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SYNTHESIS OF SPURRITE AND THE REACTION WOLLASTONITE + CALCITE ⇄ SPURRITE + CARBON DIOXIDE*

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ABSTRACT. A univariant PT curve has been located for the reaction wollastonite + calcite ⇄ spurrite + carbon dioxide. At 5000 pounds per square inch carbon dioxide pressure, the reaction takes place at about 1000°C. Theoretical considerations indicate that tilleyite is expected to have a PT stability field on the low temperature side of the above PT curve. However, tilleyite has not been synthesized and it is suggested that, the accepted composition of tilleyite may be in error, the observed breakdown of spurrite may be metastable, or the observed PT curve may end at a quintuple point involving the five phases wollastonite, calcite, spurrite, tilleyite, and carbon dioxide.

INTRODUCTION

Metamorphism of siliceous carbonate rocks was first considered systematically by Bowen (1940) who proposed that the mineralogical changes which may take place in these rocks during metamorphism were related to a progressive series of reactions of increasing decarbonation. He proposed thirteen steps, involving ten mineral phases, which were related to increasing temperatures of metamorphism and, with certain reservations, each step could be represented by a single PT curve. The PT curves can be used as geological temperature recorders, indicating the grade of metamorphism, if certain conditions are fulfilled. The reaction calcite + wollastonite ⇄ spurrite + carbon dioxide, one of the thirteen steps, will be considered here. ($3\ CaCO_3 + 2\ CaSiO_3 \rightleftarrows 2\ Ca_2SiO_4.CaCO_3 + 2\ CO_2$).

F. E. Wright (1908) first described spurrite in specimens collected by J. E. Spurr at a contact between impure limestone and a diorite, at Velardena, Durango, Mexico where it is associated with gehlenite and hillebrandite. It has subsequently been found elsewhere, and at several localities hand specimens can be collected that consist almost entirely of spurrite.

Spurrite is one of the few silicates which have apparently not previously been synthesized. Wright (1908) reported that an attempt to synthesize spurrite gave orthorhombic crystals of unknown composition. Eitel (1923) reported the synthesis of a similar phase which he believed to be a high temperature modification of spurrite, and placed the inversion at 1200°C at a carbon dioxide pressure of 90 atmospheres. However detailed data were not presented to definitely establish whether the synthetic material is a high temperature polymorph or whether it is a lime silicate.

Spurrite was synthesized reproducibly during our recent study of the system $CaO—MgO—SiO_2—CO_2$, and some information was obtained on its stability.

EXPERIMENTAL METHODS

All experiments have been carried out in cold-seal pressure vessels (Tuttle, 1949; Harker and Tuttle, 1955, p. 210) under controlled and measured pressures and temperatures. Elevated temperatures were obtained by a resistance furnace which surrounds the pressure vessel during the runs, but which can

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be removed for rapid quenching. Runs are quenched by immersing the pressure vessels in cold water. A galvanometer type controller, actuated by a thermocouple placed in the furnace above the pressure vessel, controlled temperatures to ± 2°C for short runs and ± 5°C for long runs. Pressures were generated by a pump designed by Roy and Osborn (1952) and modified by Harker and Tuttle (1955). Pressures were measured with a Bourdon gauge which gave readings reproducible to ± 3 percent.

Equilibrium determinations were carried out using as the starting materials either an analytical reagent calcium carbonate and finely ground silica glass, ground together in an agate mortar in the proportion 5 $CaCO_3$:2 SiO_2, or synthetic spurrite obtained by crystallizing some of this mixture. Samples weighing approximately 30 milligrams were used in the experiments. Carbon dioxide was always released at the beginning of the quench to prevent carbonation during quenching. Further details of the general method are given by Harker and Tuttle (1955).

