HIGH TEMPERATURE PHASES IN MONTMORILLONITES

By

GEORGES KULBICKI

University of Illinois, Urbana, Illinois

ABSTRACT

The formation of siliceous phases in montmorillonites at temperatures up to 1500°C has been studied by high temperature continuous x-ray diffraction techniques. Oriented clay aggregates on platinum slides are heated in a small platinum-wire resistor furnace placed on an x-ray spectrometer unit. The intensity of the main diffraction lines of each phase is noted versus the temperature. The nature and the temperature of formation of the different phases are closely related to the structure and composition of the sample. The important role of some cations in exchange position is emphasized.

INTRODUCTION

The reactions occurring in the clay minerals heated at high temperatures up to their melting point are of great importance in many respects, and they have been the subject of a number of studies. Various methods of investigation can be used, but the basic information given in the literature is provided by x-ray diffraction patterns of air-quenched samples, sometimes combined with D.T.A. curves. This procedure presents some drawbacks, of which the most critical is perhaps the impossibility of making continuous analysis and investigating rapid transformations taking place within a short range of temperature. Furthermore, it is time consuming and can not easily be used in a study involving a large number of samples.

On the contrary, high temperature x-ray diffraction techniques are attractive; as the reactions in the samples can be followed continuously while heating, possible modifications of the phases by cooling are prevented, and a continuous quantitative record of the transformations versus the temperature can be easily obtained. In the present work an attempt has been made to adapt these techniques to the clay minerals. The details of the procedure will be presented and a series of preliminary data will be given.

Among the different clay minerals, montmorillonite was selected as the most desirable material for the initial study. This mineral occurs with various substitutions within its lattice, so that the effect of slight variations in composition or structure, or both, can be investigated; also its high exchange capacity for cations makes possible comparisons of the effect of small quantities of various cations adsorbed on the silicate lattice.

TECHNIQUES

In recent years several models of high-temperature furnaces for x-ray diffraction have been described. The furnace used in this work was constructed by the

144

author especially to satisfy the following requirements: utilization of oriented clay aggregates, high thermal stability of the sample holder, accurate control of the temperature of the sample, small volume, and easy construction. The need for only low-order reflections (up to $2\theta = 60°$), and the use of a spectrometer-goniometer instead of photographic film, made the problem much easier.

The furnace is shown in Figure 1. The heating element is a platinum-rhodium wire coiled around a two-piece tube of refractory ceramic material. About 4 feet of 0.125 gauge wire, of 3 ohms resistance, was used. A temperature of 1600°C can be reached. A variac driven by an electric motor through a speed reducer automatically raises the temperature. By varying the initial input voltage, the heating rate can be controlled between 0° and 600°C per hour.

The sample holder is a platinum slide which is pushed along the flat side of the tube. A drop of light clay suspension is allowed to dry on the slide, giving
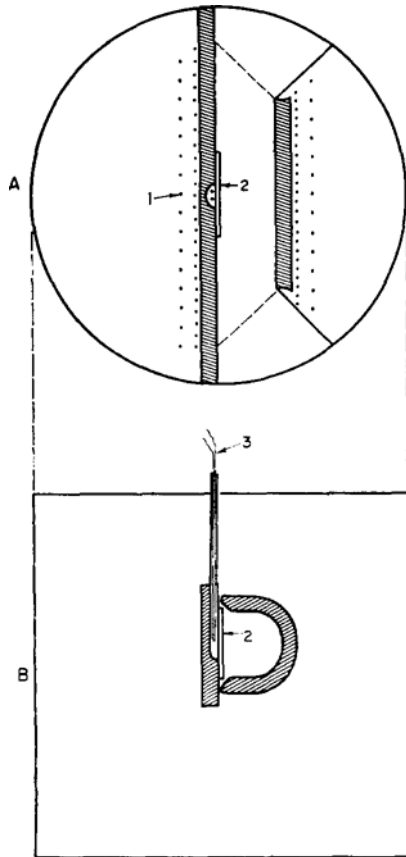

FIGURE 1. — High-temperature furnace for use with G.E. XRD-3 unit. Vertical view (A) and lateral view (B). 1, heating wire. 2, slide sample-holder. 3, thermocouple.

a thin, oriented clay aggregate. The weight of the sample is about 3 mg. It is important to press the slide well against the ceramic plate in order to have more thermal stability of the sample. A thermocouple is placed directly in contact with the back of the sample holder. The gradient of temperature on the slide can be checked easily: two Pt-Rh wires connected to the slide at two points constitute a differential thermocouple; the difference of temperature thus recorded between the center and the edges of the slide never exceeded 10°C, even with the higher heating rate used. This very satisfactory result is due to the high conductivity of the Pt slide. As the sample is very thin, it can be assumed that the temperature throughout the sample is uniform.

