

SYNTHESIS AND STABILITY OF MINERALS IN THE SYSTEM $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ *

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ABSTRACT

Phase equilibria in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ were studied in order to obtain further information on the stability of metamorphic minerals and mineral assemblages. The equilibria are described in terms of composition triangles, of phases in equilibrium with H_2O . Seventeen sets of triangles are given to describe changing equilibria with increasing temperature, at a constant water pressure of 10,000 psi. Syntheses of phases and equilibrium data are discussed, along with factors influencing the attainment of equilibrium.

At low temperatures montmorillonite "solid solutions" cover a large field in the high-silica portion of the diagram, whereas mixtures high in magnesia yield aluminian serpentine, in combination with other phases. Alumina hydrates and kaolinite dominate the high-alumina portion of the diagram in this temperature range. Aluminian serpentine at higher temperatures gives way to clinocllore. Cordierite, the only anhydrous ternary phase encountered, is stable in equilibrium with H_2O above ca. 500°C ., and the stable joins, quartz-cordierite- H_2O and cordierite-spinel- H_2O , divide the quaternary system into two areas: that part dominated by the alumino-silicates, and the area involving magnesium silicates. In the alumina-silica side of the system pyrophyllite is the hydrate stable to the highest temperature, 575°C .; but in the magnesia-silica side, talc is stable to a much higher temperature, 780°C . Applications of the data obtained to geologic problems are discussed.

INTRODUCTION

An understanding of the phase equilibria among common metamorphic minerals is of the utmost importance for a correct interpretation of the manner of formation of metamorphic rocks. The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ is of considerable interest, for it contains a large number of common metamorphic minerals, among them the anhydrous minerals, spinel, enstatite, forsterite, andalusite, kyanite, sillimanite, mullite; the alumina hydrates; clays of the kaolinite and montmorillonite groups; and chlorites and amphiboles. The determination of the phase equilibrium relations among the various minerals would provide information on formation of certain mineral assemblages, and furthermore provide a framework for the systematic addition of other components.

Moreover, the importance of this system is not limited to metamorphic rocks: it is also the basic system conditioning the relations among the minerals formed in argillaceous sediments. It is the only quaternary system involving not only typical but all the common clay minerals, and as such its study is basic to the whole field of clay and soil mineralogy.

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Besides these general considerations the solution of several specific problems in metamorphic and sedimentary petrology could be greatly furthered by the knowledge of phase equilibria in this system. Such problems involve for instance the determination of the conditions of stability of assemblages involving cordierite, one of the more common metamorphic minerals. Thus, the cordierite-forsterite-spinel combination (a stable triangle at solidus temperatures in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$) is incompatible with the association, cordierite-enstatite-spinel (a more common metamorphic assemblage). Other problems include the alternative between the stable associations of cordierite and corundum, or of mullite and spinel; both combinations occur in nature, but they represent a "crossed" relationship on the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ diagram.

A determination of the phase equilibria in the four-component system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ involves the equilibria in the four bounding ternary systems, which have been described in some detail. Envisioning the system as a tetrahedron with $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ as the base and H_2O at the apex, the other three sides are composed of the ternary systems, $\text{MgO-SiO}_2\text{-H}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$. The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ was investigated by Rankin and Merwin (1918) and later modified by Bowen and Greig (1924), Greig (1927), and recently by Foster (1950) and Keith and Schairer (1952). The system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ was studied by Bowen and Tuttle (1949), the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ by Roy and Osborn (1952*a*, 1954) and the system $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$ by Roy, Roy and Osborn (1953). The present work in the quaternary system (see Roy, 1952) was carried out contemporaneously with that of Yoder (1952) in an attempt to add to the previous knowledge and obtain a more complete picture of the quaternary equilibria.

The importance of H_2O as a component for study of equilibria in metamorphic mineral systems has been ably demonstrated in the studies of the systems $\text{MgO-SiO}_2\text{-H}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ and $\text{MgO-Al}_2\text{O}_3\text{-H}_2\text{O}$ referred to above, and in other hydrothermal studies. The use of H_2O as one component enables one to study certain anhydrous mineral equilibria at subsolidus temperatures which may approach the temperature of formation of "high-rank" metamorphic rocks. In addition, at successively lower temperatures various hydrates are stable in the presence of excess H_2O , and the "lower-grade" metamorphic rock mineral families of amphiboles and chlorites are encountered. At still lower temperatures the layer lattice clay minerals are stable.

EXPERIMENTAL

Equipment

A hydrothermal assemblage employing several types of high-pressure vessels was used, enabling the attainment of water pressures up to a

maximum of 40,000 psi and temperatures up to 900° C. The following types of pressure vessel were used, some of which are standard equipment, and others developed in this laboratory: (1) Morey-type closed bomb (Morey and Ingerson, 1937) of 20 cc. capacity, top of 41–50 Cr-Mo steel and bottom of 18-8 stainless steel. The practical upper temperature limit was 550° C. at 10,000 psi, (2) 4 cc. capacity bomb of the above type, top and bottom both of 316 stainless steel. Temperatures of 600° C. at 10,000 psi were easily maintained. These have the further advantage of being cheaper, (3) Tuttle apparatus (Tuttle, 1949), using various sizes of small capacity stainless steel, Inconel-X and Stellite vessels. Temperatures up to 900° C. at 5,000 psi could be sustained, (4) "Test-tube" bomb (Roy and Osborn (1952*b*)) essentially a thick-walled steel test-tube attached to pressure tubing by a cone-in cone seal, about 8–9 inches long, $\frac{3}{4}$ – $1\frac{1}{2}$ inches outer diameter and $\frac{1}{8}$ – $\frac{1}{4}$ " i.d., made of stainless steel, Inconel-X and Stellite. Temperatures up to 850° C. at 5,000 psi could be maintained indefinitely using the latter alloy. Shorter runs of several hours could be made up to 925° C.

Pressure was generated by three types of pumps: (1) A piston-type pump operating on water, supplied by American Instrument Company, (2) A pump manufactured by Sprague Instrument Company, based on the pressure multiplying piston working off laboratory air pressure and supplying a relatively large volume of fluid per stroke, was used up to 25,000 psi, (3) A "jack-type" pump (Roy and Osborn, 1952*b*) in which the pressure is generated by compression of water in a stainless steel chamber by a commercial "jack." This pump was most useful for attaining high pressures quickly.

The vessels were attached by pressure tubing through a system of valves and bourdon-type gauges to the pumps described above, so that each vessel could be independently maintained at a specific temperature and pressure. The vessels were heated in chromel-wound furnaces, the temperatures being automatically regulated.

An additional assemblage used was a grinding apparatus (Roy and Osborn, 1952*b*) consisting of closed Morey-type bombs containing the sample, a determined quantity of water, and several stainless steel rods. The bombs were attached to shafts and rotated by a chain drive, and heated in chromel-wound furnaces. The samples were thereby subjected to grinding action while they were heated under H_2O pressure. Satisfactory runs could be made up to only 450° C. at approximately 10,000 psi.

In general, the accuracy of the temperature control was of the order of $\pm 3^\circ$ C., but considering the differences among the different types of vessels an overall reproducibility of $\pm 5^\circ$ can be attained in the not unfavorable cases. Especially since the effect of pressure was slight in most cases, no effort was made to calibrate the pressure gauges, except to check

several gauges against one another. Pressures are therefore only accurate to about $\pm 3\%$ of the value given.

Starting Materials

Natural minerals, synthetic minerals, and various chemical mixtures, which in some cases required purification, were used as starting materials. Among the natural minerals used were the following: Cordierite from Möreländ, Kragero, Norway, U. S. National Museum, No. R-6993; spinel (ruby) from Ceylon, Genth collection, No. 234.2, The Pennsylvania State University; sapphirine from Fiskernäs, Greenland, USNM No. 94335; andalusite from Custer, S. Dakota; kaolinite from Macon, Georgia, A.P.I. No. 3; Langley kaolinite, and Florida kaolinite; clinocllore from Westchester, Chester County, Pa., Genth collection, No. 468.4. Synthetic minerals were prepared as described in the section on synthesis.

In some cases mechanical mixtures of reactive C.P. oxides were used; e.g., MgO or MgCO₃, γ -Al₂O₃, and silicic acid. In the glass-forming area glasses were prepared, but most frequently used was a mixture prepared from solution which could be made for any composition. Magnesium and aluminum nitrates were dissolved together in a minimum amount of water, ethyl orthosilicate was dissolved in alcohol, the two solutions mixed together in excess alcohol, evaporated gently until a rigid gel formed, and heated to about 400° C. to decompose the salts, leaving an intimate oxide "gel," possessing little if any long range order. The general applicability, the relative ease of making the mixtures combined with the rapidity of operation lead us to recommend the method for phase equilibrium studies in both "dry" and "wet" systems.

Techniques

The samples were prepared by one of the methods described above, then a small amount of sample put in a gold or platinum envelope, and in most cases surrounded by a larger envelope containing more of the sample as a buffer. One to four samples were heated in a bomb at the desired temperature and pressure for periods from a few hours to several weeks, the longer periods usually being required to approach a condition of equilibrium. In some cases the grinding apparatus was used, particularly to study the decomposition of a mineral which was not realized by ordinary hydrothermal treatment. After a run the bomb was quenched in a vessel or stream of water, in attempt to arrest the equilibrium, requiring usually less than 15 seconds to reach 100° C. and $\frac{1}{2}$ to 5 minutes to reach room temperature. It should be mentioned that in no case other than for the brucite-periclase transition was difficulty in arresting the equilibrium encountered using the technique described.

