the mineral, with interstitial glass. If the grain be rather large, the center may be unchanged with a fringe of crystals and glass around the outer edges.

The optical orientation of the crystals thus formed is opposite to that of the original grain. Firing to higher cones serves to enlarge the size of the crystals somewhat and to complete the breakdown of the larger grains. The volume changes are small, only a slight expansion taking place.

CYANITE—The change in cyanite does not appear to be as abrupt as in andalusite. The increase in the cleavage cracks crossing the length of the fragments and the incipient formation of fibrous crystals seem to indicate that at cone 11 a point is being approached where marked changes will occur. These changes actually occur at cone 12, but the microscopic changes are more pronounced than the megascopic appearance would indicate.

The same components are formed as in andalusite; namely, mullite and interstitial glass; but these constituents have developed an entirely different structure and relationship to the original grain from that observed in the andalusite burns. They occur in irregular areas, each grain frequently containing several crystal areas. In any one of these areas the crystals may be parallel to each other but of decidedly different orientation from that of the other areas in the same grain. Adjacent areas interlock more or less with each other.

There is a very marked increase in volume at the dissociation point, much greater than that which takes place in andalusite.

SILLIMANITE—Sillimanite shows no change megascopically or microscopically, inclusive of cone 15. This is in complete accord with the observations of Bowen and Greig.

The volume change is not as great as in cyanite, but is greater than that of andalusite. Because no dissociation is observable microscopically, it seems probable that it is due in part to the formation of cracks produced by thermal expansion or to the associated minerals.

THE SIGNIFICANCE OF THE CHANGES

Monotropism and Ceramic Ware

It has been shown that the minerals of the sillimanite group break down at certain points with accompanying mineralogical and volume changes. This brings up a factor which is of extreme importance from the practical standpoint, that of monotropism and its relation to ceramic ware.

If minerals undergo change or inversion to a different crystalline substance of identical chemical composition when heated below their melting or disintegration points, the change may be of two kinds; that is, it may be a temporary or a permanent change. In the case of a temporary change, where the original crystalline condition returns when the mineral is cooled, it is referred to as enantiotropic. If the change is permanent, the mineral is said to be monotropic in its reaction toward heat. In either case the change may be rapid or slow, a quality inherent in the substance itself.

The Silica Minerals—A classic example of enantiotropism and one which has a distinct bearing on the ceramic industry is that of the mineral quartz.[22] When quartz is heated or cooled a number of crystalline forms (seven in all) may be produced, depending upon the temperature and time factors. The more important of these inversions may be conveniently expressed in the following table. The inversion from the α- to the β- form of the same mineral is usually rapid while the change from one mineral to another is much slower.

α-quartz $\rightleftarrows$ β-quartz	570-575°C, rapid
β-quartz $\rightleftarrows$ β_2-tridymite	870° , slow
β_2-tridymite $\rightleftarrows$ β-cristobalite	1470° , slow
β-cristobalite $\rightleftarrows$ glass	1710°

In the absence of a flux the change from β_2- tridymite to β-cristobalite is easier than that from β-quartz to β_2-tridymite; hence, we frequently find that β-quartz may invert to β-cristobalite without passing through the β_2-tridymite stage. This is what happens ordinarily in the original burning of silica bricks. The tridymite develops in them in large measure subsequent to, rather than before, the formation of cristobalite, under conditions of long continued heating at some temperature above 870°C and below 1470°C.[23] Moreover, the greatest expansion in silica bricks takes place when quartz inverts to one of the tridymite or cristobalite forms. Thus, although the silica minerals are enantiotropic, the reversion is so slow that once inversion has been accomplished to tridymite or cristobalite, the ware takes on practically a monotropic character.