RESULTS

Spurrite was found to break down to wollastonite and calcite with decreasing temperature within the CO_2 pressure range investigated. It can be readily synthesized on the high temperature side of the univariant PT curve shown in figure 1, and it crystallizes readily in the presence of CO_2. (For example, a mixture of calcite and silica glass will crystallize almost completely to spurrite in six days at 950°C and 2,500 pounds per square inch CO_2 pressure.) Unlike the synthetic materials of Shephard (Wright, 1908) and of Eitel (1923) the material produced under the conditions now described appears from its x-ray powder diffraction pattern and optical properties to be identical with natural spurrite. The x-ray powder diffraction patterns of the synthetic spurrite and two natural spurrites (one from the type area) are shown in figure 2. The optical properties compare as follows:

Synthetic		*Natural*
n_α	$= 1.638 \pm .002$	$1.640 \pm .002$
n_β*	$= 1.671 \pm .002$	$1.674 \pm .002$
n_γ	$= 1.676 \pm .002$	$1.679 \pm .002$
γ-α	$= .038$	.039
2v**	$= 40° \pm 5°$	40
Sign (–)		(–)
Twinning: polysynthetic		polysynthetic
Dispersion: crossed		crossed

* Calculated from 2v, α and γ.

** Estimated from centered acute bisectrix interference figure.

Pseudowollastonite is commonly produced metastably in experimental studies of systems in which $CaSiO_3$ appears as a phase; however, in this investigation wollastonite was produced in all experiments. X-ray powder diffraction patterns of the synthetic wollastonite, together with pseudowollastonite and natural wollastonite, are shown in figure 3. The intensity differences be-

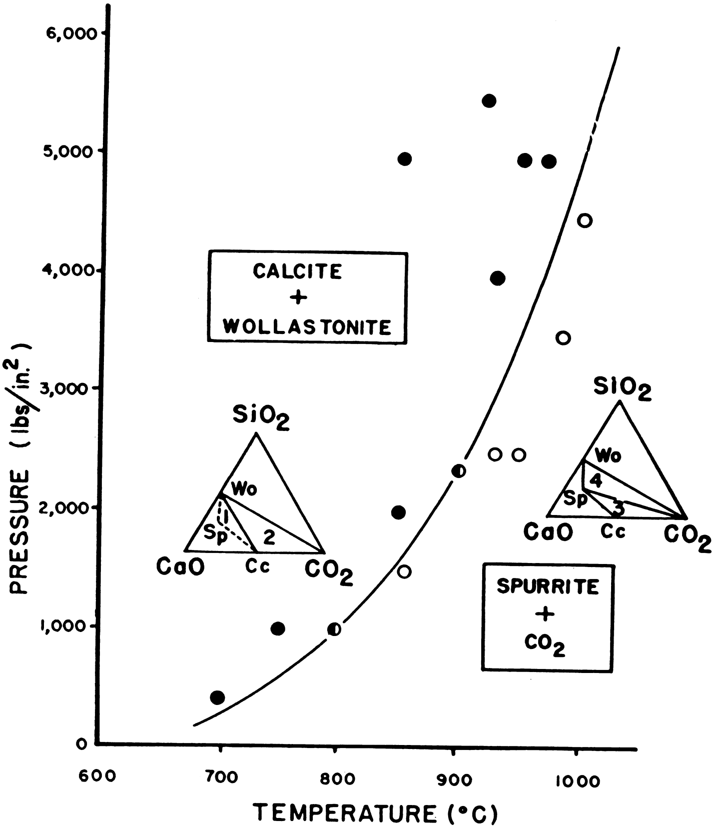

Fig. 1. Pressure (CO_2)-temperature curve for the univariant reaction $3CaCO_3 + 2CaSiO_3 \rightleftarrows 2Ca_2SiO_4.CaCO_3 + CO_2$. Wo = Wollastonite, Cc = Calcite, Sp = Spurrite. The numbers correspond to the assemblages discussed on page 5.

tween the lines of the natural and synthetic wollastonite is a result of orientation in the natural material.