Identification

The phases present in the products were identified in all cases by their x-ray diffraction patterns, using either Norelco 90° instrument or a G.E. XRD-3 165° diffractometer, employing filtered Cu radiation. Usually the samples were also studied under the petrographic microscope, though in most instances the crystal size of the product was too small to enable positive identification optically. When necessary, observations were

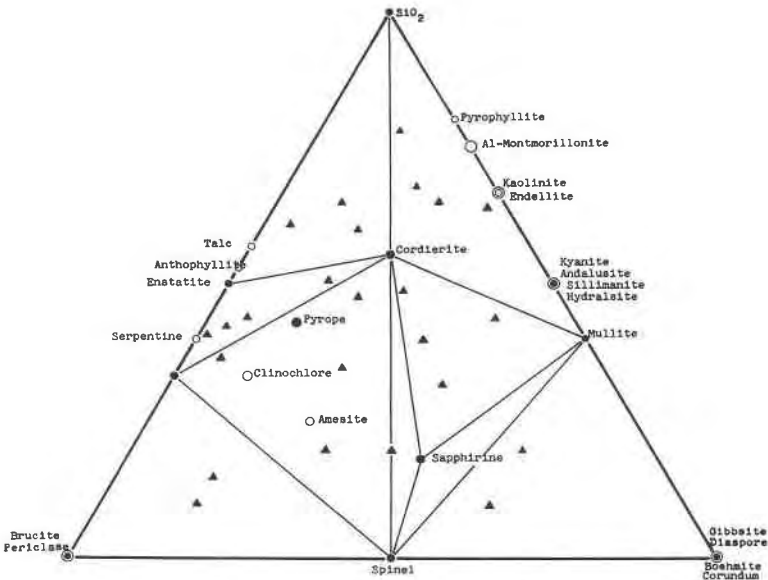


FIG. 1. Compositions studied in the system $MgO-Al_2O_3-SiO_2-H_2O$, projected on the $MgO-Al_2O_3-SiO_2$ base.

Open circles are used to indicate the compositions of hydrated minerals (which do not lie on the base of the tetrahedron) and solid circles, anhydrous mineral phases. Triangles show the compositions of other mixtures studied.

made under the electron microscope, RCA EMU model; and differential thermal analysis was employed for certain problems.

RESULTS

Synthesis of Minerals

Minerals encountered. The composition of minerals occurring in the system $MgO-Al_2O_3-SiO_2-H_2O$ is given in Fig. 1 as a projection on the $MgO-Al_2O_3-SiO_2$ base, along with other points representing compositions of mixtures used. In addition to the simple oxide components, the minerals synthesized in the present study were the following:

	<i>Anhydrous</i>		<i>Hydrous</i>
Mullite	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	Brucite	$\text{Mg}(\text{OH})_2$
Andalusite	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$	Gibbsite	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Enstatite	$\text{MgO} \cdot \text{SiO}_2$	Boehmite, Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Forsterite	$2\text{MgO} \cdot \text{SiO}_2$	Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Spinel	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	Hydralsite	$2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$
Cordierite	$2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$	Pyrophyllite	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
		Talc	$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
		Montmorillonite	variable, Mg-Al-Si
		Clinochlore	$5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$
		Aluminian Serpentine	$5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$

Absences. Notable absences among the anhydrous minerals synthesized are sillimanite, kyanite, pyrope and sapphirine, and among the hydrous minerals the anthophyllite-gedrite amphiboles. All attempts to synthesize these minerals as equilibrium phases failed. The synthesis of sillimanite has been reported previously (Morey, 1942; Balconi, 1941; Michel-Levy, 1950), but because of similarities to mullite, it is doubtful if identification of the product of synthesis was positive. The synthesis of kyanite or pyrope has not been reported. Sapphirine was found to have a small stability field in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ at liquidus and solidus temperatures (Foster, 1950, Keith and Schairer, 1952), but was not encountered in the present study as a stable phase at lower temperatures (below 900°C .) in the presence of excess water. It has been decomposed, however, by grinding at 390°C . and 5,000 psi.

Syntheses of Interest

Andalusite was synthesized in the present study, probably for the first time. Synthesis was achieved from alumina-silica mixtures only in the presence of seeds of natural andalusite. The addition of a small amount of MgO, however, apparently aided the crystallization, and andalusite was formed from such mixtures in the absence of seed crystals. Hydrothermal treatment of various kaolinite samples (Langley, Macon and Florida) also yielded the mineral, and it is suggested that the presence of impurities may play a role in its formation. No definite stability range was established, but andalusite formed in the temperature range $450\text{--}700^\circ\text{C}$., with H_2O pressures of 10,000 to 30,000 psi, higher pressures definitely favoring its formation. It is conceivable that andalusite is metastable in this pressure range and that mullite is the only stable aluminosilicate below 30,000 psi. A more complete description of the synthesis is given by Roy (1954).

Hydralsite has been described by Roy and Osborn (1952*a*, 1954) in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, and is believed to be a micaeous type of crystal, related to pyrophyllite, but having a composition of approximately

$2Al_2O_3 \cdot 2SiO_2 \cdot H_2O$. This phase was also formed as one product from mixtures in the system $MgO-Al_2O_3-SiO_2-H_2O$, at temperatures ranging from about 410 to 550° C., with H_2O pressures of 5,000 to 20,000 psi. Whether or not Mg^{2+} enters the structure has not been established. The apparent "stability" of this phase in the presence of Mg^{2+} , however, suggests that such a structure is the easiest one to form from mixtures relatively high in alumina, above the upper stability temperature of kaolinite, in the absence of large cations which would bring about the formation of a true mica.

Serpentine phases. The question of the control of morphology by composition was investigated by Roy and Roy (1952, 1954) by synthesizing a large number of serpentine-like phases containing ions of varying sizes in both the tetrahedral and octahedral layers. It was established that composition was a necessary but not sufficient consideration in determining the morphology of the mineral formed. Starting with chrysotile, $Mg_6Si_4O_{10}(OH)_8$, and attempting various substitutions, the most important among the substituent ions was Al^{3+} for Mg^{2+} and Si^{4+} . It is of considerable interest to note that the substitution was not of the heptaphyllitic-octophyllitic variety—that is, the introduction of Mg^{2+} ions into the vacant octahedral lattice positions of the octahedral layer in kaolinite, or the formation of vacant sites by substituting Al ions into the octahedral Mg layer of chrysotile. In other words, there is no solid solution between kaolinite and chrysotile.* The substitution takes place only by the very common mechanism of the exchange of $2Al^{3+}$ ions for $1Mg^{2+}$ and $1Si^{4+}$ ion. Along a composition line extending outwards from the chrysotile composition a single "aluminian serpentine" phase is obtained, up to and including the composition $5MgO:1Al_2O_3:3SiO_2$. This composition corresponds to the substitution of $2(Al^{3+})$ ions for $(Mg^{2+} + Si^{4+})$ in the chrysotile formula. Further data obtained on a mixture with higher Al_2O_3 content (see Table 1, mixture XL1, reaction 14) ($50:30:20$, $MgO:Al_2O_3:SiO_2$) indicate that, although from this composition at temperatures between 350° C. and 640° C. a serpentine phase is obtained along with other phases, the serpentine phase is not identical with that obtained from the $5MgO:1Al_2O_3:3SiO_2$ composition—the basal spacings being somewhat smaller—7.07 Å rather than 7.17 Å. This would indicate that the limit of the substitution is not reached when $1Mg^{2+}$ and $1Si^{4+}$ ion have been replaced by $2Al^{3+}$ ions and may extend as far as amesite. The actual extent of solid solution and the relation to

* That such solid solution does not exist or at least is not extensive is further demonstrated by the fact that the montmorillonite field intersects the chrysotile-kaolinite join (see triangles 1-4, Fig. 3).

TABLE 1. PHASE EQUILIBRIUM DATA FOR THE SYSTEM MgO-Al₂O₃-SiO₂-H₂O

MgO	Compo- sition Mol. % Al ₂ O ₃	SiO ₂	Run No.	Temp. °C.	Press. psi	Time days	Phases Present*
2. Magnesium Montmorillonite \rightleftharpoons Talc+H ₂ O							
43		57	5251	230	5,000	5	Monty?
43		57	5252	230	5,000	29	Monty?
43		57	5313	275	10,000	21	Talc
4. Brucite+Diaspore \rightleftharpoons Spinel+H ₂ O							
40	25	35	5321	350	10,000	5	AS+1 boehm
			5238	495	20,000	24	AS+spinel
50	30	20	5380	350	20,000	7	Boehm+AS
26	42	32	5317	350	10,000	5	Boehm+AS?
			5241	495	20,000	24	AS+cor?+spinel?
5. Kaolinite \rightleftharpoons Hydralite+Al-M+H ₂ O							
12	44	44	5361	398	10,000	5	Kaol+1 monty
			5359	410	20,000	6	Monty+hyd+AS
3	33	64	5324	372	10,000	4	Kaol+v 1 monty
			5360	398	10,000	5	Kaol+1 hyd+monty
			5310	410	20,000	4	Monty+hyd+1 AS
9. Montmorillonite \rightleftharpoons Pyroph.+Hyd+AS+H ₂ O							
35	4	61	F-308	390	20,000	5	Monty
35	4	61	5442	425	5,000	4	Talc+monty
25	10	65	5517	365	8,000	8.5	Monty
25	10	75	5170	420	20,000	18	Monty
25	10	65	5150	475	20,000	6	Crist+?
25	10	65	5015	500	4,000	11	Talc+?
9.5	12.5	78	4511	350	20,000	7	Monty
	12.5		F-309	390	20,000	5	Monty
	12.5		5303	450	20,000	4	Monty+1 crist
	12.5		5148	470	20,000	6	Pyroph+crist
3	33	64	5379	350	20,000	7	Kaol+1 monty
	33		5310	410	20,000	4	Monty+hyd+1 kaol
10	25	65	5190	350	20,000	9	Monty
	25		5269	435	20,000	5	Monty (+v 1 hyd?)
	25		5206	450	20,000	15	Monty+hyd+pyroph
50	6	44	4793	450	5,000	7	Mont+AS
50	6	44	4816	450	10,000	11.5	Mont+AS
54	3	43	4809	410	5,000	5.5	AS
10	25	65	5149	470	20,000	16	Monty+pyroph+hyd?
			5209	490	20,000	13	Hyd+AS
12	44	44	5361	398	10,000	5	Kaol+1 monty
	44		5359	410	20,000	6	Hyd+AS+monty
	44		5291	475	20,000	6	Hyd+1 AS+V 1 monty
	44		5208	490	20,000	13	Hyd+AS?+and
22	22	56	4490	360	12,000	10	Monty+AS?
	22		5310	410	10,000	4	Monty