A heating rate of 5°C per minute was chosen after some experiments on the effect of isothermal soakings on the different reactions; this rate gives the same curves as much slower rates, provided the weight of the sample is small.

The furnace is placed on a General Electric XRD-3 x-ray unit with a counter spectrometer. The use of a spectrometer makes it possible to follow the behavior of several phases almost at the same time by manually setting the counter at angles corresponding to the main diffraction lines of each phase. In presenting the results (Figs. 2 to 11) the intensities of these lines are plotted versus the temperature.

SAMPLES INVESTIGATED

Investigations were made with montmorillonites from six different localities:

Cheto, Arizona. White, low-iron content montmorillonite; formed by alteration of volcanic ash.

Tatatila, Mexico. Pink, compact; hydrothermal origin (?).

Montmorillon, France. Pink, compact.

Belle Fourche, South Dakota. Commercial sample of "Wyoming bentonite" formed by alteration of volcanic ash.

Amory, Mississippi. Dark green, iron-rich clay; marine deposit.

Smithville, Mississippi. Same formation as the preceding sample, but weathered. No analysis available.

The fraction less than 2 microns was extracted from each sample, and the natural interlayer cations removed and exchanged by H, Li, Na, K, Cs, Mg, Ca, Ba, Al, Cu, Fe. Some data on these samples are compiled in Table 1.

RESULTS

Untreated Samples

The diagrams obtained from the untreated samples are reported in Figure 2. The first curve represents the intensity of the 003 diffraction line of the montmorillonite lattice. The 003 line has been chosen rather than 001 as it is generally stronger. All samples show a slight shift of this line (about 0.3°) accompanied sometimes by a small variation of intensity, at about 650°C owing to the departure of hydroxyl water. This diffraction line disappears above 800°C. The shape of the curve showing the loss of intensity (and, therefore, structure), and the temperature at which the intensity finally declines to zero, vary with the samples.

TABLE 1. — CHEMICAL ANALYSES AND STRUCTURAL FORMULAS OF MONTMORILLONITES

Sample	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	FeO	MgO	CaO	K$_2$O	Na$_2$O	Ign. Loss	Total	Exch. Cap.
1 [1]	59.33	0.28	20.45	2.59	0.31	4.11	2.75	0.33	0.17	9.15	99.47	145
2 [2]	61.06	—	22.25	0.07	—	4.45	3.84	—	—	8.75	100.42	—
3 [2]	60.08	—	23.21	0.98	—	3.79	1.90	0.13	0.04	9.39	99.52	—
4 [1]	63.53	0.13	21.28	3.36	0.14	2.87	0.27	0.34	1.82	6.74	100.48	95
5 [1]	58.01	0.55	19.32	6.37	0.36	3.15	1.93	0.95	0.17	9.62	100.43	95

1 [1]	[Al$_{1.51}$Fe$_{.13}$Mg$_{.40}$]	[Al$_{.07}$Si$_{3.93}$]	O$_{10}$[OH]$_2$	[Na$_{.02}$(Ca/2)$_{.37}$]
4 [1]	[Al$_{1.63}$Fe$_{.17}$Mg$_{.25}$]	[Al$_{.07}$Si$_{3.93}$]	O$_{10}$[OH]$_2$	[Na$_{.24}$(Ca/2)$_{.04}$]
5 [1]	[Al$_{1.40}$Fe$_{.32}$Mg$_{.31}$]	[Al$_{.12}$Si$_{3.88}$]	O$_{10}$[OH]$_2$	[Na$_{.02}$(Ca/2)$_{.28}$]

Sample 1. Cheto, Ariz.; 2. Tatatila, Mex.; 3. Montmorillon, France; 4. Belle Fourche, S. D.; 5. Amory, Miss.
[1] Analysis recomputed from Kerr and others (1950), neglecting H$_2$O–.
[2] Analysis recomputed from Ross and Hendricks (1945), neglecting H$_2$O–.