THE SILLIMANITE GROUP MAY BE CONSIDERED AS ESSENTIALLY MONOTROPIC—As has been previously shown, when any of the members of the sillimanite group are subjected to heating to certain temperatures which vary with the different minerals, each one breaks up into two substances. One is artificial mullite of the composition $3Al_2O_3 \cdot 2SiO_2$. The other is a glass of a highly siliceous nature occurring as interstitial matter between the crystals. The crystalline substance formed in each case apparently has the same composition. This is also true of the glass. Strictly speaking, therefore, we cannot say that the members of the sillimanite group are monotropic in character because they break down and yield two substances differing in chemical composition from that of the original mineral. However, neither under conditions of slow or rapid cooling do these two compounds unite to form one compound having the properties of any member of the sillimanite group but they remain unchanged. Therefore, for all practical purposes, from the ceramic standpoint, the members of the sillimanite group may be considered as monotropic toward heat. Although consisting of two compounds, the end product is the same in all cases.

THE PRACTICAL SIGNIFICANCE OF THE CHANGES

THE IMPORTANCE OF MONOTROPISM IN CERAMIC WARE—One of the chief requirements of ceramic ware is that it must be monotropic, or practically so, toward heat. This is especially true in the case of refractories. If a ceramic body is not monotropic, the oscillation or alternation of conditions would cause variations in the physical properties of some or all of the constituents of the refractory or other body to meet those conditions. Thus, undue expansion or contraction may be produced by a change in mineralogical composition. Hence, the special monotropic character of the sillimanite group, after burning to the cones indicated, is particularly valuable to the ceramist.

THE IMPORTANCE OF VOLUME CHANGES—In this connection, also, the volume changes occurring in andalusite, cyanite, and sillimanite may be of as great significance as the actual mineralogical changes in the practical use of these minerals. Thus, if cyanite were used in a body, it would show a large and sudden expansion at cone 12 and great strains would be set up, accompanied by the production of cracks. The result of this would be a weak, porous, and "punky" body, as is the case of many silica bricks which have been fired too rapidly. In order to correct this, it would be necessary to calcine cyanite to at least cone 12 previous to its incorporation into a body mix, but this would involve additional expense. On the the other hand the interlocking character of the mullite crystals developed from cyanite indicates a structure possessing possibilities of superior mechanical strength, which might be worth the extra effort involved in its preparation.

Sillimanite shows a smaller expansion than cyanite up to cone 15 and would be subject to the same objections given for that mineral, but not to such a great extent. However, a much higher temperature (probably at least cone 20) would have to be used to convert it into mullite and glass.

In contrast to the behavior of cyanite and sillimanite, andalusite shows only a slight expansion up to cone 15 and its decomposition has been accomplished previous to this point; namely, at cone 13. It should be possible, therefore, to introduce it into a body in the raw state without subsequent production of strains. It would probably be advisable, however, to fire any body containing andalusite to above cone 13, if it is desired to convert it into mullite and to absorb incidental strains created at the decomposition point. Bowen and Greig have suggested that owing to the regular structure developed in the breakdown of natural sillimanite where the crystalline phase is external, a body using sillimanite may be mechanically stronger than one using the artificial 1:1 Al_2O_3-SiO_2 mixture where the resulting external phase is liquid. This may also hold good in the case of andalusite; namely, that bodies in which it has been used might be stronger mechanically than those using the artificial 1:1 mixture.

Thus, from the standpoint of changes in volume produced by firing, and the development of artificial mullite, andalusite is the most desirable of the three minerals for use in ceramic ware.

CONCLUSIONS

1. Andalusite and cyanite dissociate at high temperatures into mullite and a siliceous glass, both products being the same in optical properties and chemical composition as those resulting from the breakdown of sillimanite as described by Bowen and Greig.

2. Andalusite dissociates at about cone 13, (approximately 1390°C), and cyanite at about cone 12 (approximately 1370°C). The breakdown in each case is sharp and only extends over a small range in temperature.

3. The microstructures developed in andalusite and cyanite below cone 15 are entirely different and characteristic.

4. Andalusite shows only a slight change in volume at its dissociation point, practically no disintegration or expansion being noticeable even in large fragments. Hence, it may be introduced into a body without previous calcination.

