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# THERMAL ANALYSIS AND *X*-RAY STUDIES OF SAUCONITE AND OF SOME ZINC MINERALS OF THE SAME PARAGENETIC ASSOCIATION*

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## Abstract

Sauconite is the name given to the zinc-rich members of the montmorillonite group. This paper presents the results of a differential thermal analysis study of these clays. In addition, differential thermal analysis studies are reported on a base-exchanged sauconite. Differential thermal analysis curves are given for the discredited mixtures vanuxemite and moresnetite.

*X*-ray powder data are given for the various specimens of sauconite. The products formed in the differential thermal analysis studies were identified by means of *x*-ray methods. Polymorphism was observed in zinc orthosilicate.

Differential thermal analysis of hemimorphite confirmed and extended the views of Zambonini.

* Publication authorized by the Director, Geological Survey.

## INTRODUCTION

The name sauconite was given by Roepper to a clay mineral rich in zinc found at the Uberroth Mine, near Friedensville, in the Saucon Valley of Pennsylvania. The analyses of the mineral together with a mineralogical description appeared in Genth's (1875) Mineralogy of Pennsylvania. In 1946, C. S. Ross in connection with his studies of the clay minerals restudied the type sauconite of Roepper and proved the validity of the species and showed that this mineral is a member of the montmorillonite group and is particularly related to the saponites, the magnesium-rich member. In sauconite, zinc takes the place of magnesium in the octahedral positions in the crystal structure. This is illustrated by the formula of the saponite from Cathkin Hills, Scotland

$$(\mathrm{Mg}_{2.30}\mathrm{Fe}^{+3}{}_{.45}\mathrm{Fe}^{+2}{}_{.25})(\mathrm{Al}_{.80}\mathrm{Si}_{3.20})\mathrm{O}_{10}(\mathrm{OH})_2\left(\frac{\mathrm{Ca}}{2}\right)_{.24}$$

and the sauconite from the New Discovery Mine, Leadville, Colorado

$$(\mathrm{Zn}_{2.40}\mathrm{Mg}_{.18}\mathrm{Al}_{.22}\mathrm{Fe}^{+3}{}_{.17})(\mathrm{Al}_{.53}\mathrm{Si}_{3.47})\mathrm{O}_{10}(\mathrm{OH})_2\left(\frac{\mathrm{Ca}}{2}\right)_{.23}\mathrm{Na}_{.09}$$

This paper is an additional study of this group of minerals and contains some data on the minerals belonging to the same paragenetic associations.

## DESCRIPTIONS AND CHEMICAL ANALYSES OF THE SPECIMENS STUDIED

The thermal analysis studies were made on fractions prepared by Dr. Ross in connection with the earlier study. The *x*-ray work was made on portions selected from the original samples. Sauconite no. 7 was selected from a sample submitted by Dr. A. C. Spencer of Washington, D. C.

The samples used were prepared by selecting pure fragments of the minerals, crushing them gently so as to produce a minimum of fines and selecting under a binocular microscope, so as to obtain only the purest grains. The samples thus obtained were then crushed to pass a 58 mesh cloth sieve and the resulting particles were re-examined for impurities.

*Sauconite No. 1* Locality: Coon Hollow Mine, about three-fourths of a mile north of the village of Zinc, Boone County, Arkansas. White porous layers in reddish brown sauconite. Analysis 1, table 1.

*Sauconite No. 2* Locality: Same as sauconite No. 1. Reddish brown masses. Analysis 2, table 1.

*Sauconite No. 3* Locality: New Discovery Mine, Leadville, Colorado. Massive brown material. Analysis 3, table 1.

*Sauconite No. 4* Locality: Yankee Doodle Mine, Leadville, Colorado. Mottled brownish yellow masses. Analysis 4, table 1.

*Sauconite No. 5* Locality: Liberty Mine, near Meekers Grove, Plattesville District, Wisconsin. Brown masses. Analysis 5, table 1.

*Sauconite No. 6* Locality: Uberroth Mine, one-half mile N.N.W. of Friedensville, Saucon

Valley, Northampton County, Pennsylvania. Pale brownish yellow masses. Roepper's original material. Analysis 6, table 1.

*Sauconite No. 7* Locality: Same as sauconite No. 6. Yellowish white mass. Unanalyzed.

*Sauconite No. 8* Locality: Liberty Mine, near Meekers Grove, Plattesville District, Wisconsin. Dark brown masses. Analysis 8, table 1.

*Smithsonite* Locality: Kelly Mine, Magdalena, Socorro County, New Mexico. Yellow botryoidal masses. Analyzed by W. T. Schaller and J. G. Fairchild (1938) and found to contain 0.57% Cd, 0.34% MnO, 1.56% FeO, tr. PbO, insol. in HCl = 0.02%.

*Hemimorphite* Locality: Sterling Hill Mine, Ogdensburg, Sussex County, New Jersey. Crystals selected from a mass consisting of radiating crystals.

*Saponite* Locality: Cathkin, Carmunnock Parish, County Lanarkshire, Scotland. (Sometimes given as S.S.E. of Glasgow.) Greenish brown masses. Analysis 9, table 1.

Table 1 contains the chemical analyses reported by Ross (1946) which is included here for the convenience of the reader. The analyses of the sauconites and of the saponite from Scotland were made in the Geochemistry and Petrology Branch of the U. S. Geological Survey. The sauconite analyses are arranged according to decreasing zinc oxide content, sauconite No. 1 being richest in this constituent.

Sulfur was determined on sauconite No. 4, from the Yankee Doodle Mine, Colorado, and on sauconite No. 6, from Friedensville, Pennsyl-

TABLE 1. CHEMICAL ANALYSES OF THE SAUCONITES AND A SAPONITE

| Number | 1 | 2 | 3 | 4 | 5 | 6 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| Mineral | Sauconite #1 | Sauconite #2 | Sauconite #3 | Sauconite #4 | Sauconite #5 | Sauconite #6 | Sauconite #8 | Saponite #9 |
| Locality | Coon Hollow Mine, Ark. White | Coon Hollow Mine, Ark. Brown | New Discovery Mine, Leadville, Colo. | Yankee Doodle Mine, Leadville, Colo. | Liberty Mine, Meekers Grove, Plattesville district, Wis. | Uberroth Mine, Friedensville, Pa. | Liberty Mine, Meekers Grove, Plattesville district, Wis. | Cathkin, County Lanarkshire, Scotland |
| $SiO_2$ | 33.59 | 33.40 | 35.95 | 37.10 | 38.59 | 34.46 | 38.70 | 40.16 |
| $Al_2O_3$ | 6.01 | 7.45 | 6.57 | 14.18 | 13.36 | 16.95 | 16.29 | 8.03 |
| $Fe_2O_3$ | .28 | 1.73 | 2.36 | .30 | 3.41 | 6.21 | 3.91 | 8.50 |
| FeO | | | | | | | | 3.83 |
| MgO | .70 | .78 | 1.26 | 1.10 | 1.18 | 1.11 | 1.62 | 19.40 |
| MnO | .12 | tr. | .04 | .02 | | | .06 | |
| ZnO | 39.33 | 36.73 | 33.70 | 28.19 | 23.50 | 23.10 | 22.48 | |
| CaO | 1.90 | 1.92 | .62 | 1.22 | .94 | | tr. | 1.91 |
| $Na_2O$ | .13 | .22 | .44 | .24 | .01 | | .43 | |
| $K_2O$ | .07 | .27 | .10 | .13 | .18 | .49 | .32 | |
| CuO | .10 | .13 | | .02 | | | | |
| $TiO_2$ | .03 | .15 | .07 | tr. | .31 | .24 | .30 | |
| $H_2O-$ | 10.68 | 9.78 | 11.34 | 8.82 | 10.39 | 6.72 | 7.50 | 11.15 |
| $H_2O+$ | 6.98 | 7.14 | 7.24 | 8.90 | 8.05 | 10.67 | 8.38 | 7.60 |
| $\Sigma$ | 99.92 | 99.70 | 99.69 | 100.22 | 99.92 | 99.95 | 99.99 | 100.58 |

Analysts: 1. M. K. Carron, 2. M. K. Carron, 3. J. G. Fairchild, 4. M. K. Carron, 5. M. K. Carron, 6. J. G. Fairchild, 8. S. H. Cress, 9. L. T. Richardson.

vania, by J. J. Fahey and found to be absent. These two samples were selected for this determination because their $x$-ray powder patterns contain the greatest number of lines.

All seven of the sauconites were $x$-rayed and the patterns were examined and the absence of sphalerite, wurtzite, smithsonite, and hemimorphite established.

## THERMAL ANALYSIS

### (a) *Differential thermal analysis of the sauconites*

The equipment and technique used in this laboratory in differential thermal analysis studies, together with pertinent references to the literature, are given by Faust (1948) and (1950). The samples were heated at the rate of approximately 10° to 12° C. per minute. The records were obtained as photographs.

The differential thermal analysis curves for a saponite from Scotland and for four sauconites are shown in Fig. 1 and the data, taken from these curves, are summarized in Table 2. These curves show that sauconite is closely related to saponite and all are members of the montmorillonite group. All of these curves exhibit the characteristic double breaks, in the temperature range of 150° to 290° C. of montmorillonite—Alexander, Hendricks and Nelson (1939); Grim and Rowland (1942). This double break is almost always present in the curves for the natural, untreated, members of the montmorillonite group. These breaks arise from the absorption of the heat necessary to expel the adsorbed and interlayer water (water between the basal planes in the montmorillonite structure). This interlayer water is associated with the swelling of the montmorillonite. The loss of essential, or hydroxyl, water is represented by the endothermic breaks taking place above 400° C. and its culmination is reached in the last endothermic break in the temperature range of 680°–735° C., where the sauconite structure is completely destroyed and new phases appear. The break in curve C-81 at 601° C. and the break in curve C-567 at 569° C. represent the decomposition of the halloysite, present as an admixture in the samples.