The first crystalline product to appear is beta-quartz, at temperatures ranging from 910° to 1200°C. It inverts to beta-cristobalite, which gives a maximum of diffraction intensity around 1200°C and disappears more or less gradually between 1250° and 1400°C. Then the sample melts.

Samples 1, 2, 3, and 5 also show cordierite above 1200°C; it grows as beta-cristobalite disappears. The formation of anorthite in one sample (sample 1) seems independent of the beta-quartz or beta-cristobalite crystallizations. In some samples mullite grows with beta-cristobalite, and it is the only mineral that remains when the sample melts.

It is interesting to note that the diffraction patterns of these minerals show some notable reinforcements with respect to their ordinary powder patterns. This is particularly clear with beta-cristobalite for which the 111 and 220 peaks have relative intensities of 10 to 1 instead of 10 to 3 as in the powder patterns. Also, 100 of beta-quartz (except for the clay containing Li) and 020 of cordierite are strongly enhanced. This is strong evidence that these new phases develop with preferred orientation with respect to the lattice of the montmorillonite. These relationships are being investigated further, but it can safely be concluded now that the constituents of the clay keep a certain orientation in the temperature range above 850°C and until new phases form, although no diffraction lines are recorded.

Cheto Montmorillonite

Phases developed by Cheto montmorillonite after exchange with various cations are shown in Figures 3 and 4. The raw clay carries Ca^{2+} and Mg^{2+}. In the H-clay, the formation of beta-cristobalite seems easier than in the untreated material. There is a little anorthite, and cordierite is formed at a higher temperature. Samples submitted to drastic acidic treatments, such as soaking in 50
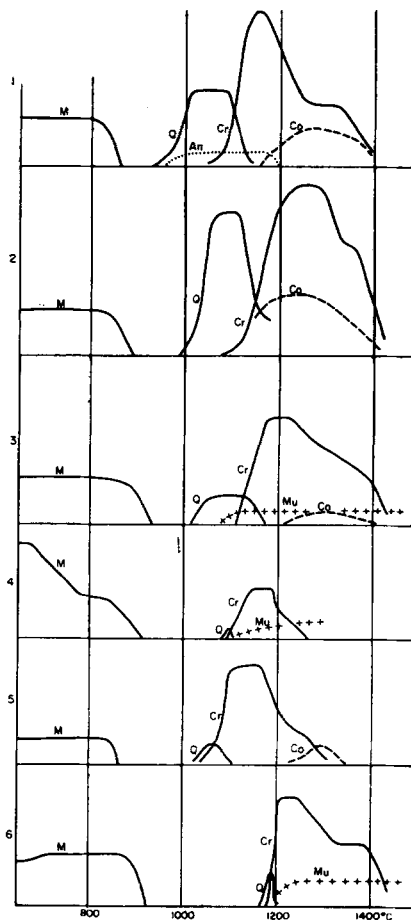
FIGURE 2. — Intensities of diffraction lines of high-temperature phases in montmorillonites from Cheto (1), Tatatila (2), Montmorillon (3), Belle Fourche (4), Amory (5), Smithville (6). Montmorillonite (M), Beta-quartz (Q), Beta-cristobalite (Cr), Anorthite (An), Mullite (Mu), Cordierite (Co), Spinel (Sp).

percent HCl for 6 hours, show similar patterns but the intensities of the reflections are greatly lowered. Alkaline cations inhibit or even prevent crystallization. At first sight it seems that the larger the cation, the greater its effect: there is no crystallization at all with K or Cs. Li extends the range of existence of beta-quartz, whereas Na prevents the formation of beta-quartz and gives beta-cristobalite directly. The same results are shown after treatment of the raw material by LiOH, NaOH, and KOH in normal solutions.