5. Cyanite shows a great increase in volume at its dissociation point accompanied by marked disintegration. This is so pronounced that unless calcined at a minimum of at least cones 12 or 13 previous to its introduction into a body, a weak and porous product would result.

6. Due to the interlocking structure of the crystal areas produced in the breakdown of cyanite, it is possible that cyanite might give a stronger body mechanically than one of the same composition made by using andalusite. Previous calcination however, would be necessary.

7. Sillimanite can probably be introduced directly into a body with but little disturbance up to cone 20, but in order to convert it into mullite it would be necessary to fire it higher than cone 20. Furthermore, it would be necessary to fire such a body to a still higher temperature in order to produce one of constant volume.

8. Unless cyanite has been previously calcined, andalusite and sillimanite are more desirable because of the great expansion of cyanite at its decomposition point.

9. Between cones 13 and 15, andalusite should be given preference over sillimanite because decomposition has been accomplished and equilibrium established at cone 13.

10. Finally, the value of andalusite lies (a) in its dissociation point being at a moderate temperature; (b) in the refractoriness of the products of decomposition; (c) in the possibilities of great mechanical strength developed by the structure formed in dissociation; and (d) in its lack of decided volume change at dissociation.

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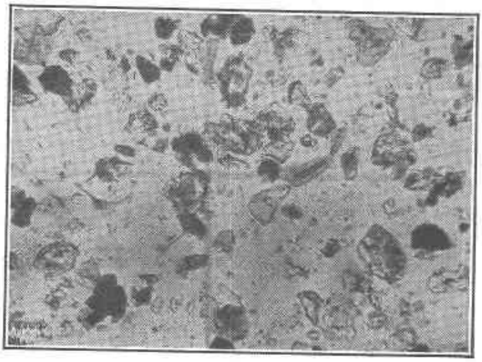

Fig. 1. Andalusite, cone 12. Note the clear unaltered grains. The black grains are mica which has decomposed. Magnification 90.

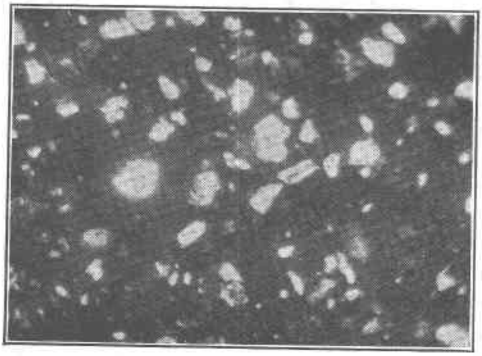

Fig. 2. Same field as Fig. 1 taken with crossed nicols. Note the strong double refraction of the andalusite.

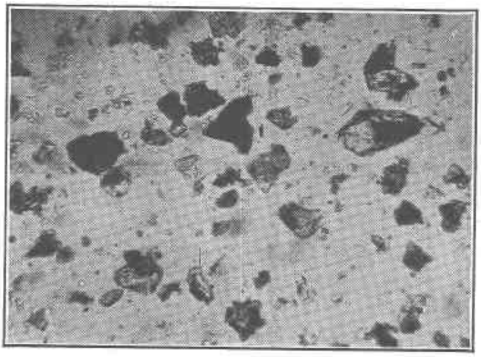

Fig. 3. Andalusite, cone 13. Note that many of the grains are clouded and have a somewhat fibrous appearance due to decomposition with the formation of fibrous crystals of mullite with interstitial glass. Magnification 90.

Fig. 4. Andalusite, cone 13. The grain in the center of the preceding photograph magnified to 315 times, showing the detail of the parallel fibers of mullite extending across the grain.