Some montmorillonites show an exothermic break above 900° C.—Alexander, Hendricks and Nelson (1939, p. 265). Grim and Rowland (1942, p. 757) have suggested that the exothermic reaction is closely related to the amount of iron present in the mineral. The greater the iron content the lower the temperature of the exothermic reaction. They associate this break with the formation of a spinel. The saponite from Scotland, shown in Fig. 1, does not show any high temperature exothermic reaction. It contains 8.50% $Fe_2O_3$ and 3.83% FeO. A possible explanation of its absence may be that the double endothermic breaks at

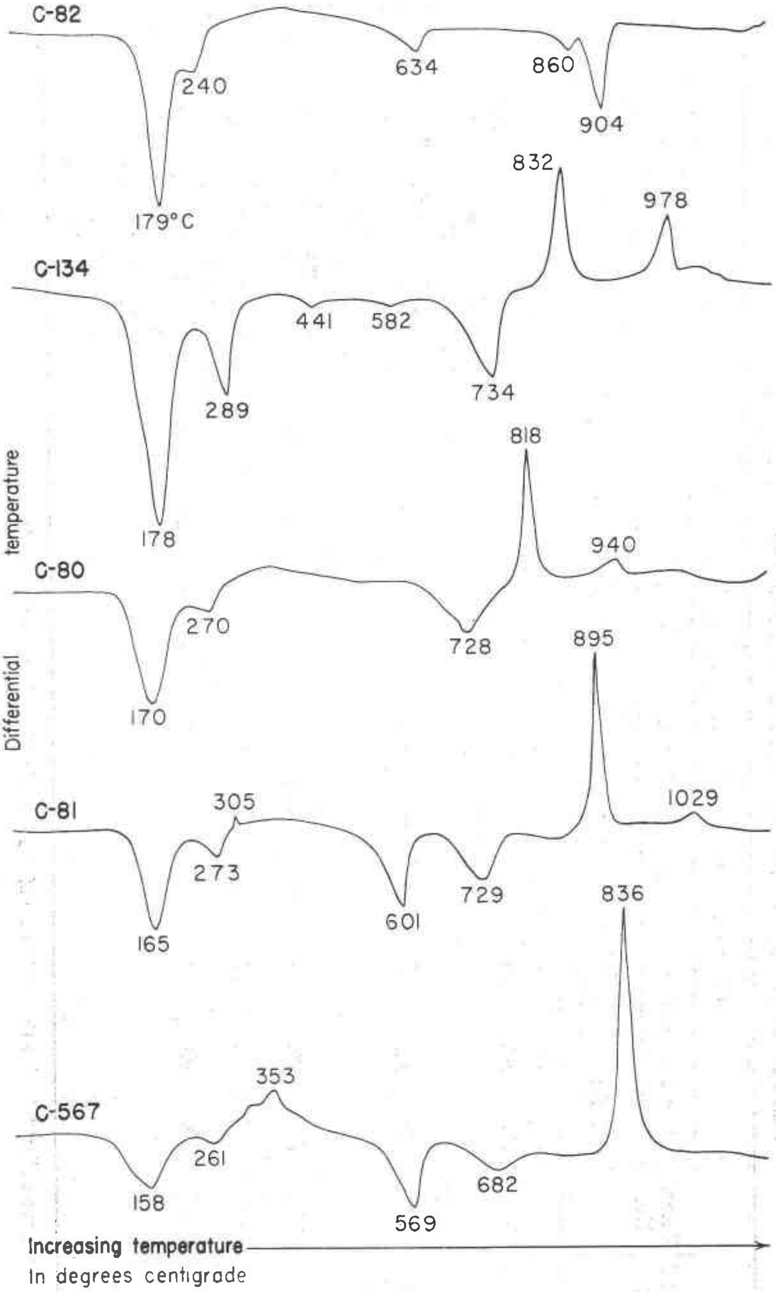

FIG. 1. Differential thermal analysis curves for sauconites and saponite. C-82 = saponite, C-134 = sauconite #2, C-80 = sauconite #3, C-81 = sauconite #4, C-567 = sauconite #6. The temperature where the curves begin, on the left, is about 25° C. the temperature of the termination of the curves, on the right, is about 1000° C.

Table 2. Observations on the Thermal Analysis Curves[1] of Saponite and Sauconite

| Mineral (ZnO content) | Record No. | Temperature of breaks in curves (Knickpunkt) | | | | | | | | | | Locality | Weight of sample used |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Low Temperature | | | Intermediate Temp. | | | High Temperature | | | | | |
| | | Endothermic | | Exothermic | Endothermic | | | Endothermic | | Exothermic | | | |
| | | ° C. | ° C. | ° C. | ° C. | ° C. | ° C. | ° C. | ° C. | ° C. | ° C. | | |
| Saponite | C-82 | 179 | 240 | — | — | 634 | — | 860 | 904 | — | — | Cathkin, Carmunnock Parish, Lanarkshire County, Scotland (S.S.E. of Glasgow). | 0.5290 grams |
| Sauconite #2 (ZnO=36.73) | C-154 | 178 | 289 | — | 441 | 582 | 734 | — | — | 832 | 978 | Coon Hollow Mine, 0.75 mile north of Zinc, Boone County, Ark. (Brown variety). | 0.5562 |
| Sauconite #3 (ZnO=33.70) | C-80 | 170 | 270 | — | — | Present | 728 | — | — | 818 | 940 | New Discovery Mine, Leadville, Colorado. | 0.4951 |
| Sauconite #4 (ZnO=28.19) | C-81 | 165 | 273 | 305 | — | 601 | 729 | — | — | 895 | 1029 | Yankee Doodle Mine, Leadville, Colorado. | 0.5082 |
| Sauconite #6 (ZnO=23.10) | C-567 | 158 | 261 | 353 | — | 569 | 682 | — | — | 836 | — | Uberroth Mine, Saucon Valley, 0.5 mile N.N.W. of Friedensville, Penna. (Roepper's material-Lehigh). | 0.3343 |

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[1] These curves were all obtained with a resistance of 600 ohms in the galvanometer circuit.

832°–978° C. represent an algebraic addition of the thermal effects accompanying the endothermic reaction associated with the breakdown of the saponite structure and the exothermic reactions involved in the crystallization of spinel.

All of the sauconites show a sharp exothermic break above 800° C. and some show a subsequent break of much lesser magnitude. The probable interpretation of these breaks will be considered in the discussion of the *x*-ray study of the decomposed materials.

The sauconites are arranged in Table 2 from top to bottom, in order of their decreasing content of ZnO. The data in this table suggest that the temperature at which the "low temperature" water is lost, is higher for the zinc-rich clays. Likewise the last well-defined endothermic break in the temperature range of 680°–735° C. takes place at higher temperatures for the zinc-rich sauconites.

### (*b*) *Differential thermal analysis of a base-exchanged sauconite*

Hendricks, Nelson and Alexander (1940) studied the hydration mechanism of montmorillonite. In this research they showed that the character of the base-exchanged ions affected the shape of the double break which occurs at low temperatures, in the differential thermal analysis pattern. They investigated montmorillonites saturated with $Li^+$, $Na^+$, $K^+$, $Cs^+$, $Mg^{++}$, $Ca^{++}$, $Sr^{++}$, $Ba^{++}$ and $H^+$.

Caillére and Henin (1944) also examined the differential thermal analysis curves of base-exchanged montmorillonites and made observations on the changes in the character of the three principal breaks. They noted the presence of an exothermic break above 850° C.

The modification of the double break of sauconite, associated with the loss of water at low temperatures, was investigated for $H^+$, $Na^+$ and $Ca^{++}$ on the brown variety of sauconite from the Coon Hollow Mine, Arkansas. These results are shown in Fig. 2 and the data are summarized in Table 3.

TABLE 3. OBSERVATIONS ON THE THERMAL ANALYSIS CURVES[1] OF NATURAL AND BASE-EXCHANGED SAUCONITE FROM THE COON HOLLOW MINE, ARKANSAS (NO. 2)

| Description of the material | Record No. | Temperature of breaks in curves (Knickpunkt) | | | | | | | | Weight of sample used |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Low Temperature Endothermic | | Intermediate Temperature Endothermic | | | High Temperature Exothermic | | | |
| | | °C. | °C. | °C. | °C. | °C. | °C. | °C. | °C. | gms. |
| Natural, untreated mineral | C-134 | 178 | 289 | 441 | 582 | 734 | 832 | 978 | — | 0.5562 |
| Ca-Na-Sauconite | C-211 | 170 | 271 | 437 | 573 | 719 | 807 | 949 | — | 0.5941 |
| Na-Sauconite | C-222 | 162 | 210 | 459 | — | 724 | — | — | 985 | 0.6480 |
| H-Sauconite | C-209 | 159 | — | — | — | 701 | 827 | 915 | 954 | 0.5024 |

[1] These curves were all obtained with a resistance of 600 ohms in the galvanometer circuit.

