

## THE LOWER LIMIT OF STABILITY OF AKERMANITE ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ )\*

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ABSTRACT. Experiments have been carried out to determine the P-T curve for the reaction, Wollastonite + Monticellite  $\rightleftharpoons$  Akermanite. The P-T curve lies above 700 and below 750°C between 30,000 and 60,000 lbs./in.<sup>2</sup>.

This P-T curve adds another line to the petrogenetic grid and, being nearly parallel to the pressure axis it must cross or intersect other P-T curves for reactions involving volatile phases.

Wollastonite-monticellite assemblages, e.g., at Crestmore, are to be expected in rocks of appropriate composition if the ultimate crystallization were at a temperature below the stability field of akermanite and in the absence of excess  $\text{CO}_2$ .

### INTRODUCTION

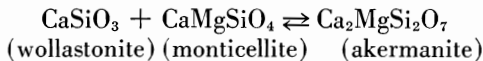
Bowen, Schairer and Posnjak (1933) found that when a glass of akermanite composition was crystallized at 1327°C. akermanite crystals alone developed. When, however, the same glass was crystallized at 1050°C., the akermanite which formed was accompanied by other crystallites identified as  $\text{Ca}_2\text{SiO}_4$ . In view of this they suggested that akermanite becomes unstable with falling temperature. Later, Osborn and Schairer (1941) found that above 1325°C. akermanite crystals grown at 1400°C. remained homogeneous but that below this temperature small euhedral crystals developed in the akermanite, and some of these had the refractive index and general appearance of diopside.

The present study shows that akermanite breaks down to wollastonite + monticellite at temperatures well below 1000°C.

### EXPERIMENTAL PROCEDURE AND RESULTS

The experimental work was carried out in cold seal pressure vessels (Tuttle, 1949) using the apparatus described in connection with studies in the  $\text{CaO-MgO-CO}_2$  system (Harker and Tuttle, 1955). In the present study, however, water was used to apply a hydrostatic pressure instead of  $\text{CO}_2$ , as it was required that the fluid phase would not react either with akermanite or with its breakdown products.

By making runs at different pressures and temperatures it has been possible to determine the P-T curve for the univariant reaction:



No hydrates were formed, so the only function of the water was to transmit the hydrostatic pressure to the solid phases and to act as a flux; water did not enter into the reaction as an active component in any other way.

The starting materials used in the runs were: (A) A fine-grained intimate mixture (Mix IV in table 1) of  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{SiO}_2$  in the molecular proportions 2:1:2 corresponding to the akermanite composition. The  $\text{CaO}$  was prepared by firing a weighed amount of  $\text{CaCO}_3$ . The  $\text{CaCO}_3$  and the  $\text{MgO}$  were the analytical reagents of the Fisher Scientific Company. Silica

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glass was used as the source of  $\text{SiO}_2$ . (B) A fine-grained intimate mixture of akermanite, wollastonite, and monticellite formed by the partial conversion of wollastonite + monticellite (in akermanite proportions) to akermanite with rising temperature. (This is Mix III in table 1). (C) Synthetic akermanite formed by the rapid crystallization of a liquid of akermanite composition.

The products of the runs were identified by their optical properties and their X-ray powder diffraction patterns.

During runs made on the high temperature side of the P-T curve akermanite developed from the two mixtures while the synthetic akermanite remained as the stable phase. On the low temperature side of the curve wollastonite + monticellite developed from the mixtures, and the synthetic akermanite broke down to wollastonite + monticellite. At  $610^\circ\text{C}$ . and 41,000 lbs./in.<sup>2</sup> akermanite broke down completely to wollastonite and monticellite in euhedral acicular and subequant crystals respectively, in ten days. Likewise, by reacting the mixtures for 15 hrs. at  $798^\circ\text{C}$ . and 58,000 lbs./in.<sup>2</sup>, pure akermanite could be prepared hydrothermally.

At pressures and temperatures closer to the P-T curve reaction rates are very much slowed down. However, it was not necessary for the reaction represented by the P-T curve to go to completion in order to ascertain on which side of the curve a given pressure-temperature condition belonged. It was sufficient to be able to detect in which direction the reaction was going. Thus the formation of a small amount of akermanite from the oxide mix or the development of a small amount of wollastonite + monticellite from the synthetic akermanite indicated conditions on the high or low temperature sides of the P-T curve respectively.