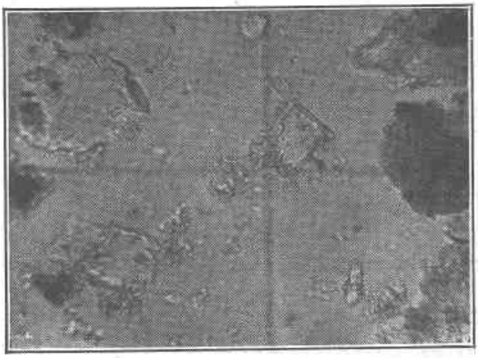

Fig. 5. Andalusite, cone 13. Showing a grain having decomposed border of fibrous crystals and glass, with a clear unaltered center. Magnification 315.

Fig. 6. Same field as Fig. 5 taken with crossed nicols. Note the strong double refraction of the unchanged center and weaker double refraction of the fibrous border.

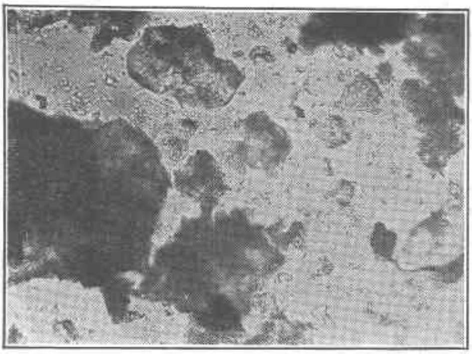

Fig. 7. Andalusite, cone 14. Showing all grains to be decomposed to aggregates of parallel fibers as contrasted to the partial decomposition of some of the grains in the cone 13 burn, Fig. 3. Magnification 165.

Fig. 8. Cyanite, cone 10. Note the clear undecomposed grains and cleavage cracks. The black grains are mica as in [Fig. 1. Magnification 90.

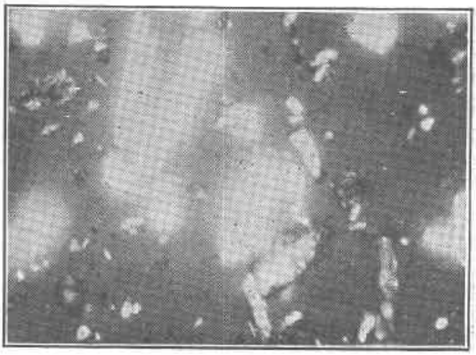

Fig. 9. Same field as Fig. 8, showing the strong double refraction of cyanite.

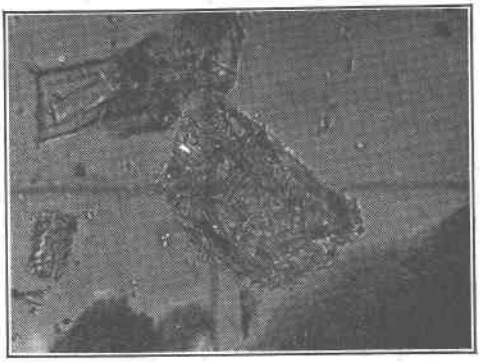

Fig. 10. Cyanite, cone 12. Showing at high magnification the intimate detail of a grain of decomposed cyanite. Note that the fibrous crystals are not parallel as compared to those in decomposed andalusite (Figs. 3 and 4), but are intricately interlocked. The clear grain is quartz. Magnification 315.

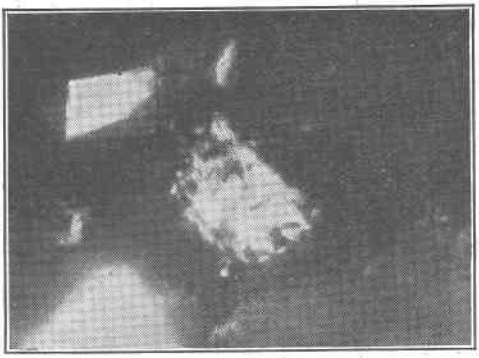

Fig. 11. Same field as Fig. 10 taken with crossed nicols. Note the mottled appearance of the large grain in the center, due to variously oriented groups of fibers. Some are in extinction, while others are light.

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