Calcium develops more beta-quartz and more anorthite than in the untreated clay.
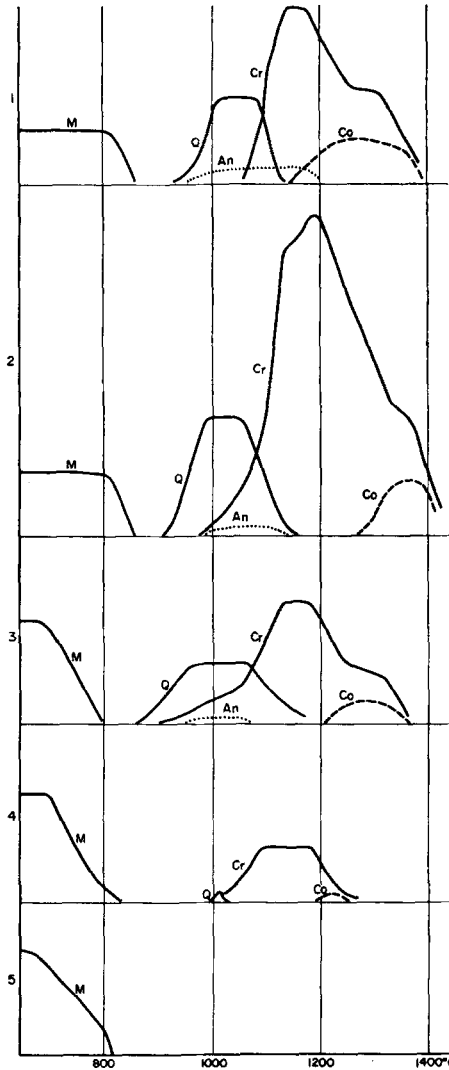
FIGURE 3. — Intensities of diffraction lines of high-temperature phases in Cheto montmoril-lonite: Untreated, (1); exchanged with H (2); Li (3), Na (4), K (5). Same notations as in Figure 2.

With magnesium, beta-quartz formation starts before 900°C, and beta-cristo-balite is simultaneously formed; the production of cordierite is intensified.

With introduction of barium, celsian replaces anorthite and a very strong reflection is given by a barium-bearing cordierite.

With aluminum, beta-quartz is formed in two stages starting at 950° and
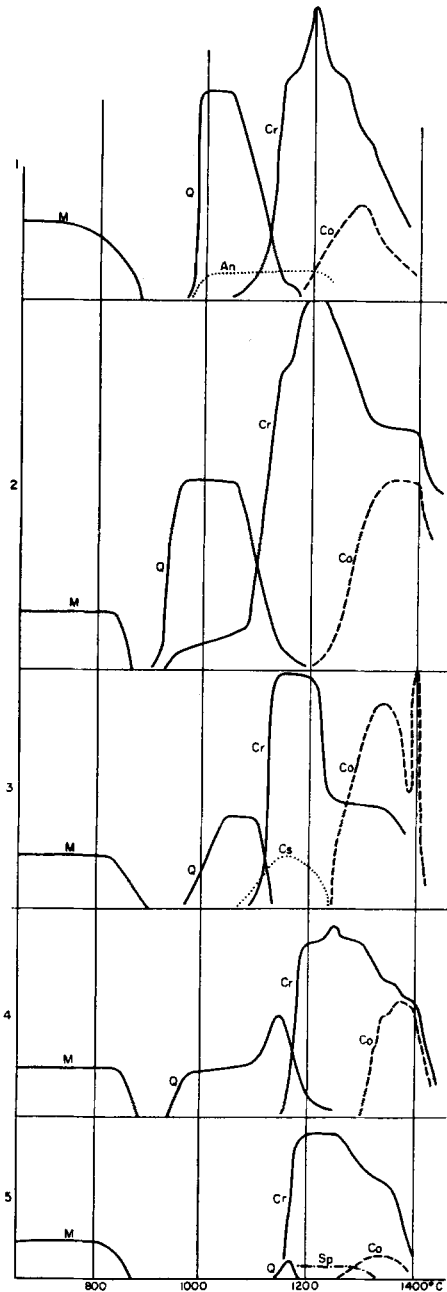
FIGURE 4. — Intensities of diffraction lines of high-temperature phases in Cheto montmorillonite exchanged with Ca (1), Mg (2), Ba (3), Al (4), Fe (5). Same notations as in Figure 2.

1150°C, and cordierite is still important. The difference between the H- and Al- samples indicates notable influence attributable only to augmented level of aluminum content.

Iron and copper enhance the formation of beta-cristobalite. Beta-quartz appears for only a short time as an intermediate phase in the crystallization of beta-cristobalite. Some spinel is also found.