TABLE 1—(continued)

MgO	Compo- sition Mol. % Al_2O_3	SiO_2	Run No.	Temp. °C.	Press. psi	Time days	Phases Present*
	22		5305	410	20,000	4	Monty+l AS
	22		5258	450	20,000	27	AS+clinocllore(+?)
	22		5152	475	20,000	6	AS+pyroph+monty?
	22		4980	520	7,500	13	Cord+talc?
	10. Pyroph+AS (or Cl)+Hyd (or and.) \rightleftharpoons Cordierite+H ₂ O						
22	22	56	5256	455	20,000	16	Pyroph+AS+?
	22		5152	475	20,000	6	AS+pyroph+Cl?
	22		4716	500	5,000	7	Cl+AS
	22		4980	520	7,500	13	Cord (+pyroph?)
	22		4939	530	8,000	10	Cord+pyroph
	22		4664	545	16,000	30	Cord+Cl+mull
22	22	56 ⁿ	4628	300	15,000	25	Cord+AS+Cl
	22	56 ^{ng}	4720	400	3,000	3	Cord+l AS?
	22	56 ^{ng}	4903	400	5,000	13	Cord+AS
	22	56 ^{ng}	5099	465	5,000	8	Cord+l AS
	22	56 ^{ng}	5110	475	5,000	20	Cord+v l AS
31	20.9	48.1	5121	515	10,000	22	Cord+AS+crist+mull?
	20.9		5118	600	20,000	20	Cl (+AS)+cord+l spinel (+cor?)
40	25	35	4990	565	5,000	13	Cord+AS+spinel
	25		5236	595	10,000	24	Cord+AS (+l Cl)+spi- nel (+l cor?)
50	30	20	4989	565	5,000	13	AS+spinel+cord?
23	28	49	5122	515	10,000	22	Crist+cord+AS+mull?
26	42	32	4984	645	5,000	15	Spinel+mull+cord+cor
	42		4987	565	5,000	13	Cord+spinel
	42		5145	695	20,000	8	Cord+cor+spinel
4	5	2	4267	450	7,500	11	AS+cor+spinel
4	5	2	5002	580	4,000	14	Cord+spinel+mull
4	5	2	4239	675	8,000	14	Cord+cor+spinel
12	44	44	5213	530	20,000	18	And+l cord+l cor+l AS
	44		5339	575	30,000	5	Cord+cor
	44		5180	715	20,000	11	Cord+cor+mull
25	15	60	4979	520	7,500	13	Qtz+cord+talc
25	10	65	5150	475	20,000	6	Crist+AS?
	10		4868	500	12,000	7	Cl+AS
	10		5155	535	20,000	8	Cl+cord
10	25	65	5240	495	20,000	24	Hyd+AS+pyroph?
	25		4978	520	7,500	13	Qtz+mull+pyroph+cord
	25		5187	525	20,000	7	Hyd+?
	25		5228	525	30,000	4	Hyd+AS
	25		5212	530	20,000	18	Cord+crist
	25		5156	535	20,000	8	Pyroph+Cl+cord
	25		5384	535	20,000	10	Cord+hyd+AS+and +mull?
	25		4949	618	8,000	19	Cord+mull+crist

TABLE 1—(continued)

MgO	Compo- sition Mol. % Al ₂ O ₃	SiO ₂	Run No.	Temp. °C.	Press. psi	Time days	Phases Present*			
12	20	68	4977	520	7,500	13	Qtz+cord+pyroph			
9.5	12.5 12.5	78	5290	500	20,000	6	Pyroph+crist+l AS			
			5154	535	20,000	8	Pyroph+crist+l cord+l AS			
11. Aluminian serpentine (or Cl?) + brucite \rightleftharpoons forsterite + spinel + H ₂ O										
70	15	15	5273	500	10,000	3	AS+bru+spinel			
			4898	510	10,000	14	Bru+AS+spinel			
			5307	525	20,000	2	AS+bru+spinel			
			5426	540	20,000	6	Bru+spinel+forst+AS			
			4950	560	5,000	23	Spinel+forst+bru			
			5418	560	20,000	1	Bru+spinel+forst+AS			
75	15	10	5023	500	10,000	1	Bru+AS+spinel			
			5314	500	20,000	2	AS+bru+spinel			
			5367	500	25,000	11	AS+bru+spinel			
			5027	510	10,000	0.5	Bru+AS+spinel			
			4897	510	10,000	14	Bru+AS+spinel			
			4974	520	7,500	13	Bru+forst+spinel			
			5308	525	20,000	2	Bru+AS+spinel			
			5226	525	30,000	4	Bru+AS+spinel			
			5205	530	20,000	2	Bru+spinel+forst			
			5233	535	30,000	3	Bru+spinel+forst			
			12. Pyroph \rightleftharpoons Mull (or and) + Qtz (Crist) + H ₂ O							
			10	25	65	5156	536	20,000	8	Pyroph+Cl+cord
5384	535	20,000				10	Cord+pyroph (?) + AS (?) + and (?) + l mull			
5175	555	15,000				10	Cord+crist+pyroph+ mull			
4953	560	5,000				23	Mull+cord+?			
5279	595	30,000				6	Cord+mull+cor?			
4949	618	8,000				19	Cord+mull+crist			
9.5	12.5	78	5154	535	20,000	8	Pyroph+crist+l cord+l AS			
			5174	555	15,000	10	Cord+pyroph+mull			
			4953	560	5,000	23	Mull+crist+cord?			
			5281	595	30,000	6	Cord+l Cl+l and+l mull			
12a. Brucite \rightleftharpoons periclase + H ₂ O										
75	15	10	4880	625	12,000	1	Forst+spinel+bru			
			4983	645	5,000	15	Forst+per+spinel			
			4875	725	12,000	2	Forst+spinel+per			
70	15	15	4881	625	12,000	1	Forst+spinel+l bru			
			4605	705	10,000	8	Forst+spinel			
14. Clinocllore \rightleftharpoons cord + forst + spinel + H ₂ O; and Clinocllore \rightleftharpoons AS										
56	11	33 ^{ng}	5492	300	5,000	120	Cl			
56	11	33 ^{ng}	5298	400	5,000	25	Cl			
56	11	33	5257	450	20,000	27	Cl+AS			
			5294	475	20,000	6	Cl(?) + AS + l talc			
56	11	33	5288	500	20,000	6	Cl (?) + AS			
			5238	495	20,000	24	Cl+AS			

TABLE 1—(continued)

MgO	Compo- sition Mol. % Al_2O_3	SiO_2	Run No.	Temp. °C.	Press. psi	Time days	Phases Present*	
	11		5132	515	23,000	16	AS	
	11		5133	515	23,000	16	AS	
	11		4975	520	7,500	13	AS	
	11		5234	535	30,000	3	AS	
	11		5153	535	20,000	8	Cl+AS	
	11		5173	555	15,000	10	AS+Cl+talc?	
	11		5139	559	23,000	9	Cl+AS	
	11		5138	559	23,000	9	AS	
	11		4988	565	5,000	13	AS	
	11		5071	605	10,000	7	AS+1 talc+1 spinel	
	11		5235	595	10,000	24	AS+1 Cl+talc+spinel	
	11		5246	600	10,000	28	AS+1 Cl+talc	
	11		5117	600	20,000	20	Cl+AS+spinel	
	11		5147	695	20,000	8	Cl+1 talc	
	11		5214	700	20,000	6	Cl+1 spinel?	
	11		5177	715	20,000	11	Forst+cord (+talc) +spinel	
	11		4958	725	6,000	22	Forst+enst+spinel	
	11		5158	735	20,000	2	Talc+forst+spinel	
	11		5141	720	10,000	8	Cord+forst (+talc) +spinel	
31	20.9	48.1	5121	515	10,000	22	Cord+AS+crist+mull?	
	11		5136	605	10,000	16	Cord+AS+talc	
	11		5118	600	20,000	20	Cl+cord+1 spinel+AS +cor?	
	11		5215	700	20,000	6	Cord+Cl	
	11		5218	715	20,000	10	Cord+forst+1 spinel	
	11		5142	720	10,000	8	Cord+spinel+talc?	
40	25	35	5022	670	10,000	7	Cord+talc+spinel	
	25		5146	695	20,000	8	Cord+Cl+spinel	
	25		4607	705	10,000	8	Talc+cord+spinel	
	25		5157	738	20,000	2	Talc+cord+spinel	
	25		5194	732	20,000	5	Cord+spinel+forst	
	25		5007	745	10,000	10	Enst+spinel+cord	
22	22	56	5258	450	20,000	27	AS+clinochlore (+?)	
	22		5256	455	20,000	16	Pyroph+AS	
			15. $Talc \rightleftharpoons Enst + qtz + H_2O$					
25	10	65	5039	750	10,000	2½	Cord+talc+crist+qtz	
	10		5183	775	15,000	5	Talc+cord (+crist?)	
	10		4448	802	8,000	6	Cord+enst+crist	
	10		5167	800	15,000	2	Cord+crist+enst	
50	30	20	5166	800	15,000	2	Cord+spinel+forst	
	30		4449	802	8,000	6	Spinel+enst	
40	25	35	5165	800	15,000	2	Cord+spinel+enst	
	25		4445	802	8,000	6	Cord+spinel+enst	

ⁿ=natural mineral.