It was considered advisable, however, to make certain that in such runs the new phases were actually steadily growing and that they were not present solely as a result of a sporadic metastable development due, say, to the variable P-T conditions to which the sample was necessarily subjected during the short period of the initial heating at the beginning of the run. Some of the runs, therefore, were repeated under a given set of P-T conditions for different lengths of time. In this way the continued growth of the stable assemblages could be observed. Mixture III was particularly useful in this respect, as it was most easy to see, by optical means and especially by the changing intensities of the X-ray powder diffraction lines, whether akermanite was increasing or decreasing in amount with respect to wollastonite and monticellite.

The successful runs made to determine the P-T curve are listed in table 1 from which figure 1 has been drawn.

#### DISCUSSION OF RESULTS

The breakdown of akermanite to wollastonite + monticellite is very different from the breakdown to calcite + diopside, which takes place at much higher temperatures in the presence of excess  $\text{CO}_2$ —see figure 2, curve I (Harker and Tuttle, unpublished data). In the breakdown to wollastonite + monticellite, akermanite becomes unstable by virtue of its own internal structure and not through any tendency to react with other phases which

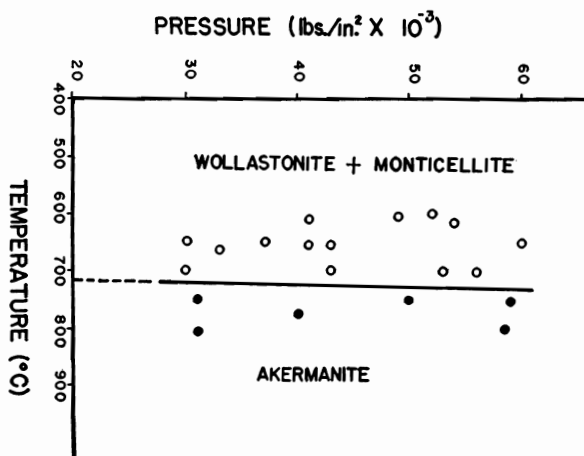


Fig. 1. P-T curve for the univariant reaction: wollastonite + monticellite  $\rightleftharpoons$  akermanite. o = runs made on the low temperature side of the P-T curve where wollastonite + monticellite is the stable assemblage. • = runs made on the high temperature side of the P-T curve where akermanite is stable.

may be present (as for example, H<sub>2</sub>O or CO<sub>2</sub>). On crossing the P-T curve for this reaction, in which solid phases only are involved, the volume change ( $\Delta V$  in the equation below) will almost certainly be both small and nearly constant in comparison with what it would be were a volatile involved. (The volume change, using density values determined at room temperature and atmospheric pressure, is in fact such that high pressures might be expected to favor the wollastonite-monticellite assemblage.) It is anticipated, therefore, from the Clausius Clapeyron equation,  $\frac{dp}{dt} = \frac{\Delta H}{\Delta V}$ , that the P-T curve will be steep and have a nearly constant slope. The curve itself will be essentially a straight line intersecting the temperature axis on the P-T diagram at a large angle, unlike the P-T curves for dehydration and decarbonation reactions which, at the lower pressures and where the fluid phase is either above the critical point or in the gaseous state, become more and more nearly parallel to the temperature axis as  $\frac{dp}{dt}$  decreases with falling pressure and temperature.

Assuming that the P-T curve is straight and has a positive slope as is suggested by  $\Delta V$ ,  $\frac{dp}{dt}$  can vary between  $\infty$  and 600 lbs./in.<sup>2</sup>/°C. Because  $\Delta H$  is infinite if  $\frac{dp}{dt}$  is infinite, it is not possible to estimate an upper limit for the value of  $\Delta H$ . As, however,  $\frac{dp}{dt}$  cannot be less than 600 lbs./in.<sup>2</sup>/°C. if the P-T curve is to be between the experimentally determined limits, then  $\Delta H$  cannot be less than about 37K.cals/mole at 750°C. or 35 K.cals/mole at 700°C.