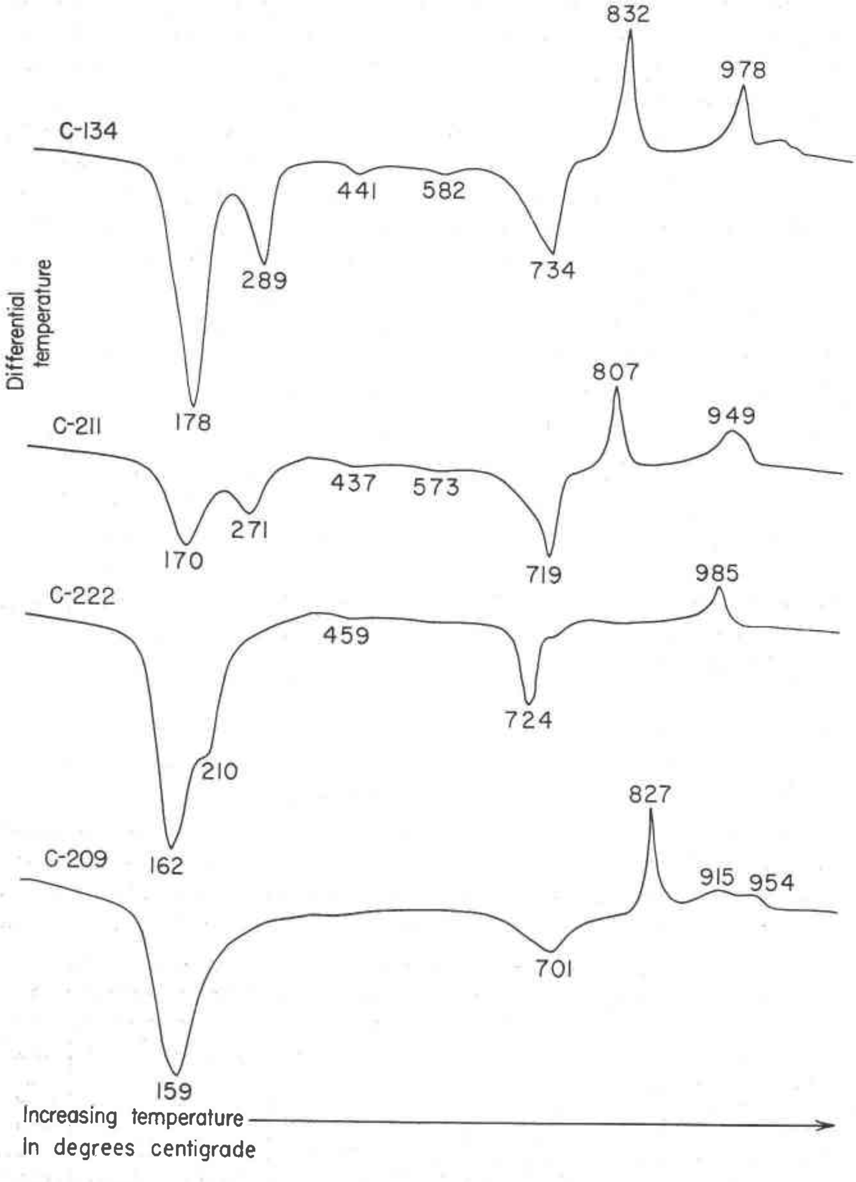


FIG. 2. Differential thermal analysis curves for sauconite #2, from Coon Hollow Mine, Arkansas. C-134=natural, untreated mineral; C-211=calcium-sodium sauconite; C-222=sodium sauconite; C-209=hydrogen sauconite.

The base-exchanged samples were analyzed for alkalies by W. W. Brannock using the flame photometer and his results are given in Table 4. These alkali determinations show that the small original quantity of $K_2O$ has not been displaced by the base-exchange experiments; the value for all samples being about 0.18%. Apparently these potassium atoms are located in sites, in the sheets, where they are held more tenaciously than that portion of the potassium which may be base-exchanged. Another possible explanation is that there are some "mixed-layers" present in the sauconite structure, the non-base exchangeable $K^+$ ions being in mica sheets.

The sodium-exchanged sauconite was prepared by treating the natural zinc clay, which is calcium saturated, with a sodium chloride solution. The calcium-exchanged sauconite was prepared by treating the sodium-exchanged sauconite with a calcium chloride solution. The chemical data in Table 4 show that the latter exchange failed to go to completion due to some mechanical difficulty, as incomplete dispersion of the clay.

TABLE 4. PARTIAL CHEMICAL ANALYSIS OF THE BROWN SAUCONITE FROM THE COON HOLLOW MINE, BOONE COUNTY, ARKANSAS

| Description of the material | $K_2O$[1] | $Na_2O$[2] | CaO |
|---|---|---|---|
| Natural Sauconite | 0.18% | 0.03% | 1.92%[3] |
| Ca-Na-Sauconite | 0.17 | 0.55 | 1.62[4] |
| Na-Sauconite | 0.16 | 1.99 | |
| H-Sauconite | 0.20 | 0.04 | |

[1,2] Analyst, W. W. Brannock.
[3] Analyst, M. K. Carron.
[4] Analyst, T. Woodward.

A study of the data in Table 3 and an examination of Fig. 2 show that this base-exchange treatment of the natural sauconite results in a modification of the double break occurring at low temperatures. The calcium-saturated sauconite shows two well-defined and clearly separate breaks. In the sodium-saturated clay the second break has lost its individual character and is represented by an inflection on the high-temperature side of the break. The hydrogen-exchanged sauconite has only one break. The low-temperature breaks, in the differential thermal curves, appear at lower temperatures for the base-exchanged sauconites than for the corresponding natural, untreated, sauconite.

These results may be explained as follows: when sauconite is dispersed in water and base-exchanged the crystal structure is so modified that the forces acting on the interlayer water are weakened resulting in the easier removal of the interlayer water at lower temperatures (Auflockern and Gitterlockern of some German authors).

### (*c*) *Differential thermal analysis of the discredited mixtures, moresnetite and vanuxemite*

Moresnetite was described by Risse (1895) from the lead mines at Altenberg, near Moresnet, and Aachen in Germany. Kenngott (1868, p. 153) later claimed that moresnetite was a mixture of hemimorphite and clay. Ross (1946) re-examined moresnetite microscopically and found a light gray to dark blue-gray zinc mineral associated with a brown material made up of micas and chlorite, and with fine-grained masses of hemimorphite.

The differential thermal analysis curve of moresnetite shown in Fig. 3, Curve C-258, was made on 0.7397 gram of the material. The curve is obviously that of a mixture of minerals. The low-temperature double breaks suggest very strongly that sauconite is part of the mixture. The *x*-ray powder photograph of this material established the presence of sauconite in the mixture.

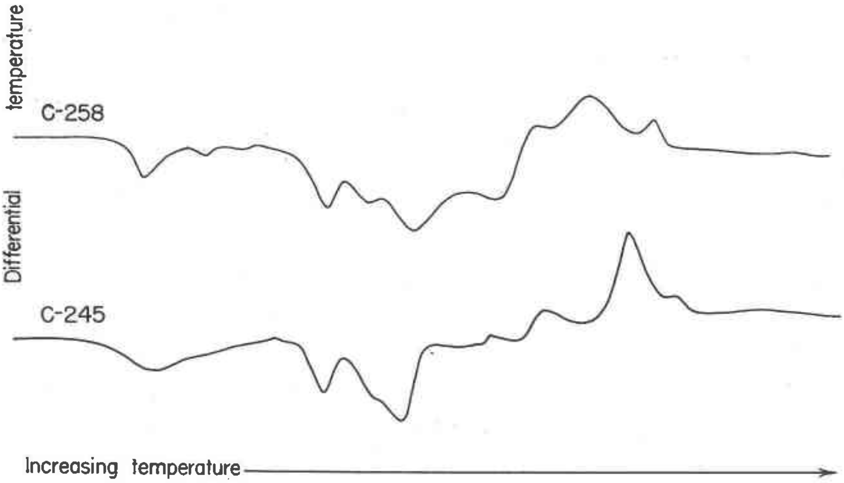


FIG. 3. Differential thermal analysis curves for the discredited mixtures moresnetite and vanuxemite Curve C-258 = Moresnetite, Altenberg, Aachen, Germany; C-245 = vanuxemite, Sterling Hill, Sussex County, New Jersey. Resistance in the galvanometer circuit is 600 ohms.

Vanuxemite was described by Shepard (1876) from Sterling Hill, Sussex County, New Jersey, as a new mineral. Cross (1877) claimed, on the basis of a chemical analysis, that vanuxemite was a mixture of equal parts of hemimorphite and halloysite. Ross (1946) on the basis of an optical study of the type material found it to be a mixture of several minerals.

The differential thermal analysis curve, C-245, Fig. 3, confirms the conclusion that this substance is a mixture of several minerals.

### (*d*) *Differential thermal analysis of smithsonite and hemimorphite*

In the study of the various specimens of sauconite it was necessary to prove the absence of smithsonite and hemimorphite in the purified fractions. This was checked by differential thermal analysis and *x*-ray methods.

### *Smithsonite*

A differential thermal analysis curve of a yellow smithsonite, $ZnCO_3$, containing 0.57% Cd, from the Kelly Mine, Magdalena district, New Mexico, is shown in Fig. 4. The curve, C-85, was obtained using 1.0113 grams of the mineral. The resistance in the galvanometer circuit was 999.9 ohms. The temperature of the break is 590° C. The dissociation of zinc carbonate yields zinc oxide as the solid phase and carbon dioxide is

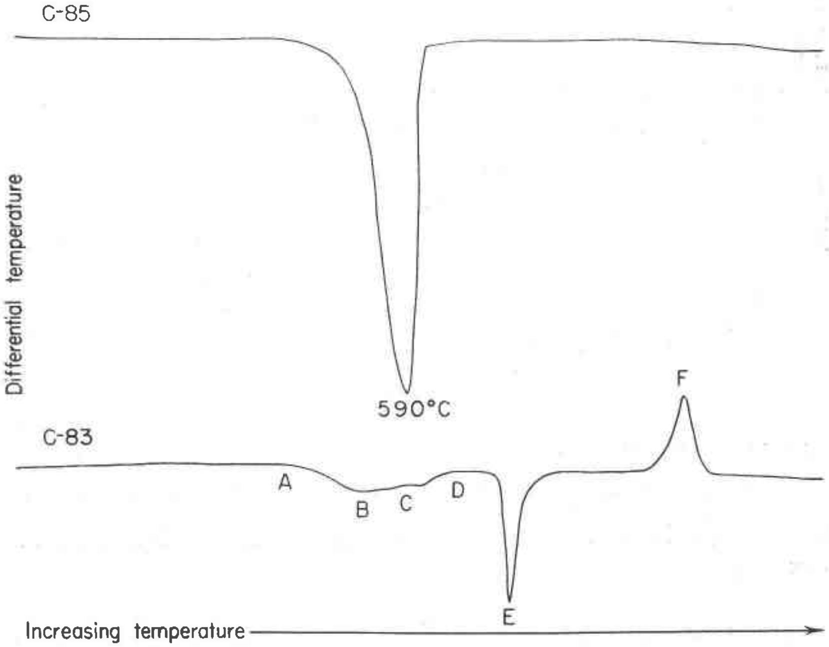


FIG. 4. Differential thermal analysis curve for smithsonite, Kelly Mine, New Mexico, C-85, and for hemimorphite, Sterling Hill, New Jersey, C-83.

lost to the atmosphere. *X*-ray examination shows the dissociated sample to consist of zincite (ZnO).