^g=grinding run.

* Abbreviations used: Monty=montmorillonite; AS=aluminian serpentine; boehm=boehmite; cor=corundum; kaol=kaolinite; hyd=hydralsite; crist=cristobalite; pyroph=pyrophyllite; and=andalusite; cl=clinochlore; cord=cordierite; mull=mullite; qtz=quartz; bru=brucite; forst=forsterite; per=periclase; enst=enstatite; l=little. Al-M=aluminum montmorillonite.

the amesite problem is a subject for further detailed investigation.*

Aluminian serpentine is obtained from the lowest temperatures investigated (350° C.) up to a maximum of 650° C. at 10,000 psi in runs as long as 3 weeks. This phase yields a sharp *x*-ray pattern in contrast to the broadened reflections in the pattern for chrysotile; electron micrographs show the reason for this since, instead of the disordered tubes of chrysotile, well-formed hexagons are obtained with this composition (see Roy and Roy, 1954). However, this composition is also that of the chlorite clinochlore, and as Yoder (1952) first showed, on prolonged heating, under certain conditions the aluminian serpentine† converts to clinochlore. Yoder obtained partial or complete conversion of the aluminian serpentine to clinochlore in some runs (at 600° C. and 15,000 psi from its own composition). While using a pressure of 10,000 psi we found it virtually impossible to convert the serpentine to a chlorite. In later runs we demonstrated that both starting material and the pressure greatly affect the rate of this reaction. Using the organic-nitrate mixtures conversion is quite rapid (thus at 535° C., 20,000 psi in 8 days most of the product is clinochlore). While no conversion has been possible below 10,000 psi and at this pressure runs as long as 24 and 28 days show only a very small amount of clinochlore, at a pressure of 23,000 psi a fair degree of conversion is achieved at the same temperature in 9 days (see data, Table 1, reaction 14). Thus whereas this does not demonstrate the existence of a "pressure bottom" for the formation of clinochlore—it does show that high pressures very greatly enhance the formation of this mineral.

The problem of the metastability of the aluminian serpentine is consequently not easily soluble; from our data it appears that clinochlore is the stable phase at least as low as 450° C., at which temperature it forms slowly at the expense of the serpentine. The fact that it does not form below this temperature and also that we were not able to decompose it by "grinding" (see Roy and Osborn, 1952*b*) at 400° C. and 5,000 psi for 3 months, still do not prove that it (clinochlore) is not stable below this temperature. However, from the fact that chrysotile is stable up to 500° C. (at 15,000 psi) one would infer that the aluminian phase (of the 5:1:3 composition, or perhaps one containing a smaller percentage of Al_2O_3) has a true stability range, and persists metastably to much higher temperatures.

* Since this work was completed, extended study has been made of the magnesia-alumina chlorites by Nelson and Roy (1953).

† While this phase is here referred to as aluminian serpentine, it may very well correspond to "antigorite" in nature—indicating therefore that the essential difference between platy antigorite and tubular fibrous chrysotile is compositional, the additional R_2O_3 giving rise to the former.

The structural relationship between the aluminian serpentine and clinochlore also constitutes a very interesting problem. The former is a 2-layer structure, and the latter a 3-1-layer structure, illustrated in Fig. 2. One can immediately see that this constitutes a special type of polymorphism. The sequence of layers is identical: brucite-silica-brucite-silica in both cases. What is involved in the transition of aluminian serpentine to clinochlore is the rearrangement of bonds, so that every alternate layer of Si^{4+} ions in the silica layer has to completely sever its bonds

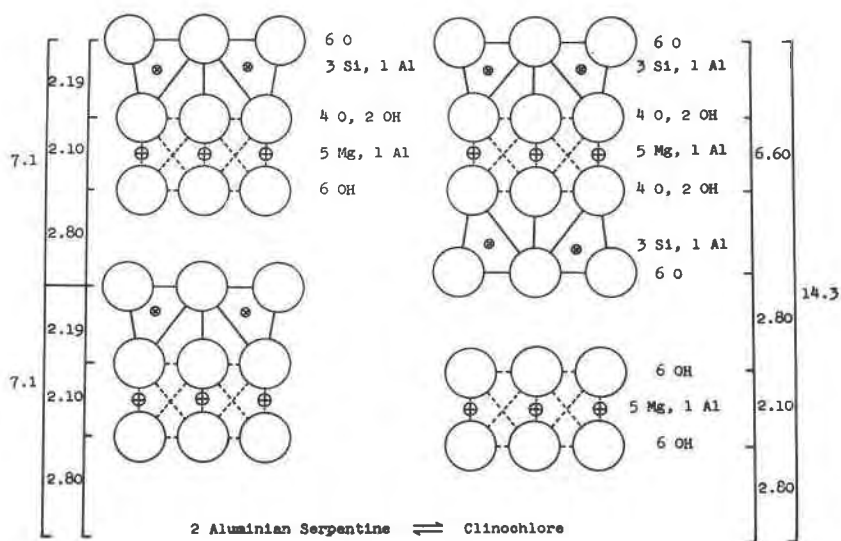


FIG. 2. Schematic diagram showing structural relationship between aluminian serpentine and clinochlore (a - b projection). Distances along the " c " axis are shown in Å.

with the O^{2-} ions of the original layer and form new Si-O bonds with the linked tetrahedra "pointing" in the opposite direction. The energy barrier to this major rearrangement must, of course, be very large and probably accounts for the extreme sluggishness of the reaction.

Montmorillonite. The synthesis of montmorillonite was achieved from a variety of compositions high in silica, and montmorillonites grown in different parts of the field were difficult to distinguish from one another because of the very small differences in lattice dimensions, or in expansion of the lattices upon introduction of a complex such as ethylene glycol. A number of compositions throughout a wide composition field produced essentially pure montmorillonite, e.g., the following molar ratios of $MgO-Al_2O_3-SiO_2$: 25:10:65; 22:22:56; 10:25:65 and 9.5:12.5:78.

In the system $Al_2O_3-SiO_2-H_2O$ (Roy and Osborn, 1952*a*, 1954) the

existence of a pure "aluminum montmorillonite" end-member was described, i.e., one with an ideal composition of about $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The possible existence of a pure magnesium montmorillonite, with a magnesia-silica ratio near that of talc, i.e., $3\text{MgO} : 4\text{SiO}_2$, was investigated. Talc was found to be stable as low as 275°C ., but at lower temperatures the x -ray pattern of the substance was much more diffuse, resembling a montmorillonite. Expansion of this lattice with ethylene glycol was attempted and the basal spacings were definitely affected but the pattern obtained was so weak that satisfactory measurable results could not be obtained (for further details see General Discussion). The substitution of as little as 4 mol. per cent Al_2O_3 in the talc composition yielded essentially a single phase montmorillonite, at temperatures up to 400°C . Approaching from the opposite side of the diagram, a large compositional area appeared to yield montmorillonite phases only.

It was hoped that information could be obtained as to whether there are two distant types of montmorillonite—i.e., the "heptaphyllitic" or beidellite type of montmorillonite, in which the octahedral layer consists largely of trivalent ions, and the "octaphyllitic" or saponite-hectorite type of montmorillonite in which the corresponding layer contains mostly bivalent ions. As discussed in a later section, it was substantiated that there is little, if any, solid solution between the higher temperature counterparts, talc and pyrophyllite, but a greater chance for extensive solid solution would be expected in the "looser" lower-temperature montmorillonite structures. The results in this aspect of the study were not positive, inasmuch as difficulty was encountered in distinguishing a high-magnesian montmorillonite from a high-aluminian montmorillonite by its x -ray diffraction pattern. A difference of about $.2\text{ \AA}$ was found in the basal spacings between the montmorillonites with less than 10 per cent Al_2O_3 and those having less than 10 per cent MgO ; the spacings for the former being 14.15 \AA and the latter 14.40 \AA (when treated and dried under identical conditions). Furthermore, using expansion with ethylene glycol, and attempting to obtain maximum resolution with $\frac{1}{3}^\circ$ per min. scanning the differences in spacing were approximately constant, 17.05 and 17.25 \AA for high magnesia and high alumina phases, respectively. While the second decimal place in the above figures is not significant the differences were real and reproducible at different times with different slides and instrument settings. The problem of the existence of solid solution among these end member types hinges on the ability to distinguish between the case where a single montmorillonite phase is present and the case in which two distinct montmorillonite phases coexist. Therefore a mechanical mixture of a high magnesia and a high alumina phase was prepared and patterns were obtained after drying at 100°C . and also after saturation with ethylene glycol. It became evident

that the x-ray data would be far from unequivocal in their application to the problem at hand. Due to the width of the peaks (rarely less than $0.5^\circ 2\theta$ at half height for the single phases) the overlap was so great that in most cases the peak appeared to be single and only in the best cases after glycol saturation was even a suggestion of resolution observed. Attempts were also made to use the "b" spacing from the 060 line as a criterion for distinguishing between dioctahedral and trioctahedral types. While the typical "end members" could be easily distinguished, considerable ambiguity was again found in intermediate compositions. Only very extensive work on the product of each run may be able, therefore, to demonstrate the definite co-existence of 2 separate montmorillonite phases.* The present study appears to be fairly conclusive only insofar as it shows the existence of relatively pure "single" phase montmorillonites extending about 10 molar per cent into the diagram from each of the ternary systems. In the central area of the diagram we have assumed—in the absence of any definite contradictory evidence—that this solid solution is continued and thus gives rise to a complete series. Such an assumption also greatly simplifies the representation of the phase relations. As mentioned before, no accurate measurements of a pure magnesia-silica montmorillonite were obtained. However, a sharp discontinuity in expansion properties of montmorillonite was shown to exist on the Al_2O_3 side. A "pure" alumina-silica montmorillonite was found to expand with ethylene glycol only to 13.4 Å.