The P-T curve for the breakdown of akermanite to wollastonite + monticellite will cross or intersect several other P-T curves which have slopes different from that of the akermanite breakdown curve. Some of the more important of these are illustrated in figure 2 representing the reactions: (a) clinocllore  $\rightleftharpoons$  forsterite + cordierite + spinel +  $H_2O$  (Yoder, 1952)—curve VI; (b) quartz + calcite  $\rightleftharpoons$  wollastonite +  $CO_2$  (Harker and Tuttle, 1956)—curve V; (c) magnesite  $\rightleftharpoons$  periclase +  $CO_2$ —curve IV; and (d) dolomite  $\rightleftharpoons$  calcite + periclase +  $CO_2$  (Harker and Tuttle, 1955)—curve III.

These curves constitute a contribution to the petrogenetic grid envisaged by Bowen (1940, p. 273) which, when accurately established on the basis of a sufficient number of P-T curves, may well provide the most satisfactory foundation for a reclassification of all metamorphic rocks on the Facies principle.

The P-T curves for dehydration and decarbonation reactions as determined in the laboratory are only strictly applicable when the partial pressures of water and carbon dioxide are known. Owing to the ability of volatiles to escape through fissures, it can only be deduced that the stable existence of a certain phase assemblage indicates that the P-T conditions have never attained the high temperature side of the P-T curve. The occurrence of wollastonite in a rock, for example, does not necessarily mean that the rock has crystallized under general P-T conditions on the high temperature side of curve V in figure 2, for this curve applies only to systems with excess  $CO_2$ . On the other hand, with P-T curves of purely solid phase reactions, it is unnecessary to consider the partial pressures of fluid phases present. This is a great advantage; it means that if akermanite occurs stably, no matter with what other phases, then P-T conditions belonging to the high temperature side of the curve *must* have been attained.

Although rocks of the right composition to bear akermanite, or wollastonite + monticellite, are unlikely to contain clinocllore, dolomite, or magnesite, nevertheless, it is possible that in a small region, representing a single set of P-T conditions, the composition of the rocks may vary sufficiently to make all the above, and other reactions possible. The usefulness of the grid would then be evident. For example, the stable occurrence of clinocllore in a rock in which akermanite-bearing strata occur would indicate that the rock crystallized under P-T conditions in the divariant region between curves VI and VII but on the high pressure and high temperature side of the cross-over. On the other hand, if clinocllore-bearing rocks were closely associated with wollastonite-monticellite-bearing rocks, then this would indicate that the P-T conditions of crystallization belonged to the divariant region between curves VI and VII but below the cross-over.

It is to be expected, as already stated above, that at least at the lower pressures the P-T curves for reactions involving solid phases only will be more nearly vertical than P-T curves representing reactions in which a fluid phase is involved. It is clear, however, that P-T curves for reactions involving fluid phases may cross one another. Curve VI, for example, crosses curves V and IV, and it is strongly suspected that curves I and II (Harker and Tuttle,

TABLE 1  
 $\text{CaSiO}_3 + \text{CaMgSiO}_4 \rightleftharpoons \text{Ca}_2\text{MgSi}_2\text{O}_7$