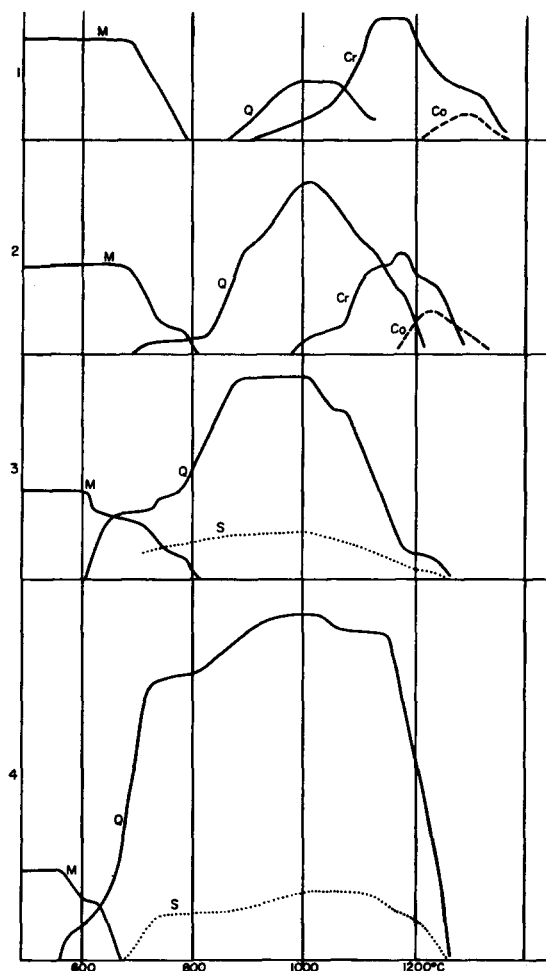In another series of experiments various quantities of chlorides of these same metals were added to the preceding samples.

FIGURE 5. — Intensities of diffraction lines of high-temperature phases in Cheto montmorillonite: Li-clay (1); Li-clay and 40 meq (2), 120 meq (3), 240 meq (4), of LiCl added. Same notations as in Figure 2. Lithium silicate (S).

With addition of LiCl to the Li-clay (Fig. 5), the intensity of beta-quartz is progressively increased while the other phases disappear. Some lithium silicate is also formed. Destruction of the montmorillonite and formation of beta-quartz are simultaneous, suggesting that beta-quartz forms in a direct reaction of LiCl with the clay and not as a late reorganization of the clay lattice after its collapse. It does not show any preferential orientation with respect to the montmorillonite. With increasing quantities of LiCl the reaction occurs in several steps, at about 600°, 700° and 850°C.

In contrast to the lithium the addition of only 40 meq of NaCl to the Na-clay melts the sample and prevents any kind of crystallization. The same thing happens with addition of NaBr, NaF, Na_2HPO_4, or Na_2SO_4 in the same proportion; the only difference is in the shape of the curve for the collapse of the montmorillonite lattice.

In order to study the influence of Na in proportions below the exchange capacity, NaCl was added to H-clay, thus presumably producing H-Na-clay (Fig. 6). As little as 25 meq of Na produces a notable modification of the beta-quartz crystallization. With 50 meq, the curve is very similar to the one given by Na-clay. More Na affects only the intensities of the reflections and the collapse of the montmorillonite.

On addition of $CaCl_2$ to the Ca-clay (Fig. 7), the suspensions flocculate and the orientation of the samples on the slide becomes very poor; it follows that the recorded intensities are low. Nevertheless one can make some comparisons. Up to 500 meq of Ca, there is a progressive disappearance of beta-quartz and then of beta-cristobalite. There is no cordierite but much more anorthite.

With $MgCl_2$ (Fig. 8), the most important effect is the formation of a great deal of cordierite and of some enstatite. The addition of $BaCl_2$ strengthens also the formation of Ba-bearing cordierite.

Other Samples

Montmorillonite from the type locality at Montmorillon, France, prepared with various cations reacts in the same general way as the Cheto samples, but all the temperatures are somewhat higher (Fig. 9). Unlike Cheto, some mullite is formed which seems unaffected by the exchanged cations.

Some diagrams made with Mississippi and Wyoming montmorillonites are reported in Figures 10 and 11. They are in general characterized by low intensities of the diffraction lines and a large gap between the collapse of the montmorillonite lattice and the appearance of beta-quartz. With the exception of Li-clay, they do not show great differences from one another.