### *Hemimorphite*

A differential thermal analysis study of hemimorphite is of considerable interest for it confirms and extends the earlier views of Zambonini (1908). Zambonini found that when hemimorphite was heated to 480° C. it lost one-half of its water and remained transparent. The remaining one-half of its water was lost at higher temperatures. A study of the crystal structure of hemimorphite by Ito and West (1932) confirmed this conclusion and they assigned the formula $(OH)_2Zn_4Si_2O_7 \cdot H_2O$.

The differential thermal analysis curve, C-83 in Fig. 4, furnishes a clear-cut demonstration of the process of dehydration of hemimorphite. The "low-temperature" water is lost more or less continuously over a span of temperatures (393°–657° C.). See Table 5. This water is represented by the $H_2O$ molecules in the structure. According to Ito and West (1932) the water molecules are loosely held in the structure and are located on the digonal rotation axis. These water molecules can be removed without destroying the crystal structure.

TABLE 5. OBSERVATIONS ON THE DIFFERENTIAL THERMAL CURVE OF HEMIMORPHITE

| Letter on curve C-83, Fig. 4 | Temperature | Observations |
|---|---|---|
| | °C. | |
| A | 393 | Beginning of loss of "low temperature" water |
| B | 526 | Temperature of first maximum on curve |
| C | 612 | Beginning of secondary shoulder |
| D | 657 | Completion of the loss of "low temperature" water |
| E | 740 | Loss of the "high temperature" water |
| F | 971 | Transformation into willemite |

The "high-temperature" water is tied up in the hydroxyl groups and it is necessary to disrupt the crystal structure completely to free this water. Each hydroxyl group is shared by two zinc atoms and is firmly bound in the structure. The steepness of the break on the low-temperature side shows that the destruction of the crystal structure, with the expulsion of the hydroxyl, took place promptly. The break is narrow, and its maximum appears at 740° C. The high-temperature side of the break is spread out to about 790° C., and heat was being consumed in the process over this range of temperature. Thereafter, the curve is essentially flat until the appearance of the exothermic break at approximately 915° C., an interval of about 125°. The temperature of the maximum point on the exothermic break is 971° C. This exothermic break is spread out on both the low and high-temperature sides of the maximum.

In order to interpret the origin of the exothermic break at 971° C. it became necessary to study the polymorphism of $Zn_2SiO_4$. A brief review is given here of the polymorphism of $Zn_2SiO_4$, summarized from Ingerson, Morey and Tuttle (1948). Schleede and Gruhl (1923) observed that the rate of cooling of a melt of Mn-activated $Zn_2SiO_4$ determined the color of its fluorescence. Melts cooled slowly gave a green fluorescence, melts cooled rapidly gave a yellow fluorescence while melts that were suddenly chilled gave a red fluorescence. They also observed that the yellow and red-fluorescing polymorphs changed to the green-fluorescing willemite when heated to 900° C.

Leverenz and Seitz (1939) designated the green, yellow and red-fluorescing polymorphic forms as $\alpha$-, $\beta$-, and $\gamma$-$Zn_2SiO_4$, respectively. They found that the $\beta$-form inverts to the $\alpha$-form when heated at 900° C., and that the $\gamma$-form inverts to the $\alpha$-form as low as 300°–400° C. The $\alpha$-form of $Zn_2SiO_4$ corresponds to the mineral willemite.

Ingerson, Morey and Tuttle (1948) studied the transformation of the various polymorphic forms of $Zn_2SiO_4$. They state:

> When $\gamma$-$Zn_2SiO_4$ is heated it changes first to $\beta$-$Zn_2SiO_4$ and then to $\alpha$-$Zn_2SiO_4$. Longer heating is required to effect complete transformation at lower temperatures. For example, at 900° C. the $\gamma$-form goes to $\beta$- in 5 minutes, but at 950° C. for the same time $\gamma$- goes to $\alpha$-. If $\gamma$- is heated to 1000° C. for 1 minute it is transformed to $\beta$-. After 2 minutes both $\alpha$- and $\beta$- are present, whereas in 3 minutes transformation to $\alpha$- is complete. A cooling rate intermediate between the chilling to $\gamma$- and the slow cooling, which always produces alpha, sometimes gives rise directly to the $\beta$-form.

The study of the polymorphism of $Zn_2SiO_4$ required for this research was greatly facilitated by Dr. Ingerson who very kindly supplied me with several specimens of $Zn_2SiO_4$ which he had prepared in connection with the above-mentioned studies. These samples formed the standards adopted here. Dr. J. F. Schairer of the Geophysical Laboratory kindly inverted a sample of willemite into a mixture of the various polymorphs.

Powder diffraction data were obtained from a sample showing a strong yellow fluorescence, considered here to be the $\beta$-form, and from a substance with yellowish-pink fluorescence, considered here to be the $\gamma$-form. One specimen with a reddish fluorescence gave an *x*-ray pattern having only a few diffuse lines.

A sample of hemimorphite was heated in the differential thermal analysis apparatus to a temperature of 761° C., the furnace was then pulled away from the sample support, and the dissociated material was allowed to cool down to room temperature. The record of the thermal behavior of this dissociated material is shown in Fig. 5. A fluorescent lamp

(Mineralight) was held above the cooling material to observe the character of the fluorescence. The results of the fluorescence test on the hot material were not convincing. The cold material exhibited a pale pinkish fluorescence. It should, however, be emphasized that this product was not activated by manganese.

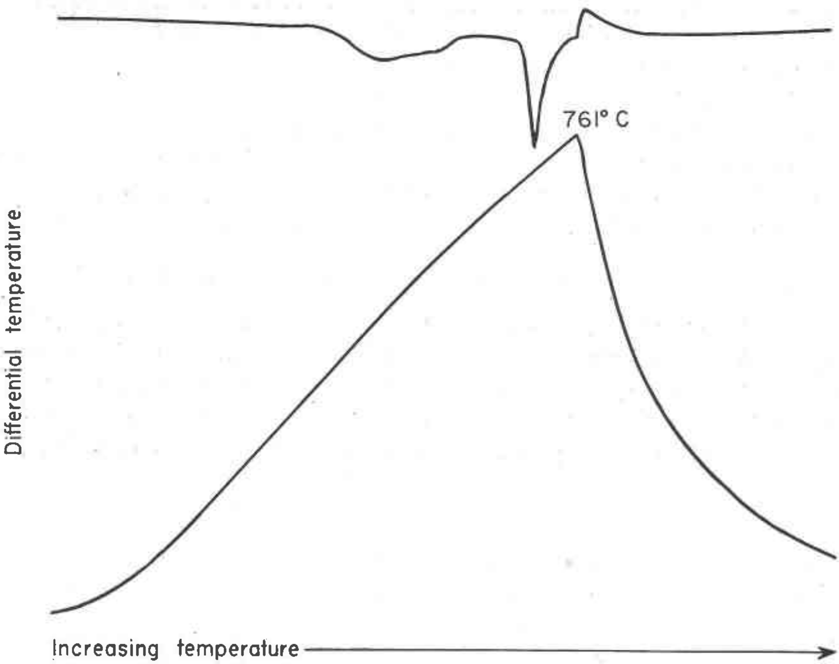


FIG. 5. Differential thermal analysis curve of a sample of hemimorphite from Sterling Hill, New Jersey, C-642, which was heated to 761° C. and then cooled down by removing the furnace.

The thermal behavior of the substance on cooling from 761° C. to nearly room temperature is shown in curve C-642, Fig. 5. A comparison of this figure with curve C-83 in Fig. 4 shows the appearance in curve C-642 of an exothermic reaction beginning at 761° C., which occurred as soon as the sample was cooled, whereas such a break in the curve does not appear in curve C-83. In addition curve C-642 does not show the exothermic break at 971° C. exhibited in curve C-83.

*X*-ray powder diffraction data obtained from these materials show that the hemimorphite heated to 761° C. consists of the $\beta$-form of zinc silicate, as defined by Ingerson, Morey and Tuttle (1948). The sample of hemimorphite heated to about 1100° C. consists of willemite, the $\alpha$-form of zinc silicate. From these data we may conclude that the exothermic break at 971° C. represents the transformation of some polymorphic form of zinc silicate to the $\alpha$-form, willemite.