Run	Initial materials	Pressure lbs./in. <sup>2</sup>	Temp. °C.	Time hrs.	Products
1011	Mix III	60,000	650	96	Ak —> Wo + Mo
1012	Ak	"	"	"	Ak + Wo + Mo
1168	Mix IV	59,000	750	5	Wo + Mo + Ak
1160	"	"	"	16	Ak + Wo + Mo
1169	Mix III	"	"	5	Wo + Mo —> Ak
1161	"	"	"	16	Wo + Mo —> Ak
1170	Ak	"	"	5	Ak
1162	"	"	"	16	Ak
1154	Mix IV	58,500	798	15	Ak
1155	Mix III	"	"	"	Ak
1156	Ak	"	"	"	Ak
1050	Mix III	56,000	700	48	Ak —> Wo + Mo
1051	Ak	"	"	"	Ak + Wo + Mo
1086	Mix III	54,000	615	240	Wo + Mo
1087	Ak	"	"	"	Wo + Mo + Ak
1033	Mix III	53,000	700	168	Ak —> Wo + Mo
1034	Ak	"	"	"	Ak + Wo + Mo
1052	Mix III	52,000	600	40	Ak —> Wo + Mo
1053	Ak	"	"	"	Ak + Wo + Mo
1094	Mix III	49,000	605	120	Wo + Mo
1095	Ak	"	"	"	Ak + Wo + Mo
986	Mix III	43,000	655	192	Ak —> Wo + Mo
987	Wo + Mo	"	"	"	Wo + Mo
989	Ak	"	"	"	Ak + Wo + Mo
969	Mix III	"	700	168	Ak —> Wo + Mo
970	Wo + Mo	"	"	"	Wo + Mo
972	Ak	"	"	"	Ak + Wo + Mo
1102	Ak	"	"	2	Ak (+ Wo + Mo)
1101	Mix III	"	"	"	Ak —> Wo + Mo
925	Mix III	41,000	610	240	Wo + Mo
926	Ak	"	"	"	Wo + Mo
1060	Mix III	"	655	"	Ak —> Wo + Mo
1061	Ak	"	"	"	Ak + Wo + Mo
1015	Mix III	40,000	775	216	Ak
1016	Ak	"	"	"	Ak
891	Mix III	37,000	650	72	Ak —> Wo + Mo
892	Ak	"	"	"	Ak + Wo + Mo
953	Mix III	33,000	665	120	Ak —> Wo + Mo
954	Ak	"	"	"	Ak + Wo + Mo
1134	Mix IV	30,000	650	168	Wo + Mo
1135	Mix III	"	"	"	Ak —> Wo + Mo
1136	Ak	"	"	"	Ak + Wo + Mo
1137	Mix IV	"	700	24	Wo + Mo (+ Ak)
1157	"	"	"	192	Wo + Mo
1138	Mix III	"	"	24	Ak —> Wo + Mo
1158	"	"	"	192	Ak —> Wo + Mo

TABLE 1 (Cont.)



Run	Initial materials	Pressure lbs./in. <sup>2</sup>	Temp. °C.	Time hrs.	Products
1139	Ak	"	"	24	Ak
1159	"	"	"	192	Ak + Wo + Mo
1116	Mix IV	31,000	750	24	Ak + Wo + Mo
1122	"	"	"	"	Ak
1117	Mix III	"	"	"	Wo + Mo $\longrightarrow$ Ak
1123	"	"	"	"	Ak
1118	Ak	"	"	"	Ak
1124	"	"	"	"	Ak
1111	Mix IV	"	805	1-1/3	Wo + Mo
1113	"	"	"	14	Ak + Wo + Mo
1106	"	"	"	44	Ak (+ Wo + Mo)
1114	Mix III	"	"	14	Ak
1107	"	"	"	44	Ak
1112	Ak	"	"	"	Ak
1115	"	"	"	"	Ak
1108	"	"	"	"	Ak

Legend: Mix III = Fine-grained intimate mixtures of Ak, Wo and Mo.

Mix IV = Fine-grained intimate mixture of CaO, MgO and SiO<sub>2</sub> (glass).

Ak = Akermanite, Wo = Wollastonite, Mo = Monticellite.

Products occurring only in trace amounts are shown in parentheses.

unpublished data) may intersect each other at pressures and temperatures somewhat higher than these for which data have so far been obtained.

Just as the clinocllore P-T curve is a dehydration curve involving excess water, curves I to V are decarbonation curves and only apply to systems containing excess CO<sub>2</sub>. The reaction wollastonite + monticellite  $\rightleftharpoons$  akermanite could not take place in the same system as these decarbonation reactions because in the presence of excess CO<sub>2</sub> akermanite and monticellite become unstable, reacting to form calcite + diopside and calcite + diopside + forsterite respectively, at much higher temperatures—see curves I and II. Also, above at least 15,000 lbs./in.<sup>2</sup> wollastonite becomes unstable in the presence of excess CO<sub>2</sub>, reacting to form calcite + quartz (see curve V) at higher temperatures than those at which akermanite breaks down to wollastonite + monticellite in the absence of CO<sub>2</sub>.