DISCUSSION

The diagrams indicate the transformations that take place when montmorillonite is heated. They show the extreme sensitivity of recrystallization to variations within the structure and to even small variations in adsorbed cations. The explanation of these variations is a difficult matter and only a beginning can be made at this time. In that connection the following suggestions are offered.
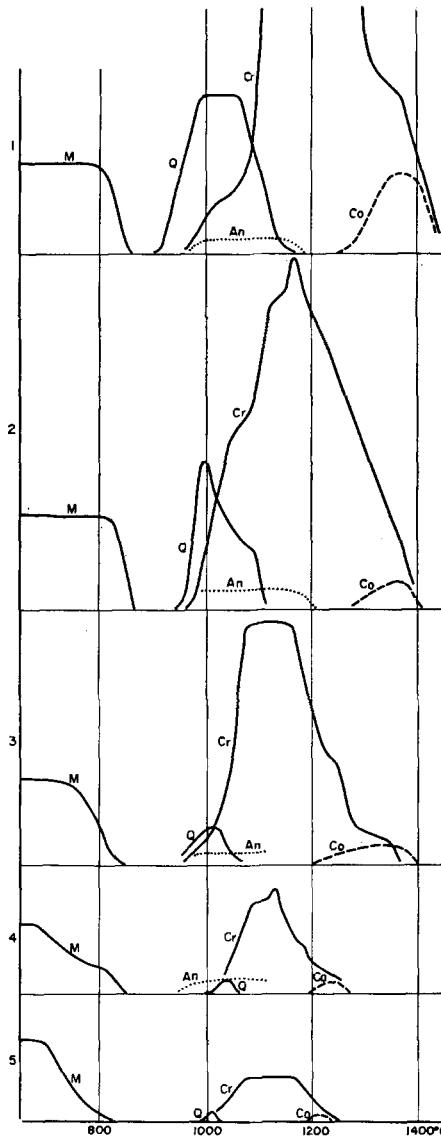
FIGURE 6. — Intensities of diffraction lines of high-temperature phases in Cheto montmorillonite: H-clay (1); H-clay and 25 meq (2), 50 meq (3), 125 meq (4), of NaCl added; Na-clay (5). Same notations as in Figure 2.

A careful examination of the diagrams shows two groups of new phases. In the first group, quartz, cristobalite, and perhaps cordierite are directly related to each other; as the temperature increases, quartz inverts to cristobalite which
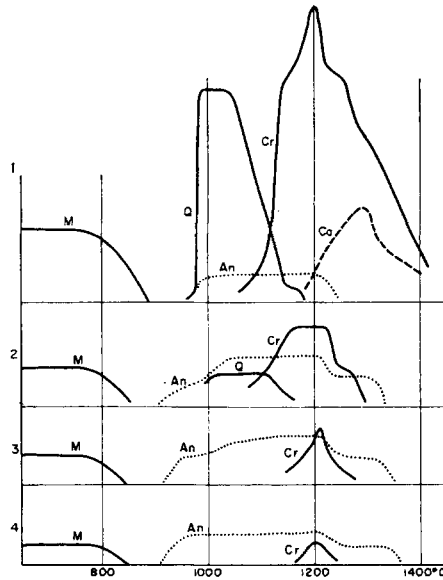
FIGURE 7. — Intensities of diffraction lines of high-temperature phases in Cheto montmorillonite: Ca-clay (1) ; Ca-clay and 100 meq (2), 200 meq (3), 500 meq (4), of CaCl₂ added. Same notations as in Figure 2.

later disappears as cordierite grows; they are oriented with respect to the clay lattice and give strong diffraction lines. On the contrary the second group, made up of feldspars, enstatite, mullite, and spinels, develop independently; they show no preferential orientation and produce relatively weak diffraction lines. A simple explanation would be to suppose that the latter come from impurities or from clay particles extraneous to the montmorillonite, but this would be wholly hypothetical and a more general explanation should be considered.

It is reasonable to think that the growing of large crystals of quartz or cristobalite is difficult or perhaps impossible without the departure of at least a part of the interlayer and octahedral cations. We can thus suppose that the crystallization of silica would follow the migration of these cations from the center toward the edges of the particles. There, these cations would enter into combinations with magnesium, aluminum, and silica, giving such phases as feldspars, enstatite, mullite, or spinels. The major phases, formed throughout the particles with a large part of the silica, give strong diffraction lines of which some are reinforced. The other phases, developed with relatively small quantities of cations, growing from many separate nuclei, give poor diffraction lines and no preferential orientation.