From the data in Table 1 (reactions 2 and 9) it is seen that montmorillonite of apparently variable composition covers a large field at temperatures of about $350^\circ C.$ or lower, but at higher temperatures the composition range becomes more limited. In the system $Al_2O_3-SiO_2-H_2O$ (Roy and Osborn, 1952a, 1954) the upper stability temperature of aluminum montmorillonite was set at about $420^\circ C.$ The substitution of Mg into this lattice apparently increases the upper stability temperature of montmorillonite to about $480^\circ C.$ A considerably extended investigation would be required to determine the composition of montmorillonite having the maximum stability temperature, but from the data obtained, its anhydrous composition must lie within the area bounded by the following compositions: 9.5:12.5:78, 25:10:65, and 10:25:65, $MgO:Al_2O_3:SiO_2$. A ratio of 15:15:70, in the center of this area, may therefore be suggested as the composition of the "ideally" stable montmorillonite.

Equilibrium Data

General statement. The results of more than 1,000 runs are summarized in Table 1. It would be extremely lengthy to include all the data, so

* This work is now in progress with a variety of synthetic montmorillonites.

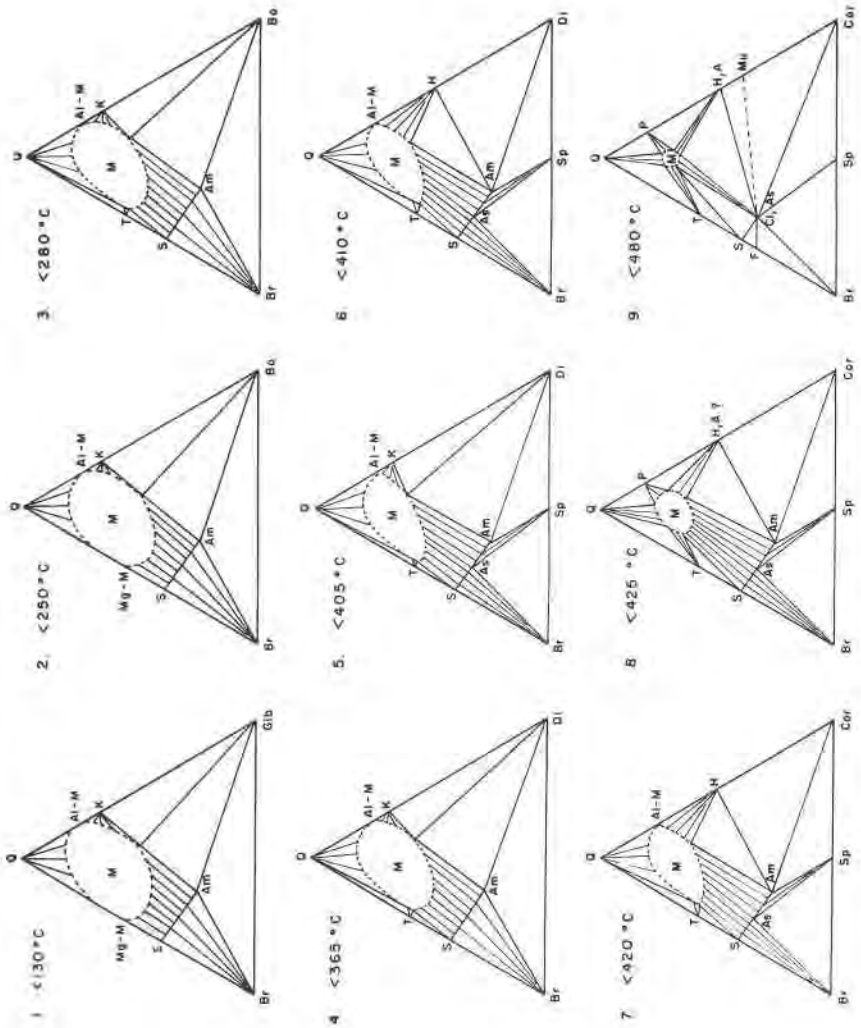
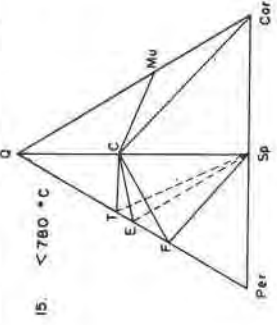
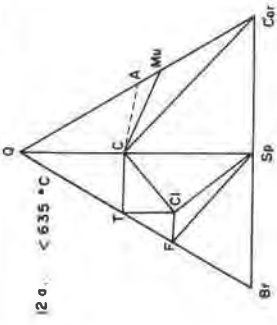
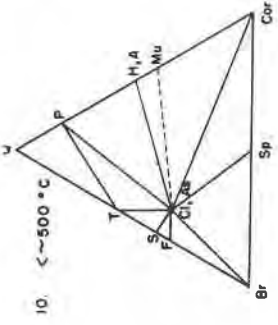
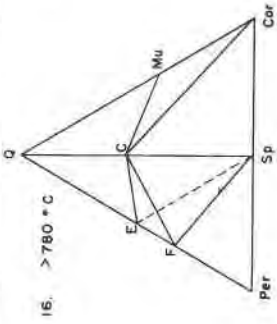
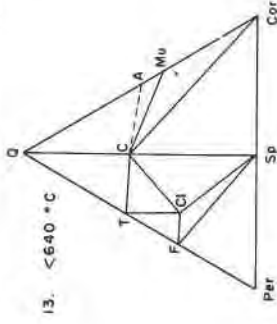
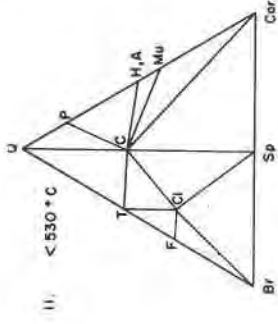
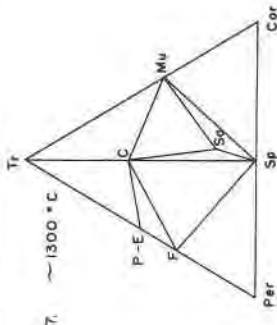
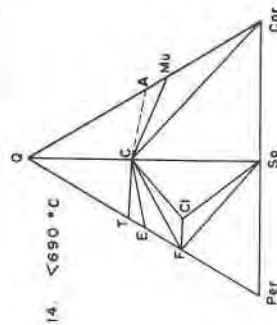
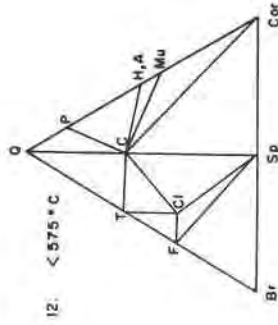


FIG. 3. The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ showing compatibility triangles at a water pressure of 10,000 psi.

Abbreviations used: Br=brucite; Gib=gibbsite; S=serpentine; Mg-M=magnesium montmorillonite; M=montmorillonite; K=kaolinite; Al-M=aluminum montmorillonite; Q=quartz; Bo=boehmite; Am=amesite; T=talc; Di=diaspore; As=aluminian serpentine; Sp=spinel; H=hydralsite; A=andalusite; P=pyrophyllite; F=forsterite; Cl=clino-



chlore; Mu = mullite; Cor = corundum; C = cordierite; E = enstatite; Per = periclase; P-E = protoenstatite; Tr = tridymite; Sa = sapphirine. Triangle 17 represents "dry" equilibria at atmospheric pressure (See Foster, 1950).

Although it was recognized that there was appreciable solid solution in the 14 Å chlorite phase, due to lack of many data and for simplicity triangles 9-14 show the composition of this phase as a single point of the clinochlore composition.

only part of the runs were selected in order to describe a particular transition. The equilibria determined by these data are described by the compatibility triangles of Fig. 3, which represent tetrahedra in the four-component system with water at the apex of the tetrahedron; i.e., the triangles indicate combinations of three phases in equilibrium with water. At relatively low temperatures where hydrates are stable, other combinations of phases will exist when there is insufficient water to convert the assemblage entirely to hydrates. We therefore speak of two types of equilibria: those in the presence of excess water, and "water-deficient" triangles; the results of the present study concern only the former. A somewhat detailed discussion of the water-deficient region and a general treatment of the limitations to the application of such phase equilibrium data has been given by Roy (1953).

The equilibria described are an interpretation of our knowledge of the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$, using data reported by previous workers, as well as those obtained in the present study. In some cases it will be noted that only an approach to equilibrium has been attained, i.e., in addition to the equilibrium phases others may be present. The criterion used for determining equilibrium phases in such instances is that if increasing the period of time, keeping all other factors constant, increases the proportion of a given phase, then this is the more stable phase.

Factors influencing the attainment of equilibrium. The state of the starting material was found to play an important part in the attainment of equilibrium. Resistant minerals such as corundum might never be decomposed under the most extreme hydrothermal treatment, even with the use of grinding techniques. Other materials may react slowly but eventually attain equilibrium. Glasses are ordinarily desirable as hydrothermal starting materials; however, throughout much of the present system glasses could not be formed. Mechanical mixtures of C.P. chemicals in some cases yielded true equilibrium assemblages, but in many cases it was found that long periods of time were required to approach an equilibrium attained more quickly using either glasses, or mixtures prepared by the nitrate-ethyl silicate method

An example of the comparison of the mixed oxides and the nitrate-ethyl silicate decomposition product is seen in Table 1, reaction 14, runs numbers 5138 and 5139 under the composition 5:1:3 $\text{MgO:Al}_2\text{O}_3\text{:SiO}_2$. Clinocllore is presumably the stable phase under these conditions, but with similar duration of run very little clinocllore was crystallized from the oxide mixture, whereas the other yielded a considerable amount. Further data showing the effect of starting material are given in Table 2, which describe runs under similar conditions for 5 different types of mixture. The stable phase under the conditions of the runs is cordierite;

TABLE 2. EFFECT OF STARTING MATERIALS ON A TYPICAL COMPOSITION
Cordierite Composition

Mixture	Run No.	Temp. °C.	Press psi	Time days	Phases Present*
Oxide Mixture	4012	675	10,000	4	Crist+talc+cor
Gel+MgCO ₃	4014	675	10,000	4	Talc+mull
Gel+Mg(OH) ₂ gel	4125	735	5,000	5	Cord+talc+mull
Nitrate-ethyl silicate	4269	700	8,000	5	Cord+l cor +l spinel
Glass	4202	700	5,000	7	Cord+l talc +l mullite

* Abbreviations used: Crist=cristobalite; cor=corundum; mull=mullite; cord=cordierite; l=little.

however, the first two mixtures (mixed oxides, and coprecipitated alumina-silica gel+MgCO₃) failed to yield cordierite at all. The third, (alumina-silica gel+Mg(OH)₂ gel) yielded some cordierite with a large proportion of other phases, whereas the last two (nitrate-ethyl silicate and glass) yielded mostly cordierite with only small quantities of other phases.