#### THE WOLLASTONITE-MONTICELLITE INTERGROWTHS AT CRESTMORE

The breakdown of akermanite as described in this paper may explain the occurrence of the wollastonite-monticellite assemblages in some of the contact-altered rocks at Crestmore, California (Dr. C. Wayne Burnham, personal communication). These rocks consist largely of calcium-magnesium-carbonate rocks which have some siliceous and aluminous impurities and which have suffered some metasomatism in addition to the thermal metamorphism caused by the intrusion of the quartz-bearing diorites and mon-

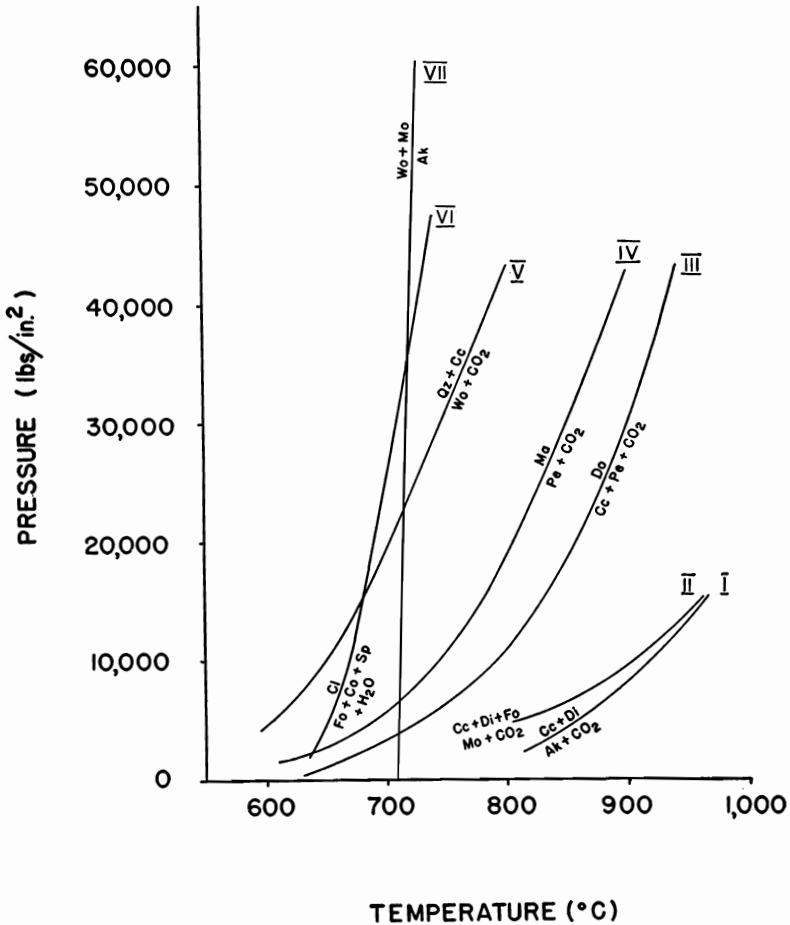


Fig. 2. P-T curve for the reactions:

- I Calcite + Diopside  $\rightleftharpoons$  Akermanite + CO<sub>2</sub>
- II Calcite + Diopside + Forsterite  $\rightleftharpoons$  Monticellite + CO<sub>2</sub>
- III Dolomite  $\rightleftharpoons$  Calcite + Periclase + CO<sub>2</sub>
- IV Magnesite  $\rightleftharpoons$  Periclase + CO<sub>2</sub>
- V Quartz + Calcite  $\rightleftharpoons$  Wollastonite + CO<sub>2</sub>
- VI Clinocllore  $\rightleftharpoons$  Forsterite + Cordierite + Spinel + H<sub>2</sub>O
- VII Wollastonite + Monticellite  $\rightleftharpoons$  Akermanite

The location of Curve III below 3,000 lbs./in.<sup>2</sup> has been taken from Graf and Goldsmith (1955).

zonites. As a result, a great variety of minerals and mineral assemblages have been produced.