Experimental results are illustrated in figure 1 and are tabulated in table 1. The PT curve represents pressures and temperatures at which the four phases of the reaction calcite + wollastonite ⇄ spurrite + carbon dioxide are stable together. Gibbs phase rule states that $P + F = C + 2$, where P is the maximum number of phases that can coexist in equilibrium; F is the number of degrees of freedom of the system, and C is the number of components in the system. Thus, when $P = 4$, $F = 1$, and for each temperature the four phases calcite, wollastonite, spurrite and CO_2 can coexist in equilibrium at only one pressure. Thus the PT curve of figure 1 indicates the pressure for each temperature at which the four phases can coexist in stable equilibrium. On either side of this curve, $P = 3$ and $F = 2$ so that regions of divariancy occur in which the following assemblages can coexist: (1) calcite + wollastonite + spurrite, (2) calcite + wollastonite + CO_2, (3)

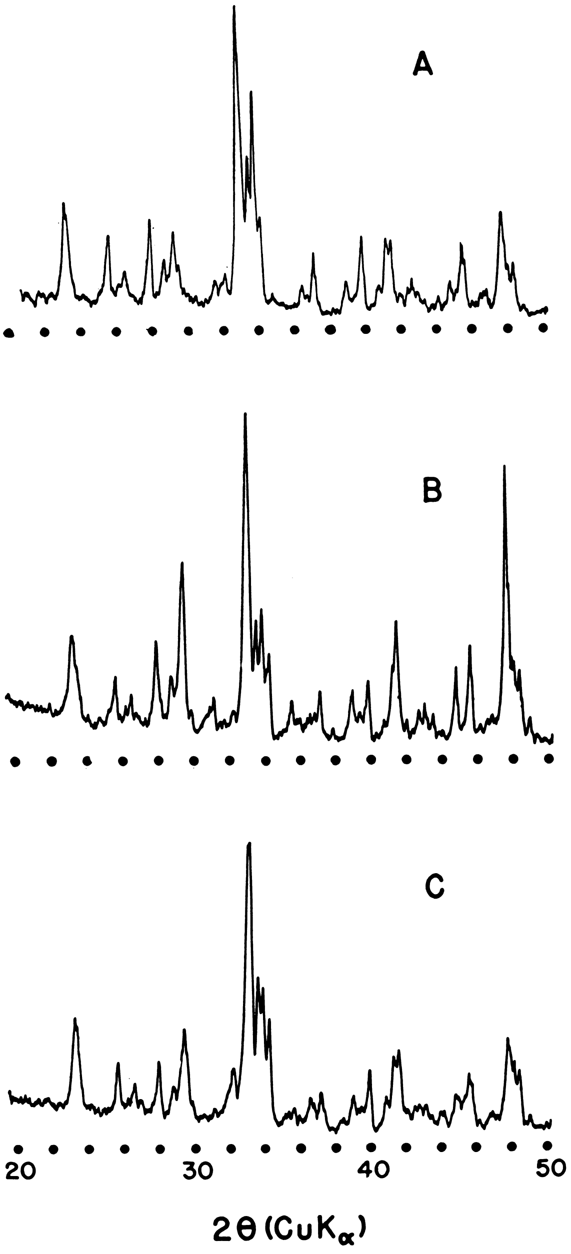

Fig. 2. X-ray powder diffraction patterns of: *A*. Natural spurrite from Velardena, Mexico; *B*. Natural spurrite from Luna Co., New Mexico; *C*. Synthetic spurrite grown at 950°C. and 2,500 lbs./in.^{2}

calcite + spurrite + CO_2, and (4) wollastonite + spurrite + CO_2. Assemblages 1 and 2 can exist stably on the low temperature side of the PT curve while 3 and 4 are stable above the curve. The triangular diagrams on either side of the univariant PT curve in figure 1 depict the range of compositions involved in this reaction. Assemblages are represented on these triangular diagrams by areas outlining compositions involved, and their numbers are shown to emphasize that the assemblages can be readily deduced from such diagrams.