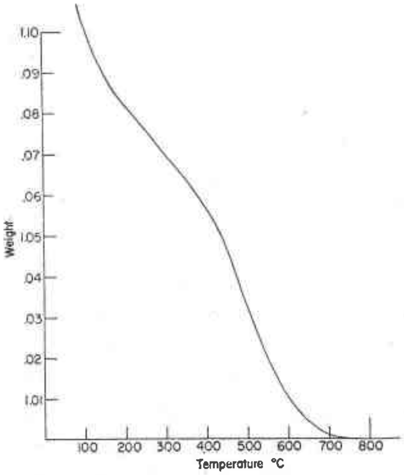
The appearance of the exothermic reaction at 761° C. in curve C-642 suggests that the form of zinc silicate produced in the dissociation of hemimorphite at 740° C. is the $\gamma$-form and that the sudden cooling brought about the transformation of the $\gamma$-$Zn_2SiO_4$ to the $\beta$-$Zn_2SiO_4$. The area of this exothermic break thus is a measure of the heat of transformation of $\gamma$-$Zn_2SiO_4$ to $\beta$-$Zn_2SiO_4$.

These conclusions are in accord with the observations of Ingerson, Morey and Tuttle (1948) mentioned earlier in this discussion.

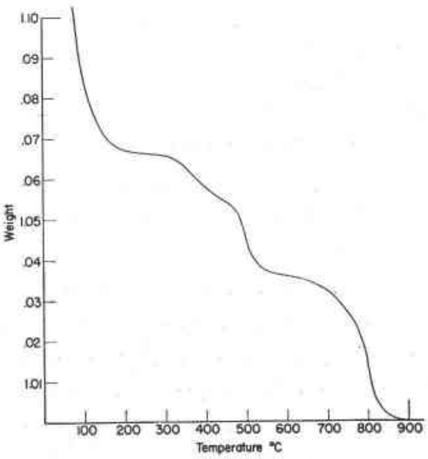
The *x*-ray powder diffraction data of the various polymorphic forms of zinc silicate and of the product, $\beta$-$Zn_2SiO_4$, produced in the differential analysis experiment C-642 will be published elsewhere.

### (*e*) *Dehydration curves for a sauconite and a saponite*

The late Dr. Perley G. Nutting, formerly a member of this laboratory, obtained dehydration curves for a sauconite and a saponite. His records have been obtained for inclusion in this paper. The experimental data are given in Table 6 and the graphical plot of the data is presented in Fig. 6. The data in Table 6 are expressed first, as the actual loss in



A



B

FIG. 6A. Dehydration curves for (A) sauconite #8, Liberty Mine, Meekers Grove, Plattesville District, Wisconsin, Record No. 358.

FIG. 6B. Dehydration curves for (B) saponite, Cathkin, Carmunnock Parish, County Lanarkshire, Scotland, Record No. 227. The ordinate is the weight of the sample at each temperature divided by the final weight at 960° C.

TABLE 6. THERMAL DEHYDRATION DATA FOR SAUCONITE AND SAPONITE

| Sauconite #8 | | | Saponite | | |
|---|---|---|---|---|---|
| Liberty Mine, Meekers Grove, Plattesville District, Wisconsin | | | Cathkin, Carmunnock Parish, County Lanarkshire, Scotland | | |
| Temperature | Loss in weight | Relative weight | Temperature | Loss in weight | Relative weight |
| °C. | | | °C. | | |
| 29 | * | 1.1531 | 27 | * | 1.2293 |
| 90 | 4.09% | 1.1059 | 80 | 10.52% | 1.1000 |
| 135 | 1.09 | 1.0933 | 170 | 2.55 | 1.0687 |
| 195 | 0.90 | 1.0829 | 215 | 0.15 | 1.0668 |
| 230 | 0.33 | 1.0791 | 285 | 0.09 | 1.0658 |
| 260 | 0.35 | 1.0750 | 325 | 0.10 | 1.0645 |
| 280 | 0.22 | 1.0725 | 395 | 0.50 | 1.0584 |
| 370 | 1.00 | 1.0610 | 428 | 0.22 | 1.0556 |
| 415 | 0.76 | 1.0522 | 475 | 0.23 | 1.0528 |
| 470 | 0.93 | 1.0414 | 530 | 1.12 | 1.0391 |
| 655 | 3.27 | 1.0037 | 560 | 0.19 | 1.0367 |
| 710 | 0.27 | 1.0007 | 646 | 0.17 | 1.0346 |
| 750 | — | 1.0000 | 720 | 0.33 | 1.0306 |
| 860 | — | 1.0000 | 780 | 0.65 | 1.0226 |
| 960 | — | 1.0000 | 895 | 1.81 | 1.0001 |
| | | | 960 | 0.03 | 1.0000 |
| | 13.21% | | | | |
| | | | | 18.66% | |

* Sample allowed to come to constant weight at room temperature.

weight of the sample at a given temperature, and secondly, as relative weight. These curves, according to Dr. Nutting, conform with those given by other members of the montmorillonite group. The oxidation of the ferrous iron to ferric iron in the saponite from Scotland results in an increase in weight of the sample. This reaction is indicated by a modification of the slope of the curve. The data suggest that this oxidation took place in the temperature range from 300°–400° C.

## X-RAY STUDIES

### (a) X-ray data for the sauconites dried at room temperature

The samples studied by the $x$-ray technique were prepared as spindles with "Duco cement" as the mounting medium. Patterns were obtained using filtered copper and iron radiation. The patterns obtained with copper radiation were very satisfactory for identification, and for the measurement of all but the (001) spacing. For most samples it was necessary to measure the (001) spacing on a pattern obtained using iron radiation. The poor quality of the (001) line, on the patterns obtained with copper radiation, arises from the inability of the cameras to record good lines at low angles of scattering. Samples containing a significant amount of iron produced some fluorescence with copper radiation.

The *x*-ray data for the various specimens of sauconite are given in Table 7. The data are arranged according to decreasing zinc oxide content; sauconite No. 1 being richest in this constituent. The lines were indexed on the basis of criteria established by Hofmann, Endell, and Wilm (1933); Gruner (1935); and Nagelschmidt (1938). This will be treated more fully at another place in this paper.

The *x*-ray data for the saponite (from Cathkin, Lanarkshire, Scotland, analysis No. 9, Table 1) are given in the last column for purposes of comparison.

### (*b*) *X-ray data for the sauconites treated with ethylene glycol*

A portion of the sauconites, dried at room temperature, was ground, placed in a watch glass, covered with ethylene glycol, and allowed to stand over night. In the morning the excess liquid was decanted, and the sample was further dried by placing it on absorbent filter paper. The moist sample was mixed with "Duco cement" and formed into spindles. Patterns were obtained with copper and iron radiation. Treatment with ethylene glycol greatly improved the quality of the patterns and made it possible to measure lines which could not be clearly differentiated in the patterns of the untreated samples.

The data for the interplanar spacings of the samples treated with ethylene glycol, are given in Table 8.

A note of caution should be added here concerning the re-use of spindles containing a substance previously soaked in ethylene glycol. Samples of sauconite prepared in June and July of 1949 and stored in small cork-stoppered vials were re-used in powder cameras in May and June of 1950. It was found that the *d* spacings for the (001) line of several sauconites were smaller than those recorded for the same spindles the previous year. One of the spindles, showing this anomalous character, was soaked in ethylene glycol and re-examined by *x*-ray methods. The resulting powder pattern gave results comparable with those obtained from the freshly prepared spindle. The vapor pressure of ethylene glycol is apparently great enough to permit its loss from spindles stored over a period of a year. This behavior of stored spindles has been confirmed by J. M. Axelrod of this laboratory.

Table 7. *X*-ray Powder Data for Sauconites and a Saponite Dri

| No. 1 Coon Hollow Mine, Ark. (White) | | | | No. 2 Coon Hollow Mine, Ark. (Brown) | | | | No. 3 New Discovery Mine, Leadville, Colo. | | | | No. 4 Yankee Doodle Min Leadville, Colo. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* |
| (001) | | 3 | s | (001) | 15.4 | | s | (001) | 15.3 | | s | (001) | 15.4 | | vs |
| (002) | 7.76 | | s | (002) | 7.77 | | ms | (002) | 7.92 | | ms | (002) | 7.90 | | m |
| Duco | 5.51 | b | w | Duco | 5.58 | b | w | Duco | 5.47 | b | w | Duco | 5.48 | b | m |
| (110)(020) | 4.59 | | s | (110)(020) | 4.60 | | ms | (110)(020) | 4.60 | | ms | (110)(020) | 4.55 | | m |
| | | | | (004) | 3.87 | | w | (004) | 3.92 | b | w | (004) | 3.94 | | vv |
| | | | | | | | | | | | | Halloysite | 3.59 | | vv |
| | | | | (005) | 3.09 | | w | (005) | 3.14 | b | m | (005) | 3.16 | | w |
| | | | | | | | | | | | | | 2.83 | (?) | vv |
| (130) | 2.68 | | s | (130)(200) | 2.67 | 2 | s | (130)(200) | 2.67 | d | ms | (130) | 2.67 | | m |
| (200) | | 1 | | | | | | | | | | (200) | 2.590 | | w |
| | | | | (150) | 1.748 | | vf | (150) | 1.736 | b | vvw | | | 1 | |
| | | | | (310) | 1.718 | | vf | | | | | | | 1 | |
| (060)(330) | 1.542 | | vs | (060)(330) | 1.544 | | s | (060)(330) | 1.548 | | s | (060) | 1.554 | | s |
| | | | | | | | | | | | | (330) | 1.505 | | vw |
| (260) | 1.329 | b | w | (260) | 1.334 | | m | (260) | 1.332 | | w | (260) | 1.334 | | w |
| | | | | | | | | | | | | (400) | 1.293 | | vv |
| | | | | | | | | (440) | 1.133 | | vvvw | (440) | 1.137 | | vv |
| (190) | 1.003 | b | w | (190) | 1.005 | b | w | (190) | 1.007 | | vvw | (190) | 1.015 | | vv |
| (550)(390) | 0.890 | b | w | (550)(390) | 0.890 | b | w | (550)(390) | 0.898 | | vw | (550)(390) | 0.894 | b | vv |
| | | | | | | | | | | | | | 0.816 | b | |

vs = very strong
s = strong
m = medium
wm = weak-medium
w = weak

vw = very weak
f = faint
vf = very faint
vvf = very, very faint
vvvf = very, very, very, faint

### (*c*) *Interpretation of the x-ray powder diffraction data of sauconite*

The best powder pattern of the seven sauconites examined was found to be that of the sauconite from the Yankee Doodle Mine, Leadville, Colorado. Accordingly, this pattern was selected as the most suitable for indexing the lines and the other sauconite patterns were indexed on the basis of this as a standard.