The effect of high pressures was found in many cases to increase the rate of reaction. From the data obtained it was suggested that a pressure boundary may exist for certain reactions: for example, the transformation of aluminian serpentine to clinocllore, or of the pair, mullite-spinel to cordierite-corundum. Clinocllore was produced relatively easily at high temperatures under pressures of 20,000 psi or greater, but at 10,000 psi only extremely long runs would yield any measurable amount of clinocllore. At lower pressures clinocllore did not form. (See data on the composition 5:1:3, reaction 14, Table 1.) Compositions in the high-alumina corner of the field at relatively high temperatures (see Table 1, reaction 10, compositions 26:42:32, 12:44:44 and 4:5:2) yielded cordierite and corundum as a stable pair at pressures of about 8,000 psi or greater. At lower pressures the results were not consistent, but mullite and spinel were formed more commonly. The possibility remains that extended periods of hydrothermal treatment under low pressure would bring about a transformation attributed to high pressure, but the time required would be beyond reason, experimentally. Nevertheless, evidence points to the favored formation of one assemblage at the expense of another at higher pressures. Furthermore, the role of water pressure may be particularly significant at decreasing temperatures, where a threshold value of activation energy may not have been attained to carry out a given reaction.

Apart from increasing the *rate* of some reactions, it has been found that with one or two notable exceptions, that the dT/dP or effect of pressure on the equilibrium temperature for a reaction (at a certain pressure) is quite low in systems such as the present in the range 5,000 psi to 30,000 psi. Furthermore, it is necessary also to consider whether the total pressure is equivalent to the water pressure and whether "directional" pressure has any different effect from that of hydrostatic pressure.

Discussion of Triangles. The series of triangles of Fig. 3 is our best interpretation of the available data for this system. Particularly at lower temperatures the data are sketchy, and many of the equilibria are represented by dashed lines, where suggested compatibility triangles have been extrapolated from known relations. The triangles represent divariant equilibria with three crystalline phases in equilibrium with water, and the transition indicated by the change from one set of the triangles to the next may be represented by a univariant pressure-temperature curve along which four phases are in equilibrium with H_2O . The temperature for each transition is given for a constant pressure of 10,000 psi but for most of the equilibria, pressure within the limits studied (2,000–20,000) had little ($< \pm 10^\circ$) effect on the transition temperatures. The reactions which indicate the transition from one set of triangles to the next are summarized as follows, and this order is used in summarizing the data in Table 1:

1. Gibbsite \rightleftharpoons boehmite + H_2O
2. Magnesium montmorillonite \rightleftharpoons talc + H_2O
3. Boehmite \rightleftharpoons diaspore
4. Spinel + H_2O \rightleftharpoons brucite + diaspore
5. Kaolinite \rightleftharpoons hydralsite + aluminum montmorillonite + H_2O
6. Diaspore \rightleftharpoons corundum + H_2O
7. Aluminum montmorillonite \rightleftharpoons pyrophyllite + hydralsite + H_2O
8. Serpentine + brucite \rightleftharpoons forsterite + H_2O
9. Montmorillonite \rightleftharpoons pyrophyllite + hydralsite + H_2O + AS
10. Hydralsite + pyrophyllite + AS (aluminian serpentine) \rightleftharpoons cordierite + H_2O
- 10a. Serpentine \rightleftharpoons forsterite + talc + H_2O
11. AS + brucite \rightleftharpoons forsterite + spinel + H_2O
12. Pyrophyllite \rightleftharpoons quartz + mullite + H_2O
- 12a. Brucite \rightleftharpoons periclase + H_2O
13. Talc + forsterite \rightleftharpoons enstatite + H_2O
14. Clinocllore \rightleftharpoons cordierite + forsterite + spinel + H_2O
15. Talc \rightleftharpoons enstatite + quartz + H_2O

Triangle 1 suggests relations below 130° C. where gibbsite is the stable alumina hydrate (see Ervin and Osborn (1951)). Montmorillonite is shown to cover a large field, presumably clear to the magnesia-silica boundary, although the evidence for the existence of a pure magnesia-

silica montmorillonite is not as positive as desired, as discussed under the the section on synthesis of montmorillonite.

In *Triangle 2* gibbsite has been replaced by boehmite, and the rest of the equilibria probably remain the same. Within this temperature region also the transition, $endellite \rightleftharpoons halloysite + H_2O$ takes place, but this has been described by Roy and Osborn (1952*a*, 1954) and a separate triangle is omitted for simplicity.

Triangle 3 describes the decrease in area of the montmorillonite field, and the pure magnesia-silica montmorillonite is replaced by talc. Data which suggest this transition are given in Table 1, reaction 2.

Triangle 4 represents the replacement of boehmite by diaspore (see Ervin and Osborn (1951)). A pressure of 2,000 psi or greater is believed necessary for the equilibrium existence of diaspore, one of the few reactions in which pressure up to 30,000 psi has been demonstrated to play a decisive role. The rest of the equilibria remain about the same. Within this temperature range there is evidence for the existence of the join, aluminian serpentine-diaspore for compositions in the high-alumina corner yield mixtures of an alumina mono-hydrate* and aluminian serpentine.

Triangle 5 describes the relations with spinel entering the equilibria. The temperatures for the reaction, $brucite + diaspore \rightleftharpoons spinel + H_2O$, 365° C. is taken from the system $MgO-Al_2O_3-H_2O$ (Roy, Roy and Osborn, 1953). Evidence for the existence of a join, spinel—AS (clinocllore composition) is found in mixtures with the following compositions: 75:15:10 and 70:15:15, which yield the three phases, brucite-AS-spinel, the aluminian serpentine having a basal spacing very close to that formed from the 5:1:3 $MgO:Al_2O_3:SiO_2$ composition. On the other hand, mixtures in the high-alumina region yield aluminian serpentine with a smaller spacing, corresponding possibly to the amesite composition; hence, an additional join is shown between aluminian serpentine (amesite composition) and diaspore (or boehmite). The montmorillonite field is shown to be smaller than in *Triangle 4*, (since certain mixtures do not yield at this temperature a single montmorillonite phase) although further intensive study would be necessary to precisely delineate the field at several specific temperatures.

In *Triangle 6* kaolinite is no longer stable, and is replaced, probably for an interval of about 15° C., by Al-montmorillonite + hydralsite + water

* In this study, as in the study of Ervin and Osborn (1951) and Roy, Roy and Osborn (1953) diaspore growth took place within its stability range only in the presence of seed crystals, or else with very long runs or at high pressures (20,000 psi). Therefore in most unseeded runs, boehmite was the alumina mono-hydrate encountered.

(see Table 1, reaction 5). Mixtures in the quaternary system containing appreciable MgO yield the assemblage, montmorillonite (Al, Mg) + hydralite + aluminian serpentine (probably near the amesite composition) + H₂O.

In *Triangle 7* the equilibria are essentially the same as in *Triangle 6*, with diaspore replaced by corundum (see Ervin and Osborn (1951)). Considerable difficulty was encountered in establishing the significance of this transition in the ternary system Al₂O₃-SiO₂-H₂O, because the presence of SiO₂ tends to inhibit the transition, diaspore \rightleftharpoons corundum + H₂O.

Triangle 8 describes the relations where pure Al-montmorillonite is no longer stable (Roy and Osborn, 1952a, 1953), but gives rise to pyrophyllite + hydralite + H₂O. As previously discussed, the true stability range of hydralite has not been definitely established but recent data suggest that the maximum "stability" temperature is about the same as, or slightly lower than that of pyrophyllite. In the event it is proven that hydralite is only metastable, the above assemblage would be replaced by pyrophyllite + andalusite (or mullite) + H₂O. The establishment of an equilibrium relationship between hydralite and andalusite would be particularly significant. The composition of hydralite has not been precisely established, but is believed to be close to 2Al₂O₃ · 2SiO₂ · H₂O (see Roy and Osborn, 1952a, 1954). If this is the true composition of hydralite, andalusite cannot exist in equilibrium with H₂O within the range where hydralite is a stable phase; and even if the Al₂O₃:SiO₂ ratio in hydralite is slightly different from 1:1, joins between this and other phases in the system may prevent the existence of the join, andalusite-H₂O. Such an occurrence would explain the difficulty in achieving the synthesis of andalusite.

Triangle 9 represents the replacement of serpentine + brucite by forsterite + H₂O. This reaction is described by Bowen and Tuttle (1949). Within this temperature range clinochlore has been synthesized at the expense of aluminian serpentine, and probably is the more stable phase (see Table 1, reaction 14, runs 5257, 5258 and 5294). It is not known whether or not clinochlore is stable at much lower temperatures, since the time required to bring about the formation of clinochlore increases greatly with decrease in temperature. The equilibria involving alumina are not very definite, since clinochlore has not been crystallized from high-alumina compositions; but inasmuch as aluminian serpentine of the clinochlore composition is considered to be metastable with respect to clinochlore within this temperature range, aluminian serpentine higher in Al₂O₃ is also presumed to be metastable. Joins connecting compatible phases are therefore drawn from the clinochlore composition.