PETROLOGICAL CONSIDERATIONS

The join wollastonite-calcite is the most important feature of the triangular diagrams of figure 1 since these two minerals cannot coexist on the high temperature side of the PT curve. If they are found together with no

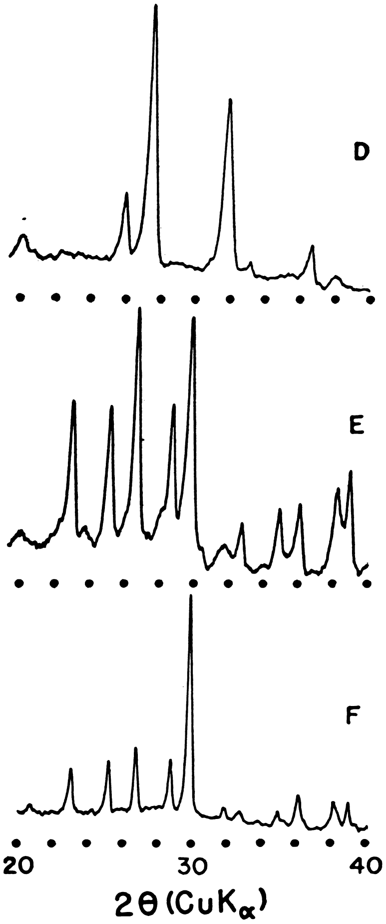

Fig. 3. X-ray powder diffraction patterns of pseudowollastonite(D), natural wollastonite(E), and synthetic wollastonite(F).

associated spurrite, then it can be assumed that the PT conditions on the high temperature side of the curve have not been attained. Calcite, wollastonite and spurrite can coexist on the low temperature side of the PT curve in the absence of CO_2 vapor, but CO_2 is probably always present during the progressive metamorphism of siliceous carbonate rocks as an additional phase, either as a dissociation product of the carbonates or as connate CO_2. Hence unless detrital spurrite is present it is reasonable to expect that the appearance of spurrite indicates that the conditions on the high temperature side of the curve have been attained.

TABLE 1

Experiments on the Reaction

$$3CaCO_3 + 2CaSiO_3 \rightleftarrows 2Ca_2SiO_4.CaCO_3 + 2CO_2$$

Run No.	Initial Material	Temp. °C.	Pressure lbs./in.^{2}	Time Hours	Result
912	CG	920	5500	72	CW
915	S	920	5500	72	CW
895	CG	850	5000	96	CW
896	S	850	5000	96	CW
984	CG	950	5000	144	CW
985	S	950	5000	144	CW
1009	CG	970	5000	72	CW
1010	S	970	5000	72	CW
1084	CG	1000	4500	38	SCW
1085	S	1000	4500	38	S
975	CG	930	4000	80	CW
976	S	930	4000	80	CW
1069	CG	985	3500	48	SCW
1070	S	985	3500	48	S
1017	CG	930	2500	144	SCW
1018	S	930	2500	144	S
874	CG	950	2500	144	S
889	CG	950	2500	48	SCW
890	S	950	2500	12	S
1038	CG	900	2250	240	CW(S)
1039	S	900	2250	240	S(CW)
1125	CG	850	2000	168	CW
1126	S	850	2000	168	CW
1109	CG	850	1500	168	SCW
1110	S	850	1500	168	S
1128	CG	750	1000	432	CW
1129	S	750	1000	432	CW
1143	CG	800	1000	240	CW
1144	S	800	1000	240	S
597	CG	700	400	120	CW