Hofmann, Endell and Wilm (1933) proposed a structure for montmorillonite which is based on the structure of pyrophyllite. According to

ROOM TEMPERATURE (WITH INDICES ASSIGNED FROM TABLE 10)

| No. 5 Liberty Mine, Meekers Grove, Wis. | | | | No. 6 Uberroth Mine, Friedensville, Pa. (Lehigh Univ.) | | | | No. 7 Uberroth Mine, Friedensville, Pa. (Spencer) | | | | No. 9 Saponite, Cathkin, near Glasgow, Scotland | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Miller ndices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* |
| (001) | 15.5 | | vs | (001) | 15.0 | | s | (001) | 15.6 | | vs | (001) | 14.8 | | vs |
| | | | | (002) | 7.44 | b | m | (002) | 7.80 | b | m | (002) | 7.71 | b | m |
| co | 5.54 | b | s | Duco | 5.37 | b | m | Duco | 5.47 | b | m | (003) | 5.14 | b | vw |
| 0)(020) | 4.52 | | s | (110)(020) | 4.51 | | s | (110)(020) | 4.58 | | m | (110)(020) | 4.59 | b | ms |
| | | | | | 4.21 | | s | | | | | | 4.34 | | vvf |
| | | | | | | | | (004) | 3.95 | | vw | (004) | 3.79 | | vw |
| | | | | Halloysite | 3.60 | | m | Halloysite | 3.59 | | vw | | | | |
| | | | | | | | | | 3.36 | | w | | | | |
| (005) | 3.3± | b | w | | | | | (005) | 3.14 | | vw | (005) | 3.09 | | m |
| | | | | | | | | | 2.87 | | vw | | | | |
| 0)(200) | 2.63 | b, d | ms | (130) | 2.68 | | m | (130) | 2.67 | | m | | | | |
| | | | | | | | | | | | | | 2.613 | | m |
| | | | | (200) | 2.571 | | m | (200) | 2.583 | | m | (200) | 2.545 | d | m |
| | | | | | 2.455 | | m | | | | | | | | |
| | | | | | 2.344 | Al | mw | (040) | 2.360 | | vw | | | | |
| | | | | | 2.233 | | vw | | 2.138 | | vw | | | | |
| | | | | | | | | | 2.001 | | w | | | | |
| | | | | | | | | | 1.851 | | vw | | 1.852 | | vvf |
| | | | | | | | | (150) | 1.747 | | w | (150) | 1.747 | | w |
| (310) | 1.71± | b | vw | (310) | 1.713 | | w | | | | | (310) | 1.703 | | w |
| | | | | | | | | | 1.640 | | vw | | | | |
| (060) | 1.545 | | ms | (060) | 1.547 | | m | (060) | 1.542 | | vs | (060) | 1.543 | b | s |
| (330) | 1.51± | | w | (330) | 1.501 | | w | (330) | 1.502 | | vw | (330) | 1.495 | | vvvf |
| | | | | | | | | | 1.459 | | vw | | 1.458 | | vvvf |
| | | | | | | | | | 1.388 | | vw | | | | |
| (260) | 1.33± | | vw | (260) | 1.331 | | vw | (260) | 1.329 | | m | (260) | 1.327 | b | m |
| | | | | | | | | | | | | (400) | 1.278 | b | vvvf |
| | | | | | 1.193 | b | vvw | | | | | | | | |
| (440) | 1.137 | b | vw | | 1.127 | b | vvw | | | | | | | | |
| | 1.077 | b | vw | | 1.081 | b | vvw | (190) | 1.010 | | w | | 0.999 | d | vvvf |
| | 0.870 | b | m | | | | | (550)(390) | 0.889 | | w | (550)(390) | 0.890 | b | vvvf |
| | 0.842 | b | w | | | | | | | | | | | | |
| | 0.818 | b | w | | | | | | 0.818 | | vw | | | | |
| | 0.793 | b | w | | | | | | 0.798 | | vw | | | | |

1—A line appears here but it is too faint to measure
2—The dark edge of the band was measured
3—Strong line present, but not measurable

Patterns for samples Nos. 1, 2, 5, 4, 7 corrected for film shrinkage.
Patterns for samples Nos. 5, 6 uncorrected for film shrinkage.
b = broad diffuse band
d = doublet, mean value used in table.

them montmorillonite is built up of units of three layers just as is pyrophyllite, but differs from pyrophyllite in that the three layer units are separated by interlayers of water. These investigators also found that the spacings of the basal reflections (00*l*) of montmorillonite vary with the water content while the other reflections are relatively unaffected. They indexed their patterns and found only lines corresponding to (00*l*) and (*hk*0) spacings. Gruner (1935) accepted most of their views but differed with them regarding the assignment of certain indices. Nagelschmidt (1938) followed Hofmann, Endell, and Wilm in the indexing of his

TABLE 8. *X*-RAY POWDER DATA FOR SAUCONITES TREATED W

| No. 1 Coon Hollow Mine, Arkansas (White) | | | | No. 2 Coon Hollow Mine, Arkansas (Brown) | | | | No. 3 New Discovery Mine, Leadville, Colorado | | | | No. 4 Yankee Doodle Min Leadville, Colorado | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* |
| (001) | 16.3 | | s | (001) | 16.6 | | s | (001) | | 3 | s | (001) | 16.1 | | vs |
| | 12.59 | b | w | | | | | | | | | | | | |
| (002) | 8.50 | | s | (002) | 8.33 | | s | (002) | 8.49 | | s | (002) | 8.40 | | s |
| Duco | 5.41 | | m | Duco | 5.41 | b | w | Duco | 5.37 | | m | Duco | 5.38 | b | m |
| (110)(020) | 4.61 | | vf | (110)(020) | 4.60 | | s | (110)(020) | 4.59 | | ms | (020) | 4.61 | | m |
| | | | | | | | | | | | | Halloysite<br>in part (110) | 4.45 | | m |
| (004) | 4.21 | | vvf | | | | | | | | | | | | |
| | | | | | | | | | | | | Halloysite | 3.63 | | [illegible] |
| (005) | 3.39 | | s | (005) | 3.34 | | m | (005) | 3.40 | | m | (005) | 3.37 | | [illegible] |
| (006) | 2.83 | b | w | | | | | | | | | (006) | 2.32 | | [illegible] |
| (130) | 2.69 | | m | (130) | 2.62 | | s | (130) | 2.68 | | ms | (130) | 2.66 | | [illegible] |
| (200) | 2.478 | | m | (200) | 2.473 | | m | (200) | 2.601 | | m | (200) | 2.579 | | w |
| (150) | 1.754 | | vvf | (150) | 1.753 | | vvf | (150) | 1.759 | | vvf | (150) | 1.754 | | vv |
| (310) | 1.706 | | vvvf | (310) | 1.715 | | vvf | | | | | (310) | 1.700 | | v |
| (060)(330) | 1.550 | b | s | (060)(330) | 1.550 | | s | (060)(330) | 1.548 | | s | (060) | 1.544 | | s |
| | | | | | | | | | | | | Halloysite<br>in part (330) | 1.491 | | w |
| (260) | 1.337 | b | w | (260) | 1.334 | | w | (260) | 1.335 | | w | (260)(170) | 1.327 | | w |
| | | | | | | | | | | | | (400) | 1.285 | b | v |
| | | | | | | | | | | | | (440) | 1.134 | b | v |
| | | | | | | | | | | | | (280) | 1.067 | b | v |
| (190) | 1.012 | b | vw | (190) | 1.010 | b | vw | (190) | 1.009 | b | w | (190) | 1.006 | b | v |
| (550)(390)<br>(00.19) | 0.895 | b | w | (550)(390)<br>(00.19) | 0.894 | b | vw | (550)(390)<br>(00.19) | 0.892 | b | w | (550)(390)<br>(00.19) | 0.891 | b | v |
| | | | | | | | | | | | | (620) | 0.844 | b | v |
| | | | | | | | | | | | | | 0.821 | b | v |

vs = very strong
s = strong
m = medium
wm = weak-medium
w = weak

vw = very weak
f = faint
vf = very faint
vvf = very, very faint
vvvf = very, very, very faint

photographs. Maegdefrau and Hofmann (1937) proposed a modification of the structure of montmorillonite to account for the absence of (*hkl*) reflections. They postulated that the three-layer units of the structure were stacked upon one another in an irregular fashion.