Expulsion of the cations from the montmorillonite lattice may occur more or less easily and at different temperatures, depending upon the nature of the cat-
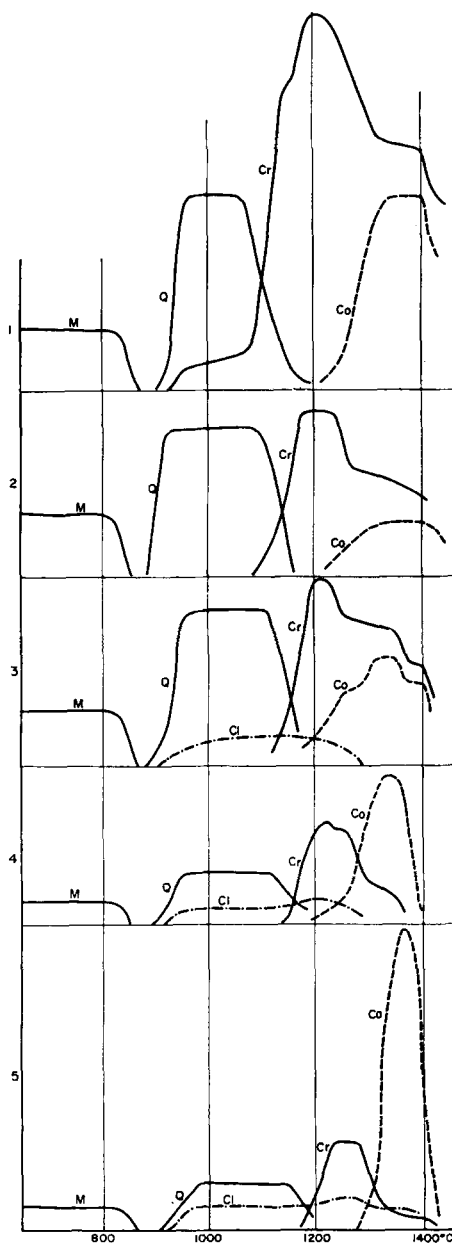
FIGURE 8. — Intensities of diffraction lines of high-temperature phases in Cheto montmorillonite: Mg-clay (1) ; Mg-clay and 100 meq (2), 200 meq (3), 500 meq (4), 1000 meq (5), of MgCl₂ added. Same notations as in Figure 2. Enstatite, Cl.
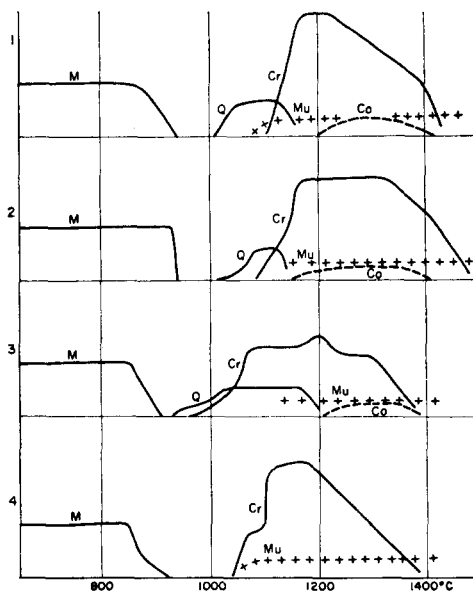
FIGURE 9. — Intensities of diffraction lines of high-temperature phases in Montmorillon montmorillonite: untreated (1); exchanged with H (2), Li (3), Na (4). Same notations as in Figure 2.

ions. Sodium, potassium, and cesium presumably promote sintering to so great a degree that otherwise observed crystallization processes were not always found. Lithium is presumed to promote crystallization by its high ability to migrate into silicate structures. The expulsion of iron can be visualized by the change in color from cream to dark brown in the sample heated over 1200°C. Incidentally, this migration is not restricted to iron in exchange position; samples with a high proportion of iron in the octahedral sheets and exchanged with hydrogen (Fig. 11, diag. 2) give exactly the same diagrams as those samples that are poor in octahedral iron but exchanged with this cation (Fig. 3, diag. 5).

The action of a large excess of such salts as Ca, Mg, or Ba chlorides (Figs. 7, 8) can now be understood. Being located outside the particles, they have little influence, if any, on the migration of the interlayer and octahedral cations and, as a consequence, they do not affect the temperature of crystallization of the silica phases. But they react with the clay on the edges and surfaces of the particles, thus increasing the proportion of the minor constituents and, at the same time, diminishing the quantity of quartz and cristobalite.