In *Triangle 10* the magnesia-alumina montmorillonites are no longer

stable, giving rise instead to talc+pyrophyllite+AS+H₂O, or pyrophyllite+AS+hydralsite (or andalusite)+H₂O (see Table 1, reaction 9). Within this temperature range, as in the previous triangle, aluminian serpentine of the clinochlore composition is probably metastable. Thus, the equilibria are represented as involving clinochlore *or* aluminian serpentine, although in most runs aluminian serpentine was the phase encountered. A unique phase of the clinochlore composition was indicated as the stable phase for simplicity because no evidence for the *stability* of a chlorite or aluminian serpentine of higher Al₂O₃ content was obtained. (See Nelson and Roy (1953) for a later discussion.)

In Triangle 11 cordierite is stable in the presence of excess H₂O, although it may be stable at lower temperatures in the water-deficient region. Considerable time is necessary to form cordierite near its lower temperature limit, and therefore, the temperature for this reaction has not been located very accurately, about $500 \pm 25^\circ$ C. (see Table 1, reaction 10). Decomposition of synthetic cordierite was effected as high as $475 \pm 20^\circ$ C., but this is unfortunately about the upper temperature limit of the grinding apparatus. Synthesis of cordierite was achieved as low as $515 \pm 10^\circ$ C. although in most runs near this temperature considerable amounts of non-equilibrium phases were still present. (For a comparison of the results of cordierite synthesis attempts at higher temperatures using different starting materials, see Table 2.) The triangles suggesting compatibility of cordierite with other phases were not definitely established down to the temperature of reaction 10, but they are presumed to be identical with those at slightly higher temperatures.

It is possible that the equilibria proceed directly from Triangle 9 to 11, without the intermediate equilibria represented by Triangle 10. The interval between the upper stability temperature of magnesia-alumina montmorillonite and the lower stability temperature of cordierite is within experimental error, considering the sluggishness of reaction producing cordierite, and the ever-present tendency to form non-equilibrium phases.

Triangle 12 represents the replacement of the join, aluminian serpentine (or clinochlore)-brucite by forsterite-spinel (see Table 1, reaction 11). Compositions in the high-magnesia corner always yielded aluminian serpentine, rather than clinochlore, as one phase. The failure to crystallize clinochlore from mixtures in this area may be explained by sluggish reaction at such low temperatures (below 530° C.) so that the true equilibrium phase clinochlore is never obtained. The aluminian serpentine obtained from the 75:15:10 and 70:15:15 mixtures had lattice dimensions identical with that of the 5:1:3 composition.

In Triangle 12a pyrophyllite is no longer stable (Roy and Osborn,

1952a, 1954), but is replaced by cristobalite+mullite (or andalusite) +H₂O (see Table 1, reaction 12). Sufficient data to delineate a stability region for andalusite were not obtained, but from natural occurrences the stability of andalusite rather than mullite would be favored within this temperature range. Experimentally it was found that higher water pressure, and in some cases prolonged duration of the run favored the formation of andalusite.

Triangle 13 the only change is the replacement of brucite by periclase+H₂O. The temperature of this reaction was taken from the ternary system MgO-Al₂O₃-H₂O (Roy, Roy and Osborn, 1953), and data given under reaction 12a (see Table 1) show that the temperature for this transition is not appreciably affected by the addition of SiO₂ to the ternary system. The temperature, 635° C. at 10,000 psi, changes considerably with change in pressure, but this would not affect other reactions, inasmuch as no other reaction involving brucite or periclase takes place within the temperature and pressure range investigated.

Triangle 14 shows the replacement of the join, forsterite+talc by enstatite+H₂O. The temperature for this reaction is taken from Bowen and Tuttle (1949), and no data conflicting with this were found. A separate triangle should probably be drawn for the reaction, talc+clinochlore \rightleftharpoons forsterite+cordierite+H₂O. This is discussed by Yoder (1952).

Triangle 15 clinocllore is no longer stable, but gives rise to the assemblage, forsterite+cordierite+spinel+H₂O. Dashed lines are drawn to indicate assemblages which are apparently less stable, but yet form readily from compositions in this area. High pressures, and long duration of runs in general tend to form the assemblage, forsterite+cordierite+spinel (+H₂O). Here again the true role of pressure is questionable—it may serve only to increase the rate of reaction; but at low pressures <10,000 psi the above-mentioned presumably stable assemblage was never attained, even with duration of runs as long as 22 days (see Table 1, reaction 14).

Triangle 16 represents the replacement of talc by enstatite+quartz +H₂O. The temperature of this transition was taken from Bowen and Tuttle (1949), and data obtained in the present study are not in disagreement with this value. Within this temperature range, also, there is a strong tendency to form the assemblage enstatite-spinel-cordierite (see data Table 1, reaction 15). Higher pressure tends to form instead the apparently more stable assemblage, cordierite-forsterite-spinel; whereas pressures of 8,000 psi or less did not form this assemblage in runs as long as 6 days.

Another step is shown by Yoder (1952), at 830° C. in which an inversion of cordierite takes place to yield a high temperature polymorph,

α -cordierite, very similar in x-ray diffraction pattern and optical properties. This area was not investigated extensively in the present study.

GENERAL DISCUSSION

Montmorillonite Formation in the System

The equilibria in the system $MgO-Al_2O_3-SiO_2-H_2O$ are basic to the problems of montmorillonite formation, inasmuch as the common cations forming the octahedral and tetrahedral layers are present. Cations which commonly fill the base exchange position, however, are absent and Mg^{2+} or a magnesia-complex must be the exchangeable cation in most cases. Three types of montmorillonites have been synthesized, which are not common in nature: pure alumina-silica montmorillonite, pure magnesia-silica-montmorillonite, and magnesia-alumina-silica montmorillonites (having *no* other cations present in the base exchange position). At low temperatures presumably approaching atmospheric conditions, the montmorillonite field covers a large area (or volume in the tetrahedron).^{*} Montmorillonites are formed from alumina-silica mixtures of about 1:3 $Al_2O_3:SiO_2$ molar ratio. Substitution of Al^{3+} for Si^{4+} in the tetrahedral layer must take place to result in an unbalance in charge, giving rise to the base exchange properties, and the base exchange position must be filled by an alumina complex such as $Al(OH)_2^+$ (see Roy and Osborn (1952*a*, 1954)). The markedly lower expansion (with ethylene glycol) of this structure (to 13 Å) may provide evidence for the influence of the tetrahedral seat of charge on the degree of expansion.

A poorly-formed structure, apparently closely related to the montmorillonites, was formed from pure-magnesia-silica mixtures of the 3:4 $MgO:SiO_2$ ratio at temperatures below 250° C. Such a structure has previously been reported (Strese and Hofmann, 1941) but only in the presence of Na^+ as a base exchange cation, not present in this study. A definite mechanism for the formation of such a structure is difficult to picture, since the base exchange essential in montmorillonite structures is attributed to unbalance in charge caused by substitution in either the tetrahedral or octahedral layers. It is not easy to show that a comparatively large, low charged ion such as Mg^{2+} would substitute for Si^{4+} in the tetrahedral layer of a clay. However, the occurrence of Mg^{2+} in tetrahedral coordination in glasses is not uncommon (Roy, 1950). Another possible explanation may be that in such a loose, imperfectly formed structure a cation deficiency exists in the octahedral layer,

* Actually the variability of composition with respect to water content is not very great compared to the variability with respect to other components, and the volume is actually a nearly flat slab.

with the deficiency in charge supplied by the base exchange cation. The possibility also remains, however, that such an imperfectly formed structure is actually only metastable; that, given sufficient time, would convert to the more stable structure, talc.

Other features of the montmorillonites have been described in the section on montmorillonite synthesis. Magnesia-alumina-silica montmorillonites of widely variable composition have been formed, in which substitution giving rise to unbalance in charge may take place in either the octahedral or tetrahedral layer, or both. Mg^{2+} (or a hydrated complex) is the exchangeable base, which is not common in itself, since in natural montmorillonites relatively small cations do not ordinarily enter the base exchange position. The existence of these montmorillonites, and the alumina-silica montmorillonite (see Roy and Osborn, 1952*a*, 1954) demonstrates the fact that a stable montmorillonite structure may be formed through the mechanism of unusual types of substitution when the more common types are not possible. In order to obtain further evidence, attempts to synthesize a "pure" gallia-silica montmorillonite having presumably the same structure as aluminum montmorillonite were made (Roy and Roy, 1954) and were successful.

The facts that the montmorillonite field covers a large area in the $MgO-Al_2O_3-SiO_2-H_2O$ diagram, and the mineral is formed stably up to fairly high temperatures, (480° C.) are rather surprising, since montmorillonite is largely a sedimentary mineral, and less commonly of hydrothermal origin—but not present in rocks commonly attributed to metamorphic processes. The addition of K_2O to the system $MgO-Al_2O_3-SiO_2-H_2O$, however, would move such compositions out of the montmorillonite field to produce micas, or under other conditions feldspars; the same would be the case with the addition of Na_2O . The question of equilibrium co-existence of a mica and montmorillonite is quite intriguing from the clay mineralogist's viewpoint.

Clay Mineral Assemblages

Within this system are included representatives of each of the clay mineral groups, and the addition of several mole per cent of potash would enable us to very closely duplicate compositions of a high proportion of clay-bearing rocks.