The authors became interested in the wollastonite-monticellite assemblages because at no stage in Bowen's decarbonation series are wollastonite and monticellite found together in stable equilibrium. That these two phases were in equilibrium with each other at some stage in the Crestmore rocks is strongly

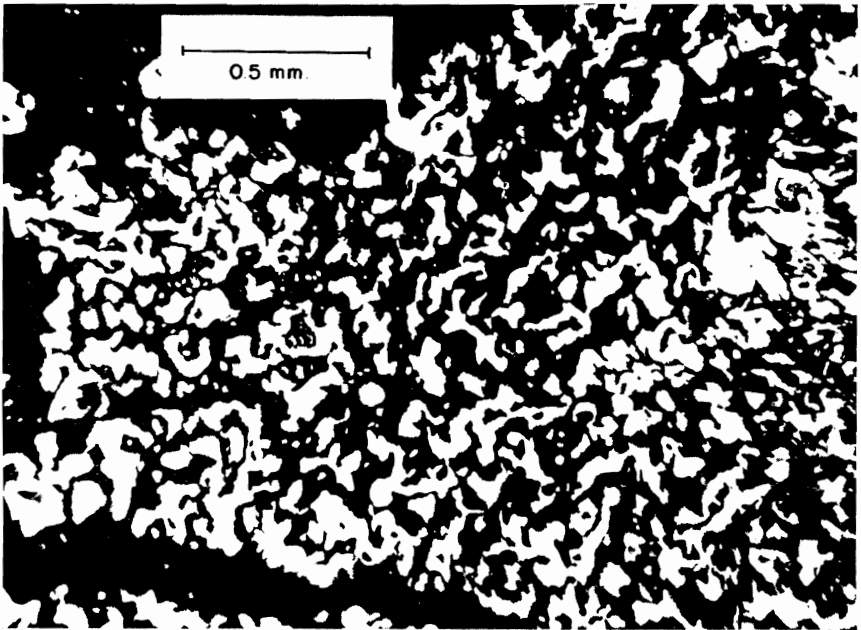


Fig. 3. Intimate intergrowth of wollastonite (in extinction) and monticellite (illuminated). Crossed nicols. Rock specimen kindly provided by Dr. C. Wayne Burnham.

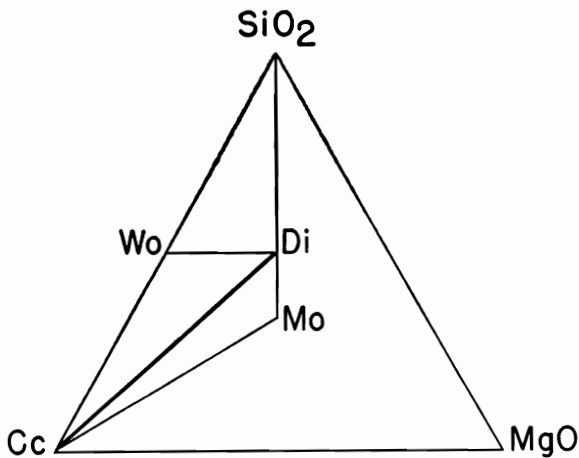


Fig. 4. Diagram illustrating the separation of the wollastonite composition from the monticellite composition by the Calcite-Diopside- $\text{CO}_2$  plane (with  $\text{CO}_2$  at the eye of the observer) in the excess  $\text{CO}_2$  part of the  $\text{CaO}$ - $\text{MgO}$ - $\text{SiO}_2$ - $\text{CO}_2$  system.

- Wo = Wollastonite
- Di = Diopside
- Mo = Monticellite

suggested by the fact that they occur in an intimate intergrowth (fig. 3). A modal analysis made on enlarged photographs of four such intergrowths gave the following results:

Wollastonite	48.85	53.00	50.91	57.24	% volume
Monticellite	51.15	47.00	49.09	42.76	% volume

yielding an average of 52.5% by volume of wollastonite and 47.5% by volume of monticellite.

In the normal course of the decarbonation of siliceous dolomitic limestones in the presence of *excess*  $CO_2$ , as deduced by Bowen from observations of natural rocks in the system  $CaO-MgO-SiO_2-CO_2$ , assemblages including wollastonite +  $CO_2$  are cut off from those including monticellite +  $CO_2$  by the calcite-diopside- $CO_2$  plane (fig. 4). The stability of a calcite-diopside- $CO_2$  assemblage is well established at temperatures above and below those at which wollastonite and monticellite normally develop during decarbonation.