Using the criteria proposed by the above-mentioned investigators the pattern of sauconite was indexed. Assuming the *d* values for (060) and for (200) the *d* values of the most probable (*hk*0) and (00*l*) planes were thylene Glycol (with Indices Assigned from Table 10)

| No. 5 Liberty Mine, Meekers Grove, Wisconsin | | | | No. 6 Uberroth Mine, Friedensville, Pa. (Lehigh University) | | | | No. 7 Uberroth Mine, Friedensville, Pa. (Spencer) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* | *Miller Indices* | *d* | *Notes* | *I* |
| (001) | 15.3 | | s | (001) | | 3 | s | (001) | 15.4 | | vs |
| | | | | | | | | Halloysite | 10.0 | | f |
| | | | | (002) | 8.39 | | m | (002) | 8.20 | | m |
| | | | | Halloysite | 7.31 | | ms | Halloysite | 7.30 | | w |
| Duco | 5.42 | b | vs | Duco | 5.48 | b | ms | Duco | 5.49 | | vs |
| | | | | (110)(020) | 4.50 | | ms | (110)(020) | 4.58 | | s |
| | | | | (004) | 4.23 | | ms | (004) | 4.09 | | w |
| | | | | Halloysite | 3.58 | | ms | Halloysite | 3.62 | | m |
| (005) | 3.48 | b | ms | (005) | 3.39 | | ms | (005) | 3.37 | | ms |
| | | | | | | | | (006)? | 2.90 | | w |
| 130)(200) | 2.62 | | m | (130) | 2.67 | | m | (130) | 2.68 | | m |
| | | | | (200) | 2.585 | | m | (200) | 2.603 | | m |
| | | | | | 2.455 | | m | | 2.512 | | vw |
| | | | | | 2.344 | Al | f | | 2.144 | | w |
| | | | | | 2.214 | | vvf | (008)? | 2.063 | | w |
| | | | | | 2.006 | Al | vvf | | 2.007 | | w |
| | | | | | | | | | 1.877 | | vw |
| | | | | | | | | (150) | 1.762 | | w |
| (310) | 1.71 | | vvvw | (310) | 1.714 | | vf | | | | |
| | | | | (00.10) | 1.678 | | | (00.10)? | 1.668 | | vw |
| 060)(330) | 1.542 | b | ms | (060) | 1.534 | | s | (060)(330) | 1.550 | | vs |
| | | | | Halloysite in part (330) | 1.497 | | w | | | | |
| | | | | (260) | 1.326 | b | vf | (260) | 1.338 | | mw |
| (440) | 1.13 | b | vw | (440)? | 1.240 | b | vvf | | | | |
| | 1.08 | b | vw | | | | | | | | |
| | | | | (190) | 1.007 | b | vvvf | (190) | 1.013 | b | mw |
| (550)(390) (00.19) | 0.908 | b | vw | (550)(390) (00.19) | 0.891 | b | vvvf | (550)(390) (00.19) | 0.895 | b | mw |
| | 0.872 | b | vw | | | | | | | | |
| | 0.846 | b | vw | | | | | | | | |
| | 0.820 | b | vw | | | | | | | | |
| | 0.791 | b | vw | | | | | | | | |

1—A line appears here but it is too faint to measure
2—The dark edge of the band was measured
3—Strong line present, but not measurable
Patterns for samples Nos. 1, 2, 3, 4, 7 corrected for film shrinkage.
Patterns for samples Nos. 5, 6 uncorrected for film shrinkage.
b = broad diffuse band
d = doublet, mean value used in table.

calculated using the monoclinic formula and the results are given in Table 9. In selecting the most probable indices the following were considered:

(1) The agreement between calculated and observed spacings.
(2) The quality of the line as indicated by the intensity and the width of the line.
(3) The specific effect of ethylene glycol upon the position of the (00*l*) spacings.

The powder diffraction data were also used to construct a diagram of the reciprocal lattice which afforded a check on the indexing of the data.

The presence of halloysite in some of the samples of sauconite was established by *x*-ray studies and confirmed by means of electron microscopy. The electron micrographs were made by Edward J. Dwornik.

TABLE 9. MOST PROBABLE INDICES OF THE LINES IN THE *X*-RAY DIFFRACTION PATTERN OF SAUCONITE NO. 4 FROM THE YANKEE DOODLE MINE, LEADVILLE, COLORADO

| Most probable index | *d* (observed) | *d* (calculated) for possible spacings | Intensity | Width of line | Expansion of basal spacings | Error in line measurement ±0.2 mm. | | Halloysite-Average pattern after G. Nagelschmidt |
|---|---|---|---|---|---|---|---|---|
| | | | | | | (−) | (+) | |
| (001) | 16.1 | 16.8 (001) | vs | 0.7 mm. | 0.7 Å | | | |
| (002) | 8.4 | Assumed (002) | s | 0.5 mm. | 0.5 Å | | | 7.49 to 7.43 m to vw |
| (020) | 4.61 | 4.63 (020) | m | 0.4 mm. | | 4.66 | 4.56 | |
| (110) | 4.45 | 4.50 (110)* | ms | 0.5 mm. | | 4.49 | 4.41 | 4.44 to 4.42 vs to s |
| | 3.63 | Halloysite | wm | 0.6 mm. | | | | 3.72 to 3.60 s to w |
| (005) | 3.37 | 3.36 (005) | m | 0.7 mm. | 0.21 Å | 3.40 | 3.35 | 3.35 to 3.31 m to w |
| (006) | 2.82 | 2.80 (006) | w | 0.8 mm. | no data | 2.836 | 2.801 | |
| (130) | 2.66 | 2.65 (130) | m | 0.6 mm. | | 2.671 | 2.640 | |
| (200) | 2.579 | Assumed (200) | wm | 0.6 mm. | | | | 2.60 to 2.57 s |
| (150) | 1.754 | 1.743 (150) | vw | broad, diffuse | | 1.760 | 1.747 | 2.36 to 2.33 s |
| | | 1.721 (240) | | | | | | 2.22 vw |
| (310) | 1.700 | 1.687 (310) | vw | broad, diffuse | | 1.705 | 1.694 | 1.71 to 1.70 s to m |
| (060) | 1.544 | Assumed (060) | s | 0.6 mm. | | | | 1.64 to 1.62 s to m |
| (330) | 1.491 | 1.499 (330)* | w | 0.8 mm. | | 1.495 | 1.486 | 1.491 to 1.486 vs to s |
| (260) (170) | 1.327 | 1.324 (260) | wm | 1.2 mm. | | 1.330 | 1.323 | |
| | | 1.324 (170) | | | | | | |
| (400) | 1.285 | 1.289 (400) | vvw | broad, diffuse | | 1.288 | 1.282 | 1.291 to 1.289 m to w |
| | | 1.292 (00.13) | | | | | | 1.239 to 1.236 m to w |
| (440) | 1.134 | 1.125 (440) | vvw | broad, diffuse | | 1.137 | 1.132 | |
| (280) | 1.067 | 1.056 (280) | vvvw | broad, diffuse | | 1.069 | 1.065 | |
| | | 1.050 (00.16) | | | | | | |
| (190) | 1.006 | 1.004 (190) | vvw | broad, diffuse | | 1.0073 | 1.0043 | |
| (550) (390) (00.19) | 0.891 | 0.900 (550) | vvw | 2.0 mm diffuse | | 0.8921 | 0.8903 | |
| | | 0.890 (00.19) | | | | | | |
| | | 0.883 (390) | | | | | | |
| (620) | 0.844 | 0.844 (620) | vvvw | broad, diffuse | | 0.8444 | 0.8431 | |
| | | 0.840 (00.20) | | | | | | |
| | 0.821 | 0.826 (630) | vvw | broad, diffuse | | 0.8210 | 0.8200 | |

* Halloysite in part.

vs = very strong
s = strong
m = medium
ms = medium-strong
wm = weak-medium

w = weak
vw = very weak
vvw = very, very weak
vvvw = very, very, very weak

### (*d*) *Identification of the phases formed in the dissociated minerals*

#### (1) *Phases present in sauconite heated to about 350° C.*

A sample of sauconite No. 2, the brown variety, from the Coon Hollow Mine, Arkansas, was heated in the differential thermal analysis apparatus to a temperature of 327° C. The heating was stopped after all the "low-temperature" water was expelled (see Fig. 7A). This "low-temperature" water represents the interlayer water and the very small amount of adsorbed water. An *x*-ray powder photograph was made of this heated material. Comparison of the powder patterns of the heated brown sauconite and of the natural sauconite shows that the basal spacings (00*l*) are smaller for the heated sauconite than for the unheated mineral, an observation that was expected. See Table 10. Otherwise, the patterns are almost identical. The background due to general scattering is much less for the heated sauconite and this decrease is chiefly due to the absence of the adsorbed water.

#### (2) *Phases present in sauconite heated to a temperature just above the dissociation point*

Zinc orthosilicate ($Zn_2SiO_4$) is one of the products formed when sauconite is dissociated. In order to determine the sequence in the polymorphic transformations of $Zn_2SiO_4$ in the differential thermal analysis, a sample of sauconite no. 2, from Boone County, Arkansas, was heated to a temperature of 866° C. and then suddenly cooled by pulling the furnace away from the sample. The record of this heating and quenching experiment is shown as curve C-643 in Figure 7B. A comparison of this curve C-134 in Fig. 1, shows that up to a temperature of about 840° C. the curves are essentially the same. The slight exothermic reaction at about 350° C. appearing on curve C-643 is probably due to the combustion of organic matter or the oxidation of ferrous iron. Above 840° C. these curves are very different. The record of the sample heated to 866° and then suddenly cooled shows a well defined exothermic break at about 870° C. Thereafter, no reaction took place and the sample cooled down to room temperature. *X*-ray examination of the resulting material shows the powder pattern to be that of $\beta$-$Zn_2SiO_4$ with an extra line probably belonging to gahnite ($ZnAl_2O_4$).

The exothermic break at 832° C., curve C-643, apparently represents the formation of $\gamma$-$Zn_2SiO_4$. Accordingly, the exothermic break at 870° C. represents the transformation of "$\gamma$-$Zn_2SiO_4$" to $\beta$-$Zn_2SiO_4$ and the area under the curve is a measure of the heat of transformation of the "$\gamma$" to the $\beta$ form.