The montmorillonites are seen in this presentation to completely dominate the picture, so that only in a small area of the system do we not have montmorillonite as *one* of the phases formed. The mode of representation, however, somewhat over-emphasizes the position of the montmorillonites. If the projection had been made on the $Al_2O_3-SiO_2-H_2O$ face the position of kaolinite would also have been striking. However, one

of the main reasons for the abundance of kaolinite in nature is that a large fraction of these clays is secondary and derived from weathering of feldspars and micas, and even rocks containing a very low percentage of magnesium. The relatively pure primary kaolinites not contaminated by phases other than alumina-hydrates must also be ascribed to a relatively "pure" (Mg-free) source area. Under all other conditions one would expect montmorillonite to be present in significant amounts. The lowest temperature triangle would imply that kaolinite-montmorillonite mixtures should not be very common in primary sedimentary deposits. On the other hand one would expect a fairly common occurrence of montmorillonites with the 7 Å (or 14 Å) chlorites, represented respectively, by aluminian serpentine and clinochlore. These low temperature triangles (1-5) also indicate (though unfortunately at these temperatures it is nearly impossible to claim that equilibrium has been attained) that the 7 Å kaolinite and 7 Å aluminian-serpentine are incompatible and that a more common assemblage would involve either of these 7 Å phases with boehmite (or gibbsite) and montmorillonite. Triangles such as 5 and 6 show that these clay mineral phases will persist to quite high temperatures (well into the metamorphic range) and indeed, the assemblage, chlorites-montmorillonites covers a large area of the compositional field. In nature the presence of K^+ transforms many of the montmorillonites into micas. It is nevertheless a remarkable fact that a montmorillonite is actually stable up to 480° C.

It is worthy of note that no case of "interlayering" effects was noticed on the x -ray patterns. The so-called mixed-layer phases (giving "interfering" x -ray patterns) composed, at least, of any combination of the phases kaolinite, montmorillonite, and chlorite (including 7 Å aluminian serpentines) must therefore be metastable assemblages which are mixtures of two phases within the context of the phase rule.

The Stability of Andalusite

Andalusite was synthesized apparently for the first time in the present study (see Roy, 1953) and its stability has been discussed also in part under the Discussion of Triangles. General difficulties arising in attempts to synthesize the aluminosilicates have been described by Roy and Osborn (1951, 1953). In the present study only suggestions of a stability region for andalusite have been obtained although the synthesis was achieved reproducibly. Several inter-related factors influence the delineation of a stability range for andalusite.

First, andalusite cannot be stable in the presence of excess water below about 400° C., inasmuch as the hydrates, diaspore and kaolinite are stable and compatible up to this temperature. In the presence of a defi-

ciency of H_2O , andalusite may be stable to low temperatures, although the slow rate of reaction at these temperatures will be an important factor in the experimental determination of a lower temperature limit under these conditions.

Second, another hydrous aluminosilicate, hydralsite, has about the same alumina-silica ratio as andalusite. The stability range of this structure has not been definitely established, but most recent indications are that it may be about as high as that of pyrophyllite ($575^\circ C.$). Andalusite has in some cases been synthesized as low as $450^\circ C.$, with fairly long duration of run and relatively high water pressures. From the compositional limitations it would be very unlikely that both structures are stable in the presence of excess H_2O in the same temperature and pressure range. Decomposition of hydralsite to yield andalusite + H_2O would be a positive indication both of a maximum stability temperature for hydralsite and a minimum for andalusite (in the presence of excess H_2O). But it has not been possible as yet to achieve such a reaction.

Third, the presence of certain impurities apparently facilitates the synthesis of andalusite. The synthesis was achieved only with great difficulty, and in the presence of andalusite "seeds," from pure $Al_2O_3-SiO_2$ mixtures,* while in the presence of small amounts of MgO , or starting with natural slightly impure kaolinites synthesis was achieved more readily.

The effect of the presence of impurities such as Mg^{2+} may also be explained on the basis of the favorable coordination conditions (6 fold) that Mg^{2+} ions would prefer. On this basis also both $(OH)^-$ and F^- ions will make it easier to form these aluminosilicate structures if they enter them. The presence of impurities may be of considerable importance when attempting to correlate experimental equilibrium data with natural occurrences, to obtain a better picture on the stability of andalusite, since in nature a host of "impurities" are available. One hopeful feature is the fact that the highest stability of a hydrate mineral in the portion of the system in which the aluminosilicates are involved is $575^\circ C.$ (pyrophyllite), and hence extended investigation by hydrothermal techniques has a possibility of yielding further information on the stability of the anhydrous aluminosilicates, which in turn may be correlated with natural mineral associations. The present position on the anhydrous aluminosilicates is therefore not much advanced over much earlier work. The data indicate that mullite is the stable aluminosilicate at pressures below say 30,000 psi from $575^\circ C.$ upwards and probably as

* Experimentally other factors such as the state of starting material were of considerable significance, but these should not affect the ultimate equilibria.

low as 400° C. In this pressure range the only possible change may be that it is metastable from 575–400° and andalusite is stable with corundum. Of course, it is not impossible that andalusite and mullite be both stable at low pressures.

The Stability of Cordierite—Corundum or Spinel—Mullite

One of the more remarkable features of the equilibria determined in the high-alumina portion of the system is the apparent compatibility of cordierite and corundum. At solidus temperatures in the system $MgO-Al_2O_3-SiO_2$, spinel and mullite coexist, but the data obtained in the present study (see Table 2, esp. reaction 10) strongly suggest that cordierite and corundum are compatible, at least below about 800° C.

The pair mullite-spinel is sometimes formed in runs of relatively short duration, whereas cordierite-corundum is formed under prolonged hydrothermal treatment; and at lower H_2O pressures, where presumably the solubility of the phases is lower and reaction would take place more slowly, the pair mullite-spinel is sometimes formed, whereas cordierite-corundum is formed almost invariably at higher pressures. The second factor suggests that a minimum pressure may be required for the formation of the assemblage, cordierite-corundum; and, indeed, it is recognized that spinel and mullite are compatible in the sanidinite facies, characterized by high temperatures and low pressures. Metamorphic field assemblages (Tilley, 1924) suggest, however, that cordierite and corundum are compatible under the conditions characteristic of the pyroxene-hornfels facies, presumably of lower temperatures and higher pressures. Extensive study, with the availability of new experimental techniques to attain higher temperatures under hydrothermal conditions might yield some information on the existence of a pressure-temperature curve for the reaction $spinel + mullite \rightleftharpoons cordierite + corundum$.

The Joins Forsterite-cordierite and Enstatite-spinel

At solidus temperatures in the system $MgO-Al_2O_3-SiO_2$, the phases, forsterite, cordierite and spinel coexist at equilibrium. These three phases are also apparently compatible in equilibrium with H_2O above 680° C. at 15,000 psi (Yoder, 1952). In the present study repeated runs at pressures of 10,000 psi or lower yielded evidence suggesting that the joins, enstatite-spinel and talc-spinel are stable. The assemblage, cordierite-enstatite-spinel appeared to be stable above 725° C. with prolonged runs at 10,000 psi; whereas at 20,000 psi similar runs yielded, cordierite-forsterite-spinel. Spinel-cordierite-hypersthene associations in nature (approximated by spinel-cordierite-enstatite) are typical of the pyroxene-hornfels facies (Tilley, 1924), rather than the assemblage,

spinel-forsterite-cordierite. The fact that spinel-forsterite-cordierite is obtained stably at the solidus temperature under atmospheric pressure and also apparently stably at lower temperatures (above about 700° C. at 20,000 psi) at high pressures would indicate that it is unlikely that the alternative assemblage, spinel-enstatite-cordierite is stable in the same temperature range under intermediate pressures. This is not positive evidence that the assemblage, spinel-enstatite-cordierite is formed only metastably, but does suggest a mechanism for its formation in nature.

SUMMARY AND CONCLUSIONS

Phase equilibria in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ have been determined by hydrothermal techniques. At the highest temperatures studied (above about 800° C. at 10,000 psi) only anhydrous minerals are stable, and the equilibria are expressed in terms of compatibility triangles of three phases in equilibrium with H_2O , differing in only a few instances from the "condensed" equilibria in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. A notable exception is the existence of the cordierite-corundum join, rather than the join, spinel-mullite. No evidence for the presence of sillimanite, andalusite or kyanite was obtained at these temperatures and pressures.

With decreasing temperature hydrated minerals enter the equilibria—first talc, at 780° C. and 10,000 psi—and then below 700° C. at 20,000 psi the first quaternary phase, clinocllore is stable. An interesting polymorphism is observed between clinocllore and "aluminian serpentine" of the same composition. A definite p - T curve for the transformation could not be determined because of the sluggishness of reaction, but higher pressures and temperatures were found to favor the formation of clinocllore. The hydration of periclase to brucite takes place at 635° C. at 10,000 psi, the temperature of the reaction changes considerably with variation in pressure. Within the smaller tetrahedron, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}\cdot\text{Al}_2\text{O}_3\text{-H}_2\text{O}$, the highest hydrate stability is that of pyrophyllite (575° C. at 10,000 psi); the upper stability temperature of hydralsite ($2\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot \text{H}_2\text{O}$), a micaceous type phase, does not exceed this temperature. Andalusite was synthesized at temperatures between about 450° C. and 700° C., but no definite stability range could be established on the basis of the data obtained.

Cordierite is no longer stable in the presence of excess H_2O below about 500° C., and the character of the equilibria is changed considerably by its disappearance. Another quaternary phase, montmorillonite, of variable composition enters the equilibria below about 480° C., and its stability field covers a large area at lower temperatures. Alumina hydrates, in place of corundum, are formed below about 400° C., at which tempera-

tures kaolinite is also stable. Below about $365^\circ C.$, spinel ($+H_2O$) is replaced by brucite+diaspore (or boehmite); i.e., spinel is no longer stable in the presence of excess H_2O . At lowest temperatures a magnesia-silica montmorillonite phase is formed at the expense of talc, in addition to the quaternary montmorillonites, which cover a large field.

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