Even in the  $CO_2$ -deficient region of the  $CaO-MgO-SiO_2-CO_2$  system, i.e., in the region below the calcite-diopside-wollastonite and the calcite-diopside-monticellite planes, the wollastonite-monticellite join is interrupted by

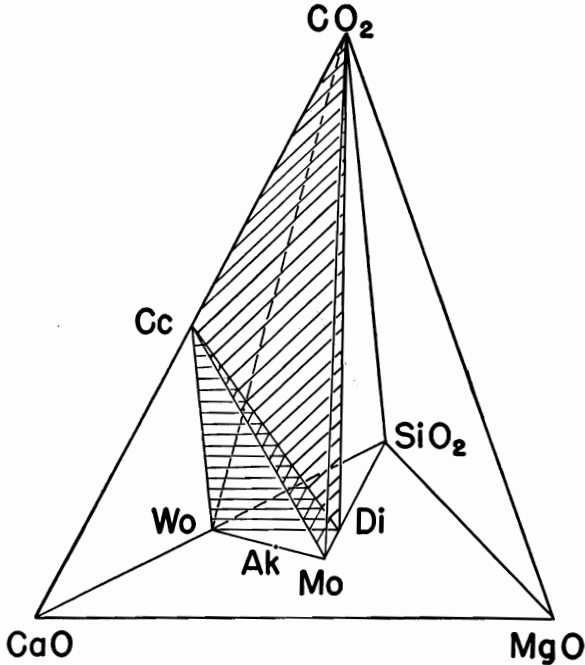


Fig. 5. The  $CaO-MgO-SiO_2$  tetrahedron showing the Calcite-Diopside- $CO_2$  plane and the  $CO_2$ -deficient region below the Calcite-Diopside-Wollastonite and the Calcite-Wollastonite-Monticellite planes (shaded).

- Cc = Calcite
- Wo = Wollastonite
- Ak = Akermanite
- Di = Diopside
- Mo = Monticellite

akermanite (fig. 5). However, now that the lower limit of stability of akermanite has been proved, there is no reason why wollastonite and monticellite should not occur in equilibrium together in  $CO_2$ -deficient systems under P-T conditions on the low temperature side of the akermanite breakdown curve.

An intergrowth formed solely by the breakdown of akermanite should consist of 45% wollastonite and 55% monticellite by volume. As mentioned above, the volume ratio averages 52.5: 47.5 instead of 45:55 in the Crestmore intergrowths. This discrepancy could be explained by the original presence of a little excess wollastonite or by impurity of the natural phases.

Clearly an important aspect to consider with reference to the application of the results to natural rocks is the effect of solid solution on the breakdown. Of the components most likely to enter into the akermanite the most important is gehlenite. No detailed work has yet been carried out on the effect of the gehlenite content on the lower limit of stability of melilite, but it has been suggested that the structure is stabilized by the addition of gehlenite and that the melilites become unstable at progressively lower temperatures as the gehlenite content is increased (Osborn and Schairer, 1941, p. 718).

Although in fact the wollastonite-monticellite intergrowths at Crestmore gave rise to the present investigation, it is possible that they have developed in some way other than by the breakdown of a melilite. They may have formed, for example, by the direct recrystallization of part of the rock which had a composition close to melilite, or they could represent an intermediate stage in the replacement of wollastonite by monticellite or vice versa. Crestmore has been noted for some time for intergrowths of different kinds (Dunham, 1933) which may have formed in a variety of ways. On the other hand, it should perhaps be pointed out that the co-existence of a melilite of say, composition ( $Ak_x, Geh_{100-x}$ ) in equilibrium with wollastonite-monticellite intergrowths does *not* provide any evidence against the formation of the intergrowths by the breakdown of the akermanitic component of a melilite of composition ( $Ak_y, Geh_{100-y}$ ), where  $y > x$ . The addition of gehlenite in solid solution must render the breakdown no longer univariant as indicated by the Gibbs Phase Rule. It is, in fact, to be expected that an original melilite ( $Ak_y, Geh_{100-y}$ ) will, if it reaches its lower limit of stability, break down to a second melilite ( $Ak_x, Geh_{100-x}$ ) + wollastonite + monticellite.

However, no matter what process caused the development of the wollastonite-monticellite intergrowths, if the two phases were in equilibrium, they must have formed on the low temperature side of the P-T curve for the breakdown of that particular melilite composition.

It will be possible to discuss more fully the usefulness of the P-T curve for the lower limit of stability of akermanite when the effect of solid solution of other components is known.

#### ACKNOWLEDGMENTS

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