TABLE 10. X-RAY POWDER DIFFRACTION DATA FOR SAUCONITE NO. 2, THE NATURAL BROWN VARIETY FROM THE COON HOLLOW MINE, ARKANSAS, AND FOR THE SAME SUBSTANCE HEATED TO 327°C.

| Sauconite No. 2 Natural Mineral | | | | Sauconite No. 2 Heated to 327° C. | | | |
|---|---|---|---|---|---|---|---|
| d spacing | Intensity | Remarks | Probable indices | d spacing | Intensity | Remarks | Probable indices |
| 15.4 | s | | (001) | 14.5 | vs | | (001) |
| 7.77 | ms | | (002) | 7.74 | s | | (002) |
| 5.58 | w | Duco band | | | | present but not measured | |
| 4.60 | ms | | (020)<br>(110) | 4.60 | s | | (020)<br>(110) |
| 3.87 | w | | (004) | 3.82 | m | broad | (004) |
| 3.09 | w | | (005) | 3.07 | m | broad | (005) |
| 2.670 | s | | (130)<br>(200) | 2.66 | ms | doublet | (130)<br>(200) |
| 1.748 | vw | | (150)<br>(240) | 1.747 | vw | | (150)<br>(240) |
| 1.718 | vw | | | | | (?) | |
| 1.544 | s | | (060) | 1.544 | vs | | (060) |
| 1.334 | m | | (260)<br>(170) | 1.331 | w | broad | (260)<br>(170) |
| 1.005 | w | broad | | 1.007 | vw | broad | |
| 0.890 | w | broad | | 0.891 | vw | broad | |

s = strong
ms = medium-strong
w = weak
vw = very weak
vs = very strong

(3) *Phases present in sauconite heated to about 1000° C.*

The products resulting from the dissociation of the various specimens of sauconite which had been heated to at least 1000° C. were examined by the *x*-ray powder diffraction method. The phases observed are wil-

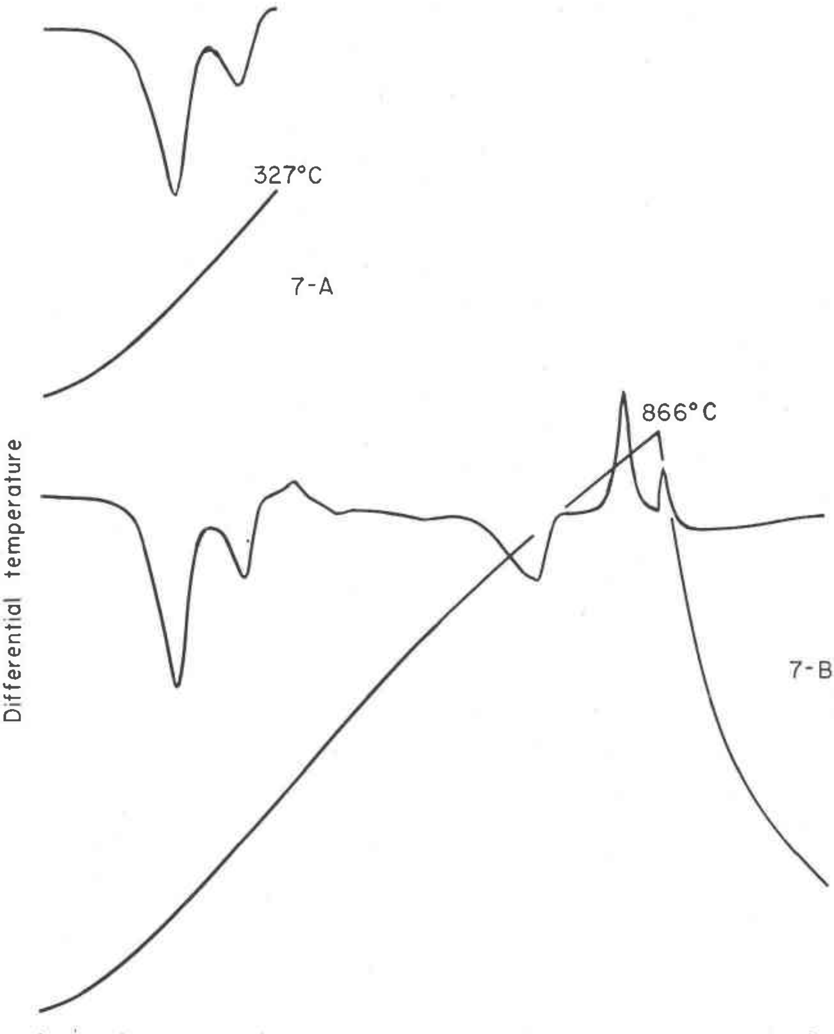


FIG. 7A. Differential thermal analysis curve of a sample of sauconite no. 2, from Boone County, Arkansas, C-639, heated to a temperature of 327° C. and then cooled by removing the furnace from the sample holder.

FIG. 7B. Differential thermal analysis curve of a sample of sauconite no. 2, from Boone County, Arkansas, C-643, heated to 866° C. and then suddenly cooled by removing the furnace from the sample holder.

lemite, gahnite, and cristobalite. A summary of these data is given in Table 11.

TABLE 11. PHASES IDENTIFIED BY X-RAY METHODS IN THE SAUCONITES HEATED TO ABOUT 1000° C.

| Sauconite used in the experiment | Record No. | Phases present | | | Relative abundance | X-ray powder pattern no. | Notes |
|---|---|---|---|---|---|---|---|
| | | Willemite $\alpha$-$Zn_2SiO_4$ | Cristobalite $SiO_2$ | Gahnite $ZnAl_2O_4$ | | | |
| Sauconite No. 2 (ZnO=36.73%) | C-134 | + | + | + | Willemite> Gahnite | 3305 | |
| Sauconite No. 2 Ca-Na Sauconite | C-211 | + | + | + | Willemite>> Gahnite | 3318 | |
| Sauconite No. 2 Na-Sauconite | C-222 | + | − | + | Willemite>>> Gahnite | 3319 | |
| Sauconite No. 2 H-exchanged | C-209 | + | − | + | Willemite>> Gahnite | 3306 | |
| Sauconite No. 3 (ZnO=33.70%) | C-80 | + | + | + | Willemite> Gahnite | 3303 | |
| Sauconite No. 4 (ZnO=28.19%) | C-81 | + | + | + | Gahnite> Willemite | 3304 | |
| Sauconite No. 6 (ZnO=23.10%) | C-175 | + | − | + | Gahnite>> Willemite | 3072 | A weak extra line appears at 3.37Å(±). This suggests the presence of mullite $(2SiO_2 \cdot 3Al_2O_3)$ |
| Sauconite No. 6 | C-567 | + | − | + | Gahnite>> Willemite | 3320 | |

The equilibrium relations in the system $ZnO$-$Al_2O_3$-$SiO_2$ have been determined by Bunting (1932). One must be cautious in attempting to correlate the results of differential thermal analysis studies with equilibrium diagrams. Differential thermal analysis experiments are almost always performed in such a manner that inequilibrium results. Nevertheless, a comparison of the results of differential thermal analysis studies with the actual equilibrium diagrams is of interest. The chemical analyses of the various sauconites studied were recalculated to a water free basis. In this calculation the very small amounts of MnO, $TiO_2$ and CuO were neglected. The $Fe_2O_3$, $Na_2O$ and $K_2O$ were combined with the $Al_2O_3$ and the resulting sum was considered as $Al_2O_3$; likewise the MgO and CaO were added to the ZnO. These "corrected" values of ZnO and $Al_2O_3$ together with the $SiO_2$ were used to calculate the mole percentages of these oxides in each of the sauconites. The resulting data were plotted on the phase rule diagram of Bunting. See Fig. 8. The phases present in these samples of dissociated sauconite are those which are predicted by an examination of the equilibrium diagram.

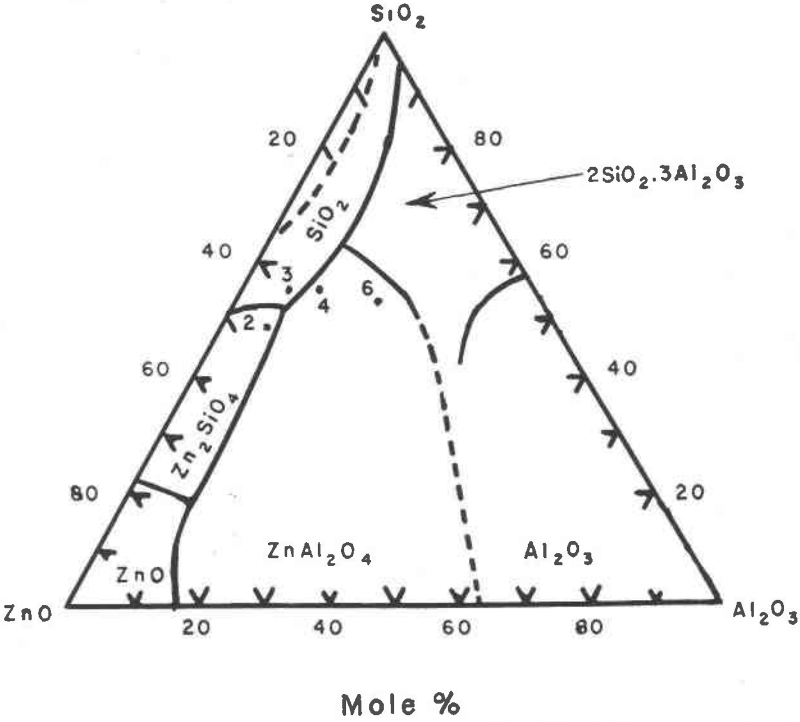


FIG. 8. Phase equilibrium diagram of the system $ZnO$-$Al_2O_3$-$SiO_2$, as determined by E. N. Bunting. The numbers 2, 3, 4, and 6 represent the composition of sauconites Nos. 2, 3, 4, and 6.

When samples of sauconite are packed in the hole in the nickel block of the differential thermal analysis apparatus and heated to a temperature of about 1000° C. they usually form as a firm cylinder. The sauconite from the New Discovery Mine yielded the firmest cylinder. This behavior is like that of certain types of montmorillonite.

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