Finally, the high-temperature transformations in montmorillonites can be interpreted as the sum of two reactions; reorganization of the silica layers and combination of the other components on the edges of the particles. The first one is the more important; it occurs in the same way in all the samples, the main variation being the temperature of initiation which depends upon the nature
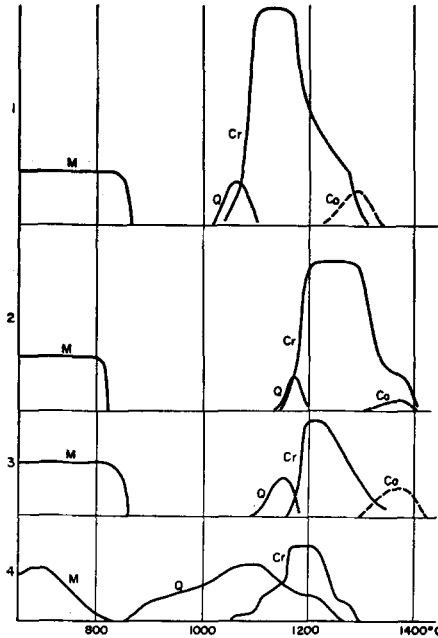
FIGURE 10. — Intensities of diffraction lines of high-temperature phases in Amory mont-morillonite: untreated (1); exchanged with H (2), Mg (3), Li (4). Same notations as in Figure 2.

of the interlayer and octahedral cations. The second one is more complex but involves only a small amount of matter.

A comparison of the diagrams with the chemical compositions and structural formulas given in Table 1 was attempted. These data reflect as exactly as pos-sible the average composition of the clay, but the samples are not homogeneous; intimate mixtures of particles having different structure and composition can not be detected; the regularity of the lattice in each particle is questionable, either because of the distribution of the ions within the sheets or because of the very possible presence of mixed layers; also, small quantities of impurities may be included in the analyzed compositions. It seems, therefore, that the accuracy of the chemical and structural data is far less than the sensitivity of the high-temperature reactions. It follows that a close correlation of the formulas and the new phases is not to be expected, and, further, that an accurate prediction of high-temperature phases can not be made from a chemical analysis of the clay.

Phase transformations are used by geologists in evaluating the conditions of metamorphism. The data presented herein show the importance of initial struc-tures and traces of some extraneous cations. In fact, these may be the control-ling factors.
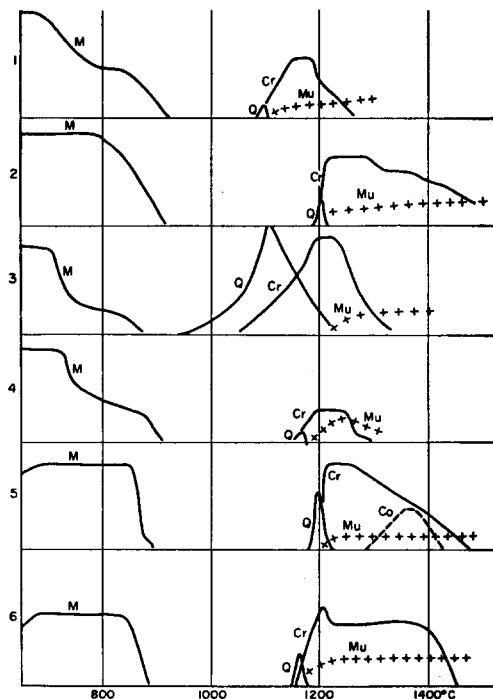
FIGURE 11. — Intensities of diffraction lines of high-temperature phases in Belle Fourche montmorillonite: untreated (1) ; exchanged with H (2), Li (3), Na (4), Mg (5), Al (6). Same notations as in Figure 2.

ACKNOWLEDGMENTS

REFERENCES

Kerr, P. F., and others, 1950, Analytical data on reference clay minerals: in Reference clay minerals, A. P. I. Res. Project 49, Prelim. Rept. 7, 161 p.
Ross, C. S., and Hendricks, S. B., 1945, Minerals of the montmorillonite group: U. S. Geol. Survey Prof. Paper 205-B, p. 23–79.