C = calcite
W = wollastonite
S = spurrite
G = silica glass
( ) = trace

It is interesting to note that calcite and quartz are stable together up to 600°C at 5000 pounds per square inch CO_2 pressure (Harker and Tuttle, 1956) while wollastonite and calcite remain stable together up to 1000°C at the same pressure; the 400°C difference in temperature between the appearance of wollastonite and that of spurrite is reflected in the common occurrence of the former at granite-limestone contacts and the latter at diabase-limestone contacts. The rare occurrence of spurrite at granite-limestone contacts is significant because if the pressure of carbon dioxide is low, spurrite should be a common mineral along with wollastonite as temperatures at these contacts are known to be at least as high as 700-750°C. *The fact that spurrite is not common at these contacts indicates that the pressure of carbon dioxide is relatively high and may well be commensurate with the rock load.* This also suggests that the vapor phase is rich in CO_2 and relatively poor in H_2O as the presence of large amounts of H_2O would lower the partial pressure of CO_2 and thereby permit calcite and wollastonite to react to give spurrite.

Another interesting feature of this study is the absence of tilleyite above and below the portion of the spurrite PT curve which has been investigated. In any decarbonation scheme tilleyite is expected to have a stability field on the low temperature side of the spurrite curve. It is expected to develop by the reaction wollastonite + calcite $\rightleftarrows$ tilleyite + carbon dioxide, and the univariant PT curve for this reaction should then be followed at higher temperatures by a curve for the reaction tilleyite $\rightleftarrows$ spurrite + carbon dioxide ($Ca_3Si_2O_7.2CaCO_3 \rightleftarrows 2Ca_2SiO_4.CaCO_3 + CO_2$).

The absence of tilleyite may be the result of failure to obtain equilibrium, the accepted composition of tilleyite may be in error, or the univariant PT curves for the reactions wollastonite + calcite $\rightleftarrows$ tilleyite + carbon dioxide and tilleyite $\rightleftarrows$ spurrite + carbon dioxide may intersect at a quintuple point. Perhaps the first mentioned possibility can be resolved by studying the breakdown of natural tilleyite and we propose to attempt this as soon as suitable material is obtained. Two analyses of tilleyite reported by Nockolds (1947) and one by Larsen and Dunham (1933) show more than 1 percent water, and although this may represent hydrated alteration products, it is suggested that water may be essential in the structure of tilleyite. The fact that tilleyite is commonly secondary after spurrite also suggests a hydrated mineral, although it is not impossible that tilleyite is replacing spurrite and wollastonite as a result of retrograde metamorphism in the presence of excess CO_2. There are two possible sets of reactions if the determined PT curve terminates at a quintuple point, one in which tilleyite is unstable at high pressures in the presence of carbon dioxide, and a second in which tilleyite is unstable at low pressures of carbon dioxide. The following assemblages appear in each of these reactions: (1) wollastonite, calcite, tilleyite, carbon dioxide; (2) wollastonite, calcite, spurrite, carbon dioxide; (3) wollastonite, calcite, spurrite, tilleyite; (4) wollastonite, spurrite, tilleyite, carbon dioxide; and (5) calcite, spurrite, tilleyite, carbon dioxide. As spurrite, tilleyite and carbon dioxide have compositions which lie on a line in the ternary system $CaO—SiO_2—CO_2$ the last two reactions (4 and 5) involve binary equilibria and these two assemblages can be reduced to the reaction tilleyite ⇄ spurrite + carbon dioxide.

The first mentioned possible quintuple point is illustrated schematically in figure 4A. Reactions which take place along each of the four curves are shown together with the compositions involved. It can be seen that tilleyite can exist only at low carbon dioxide pressures with this arrangement of curves. This quintuple point was proposed by Korzhinsky (1937) as one of a series of changes that may take place at depth as a result of increasing pressure. The second possible quintuple point is illustrated in figure 4B and here tilleyite would have a minimum pressure at which it is stable. In each instance the nearly vertical curve involves only solid phases and to realize this reaction it would be necessary to work in the "vapor deficient" region. Either of the quintuple points described above would explain the fact that spurrite is of more common occurrence than tilleyite because spurrite could develop from calcite + wollastonite in the presence of excess CO_2 throughout the entire range of pressures shown, whereas the pressures at which tilleyite could de-

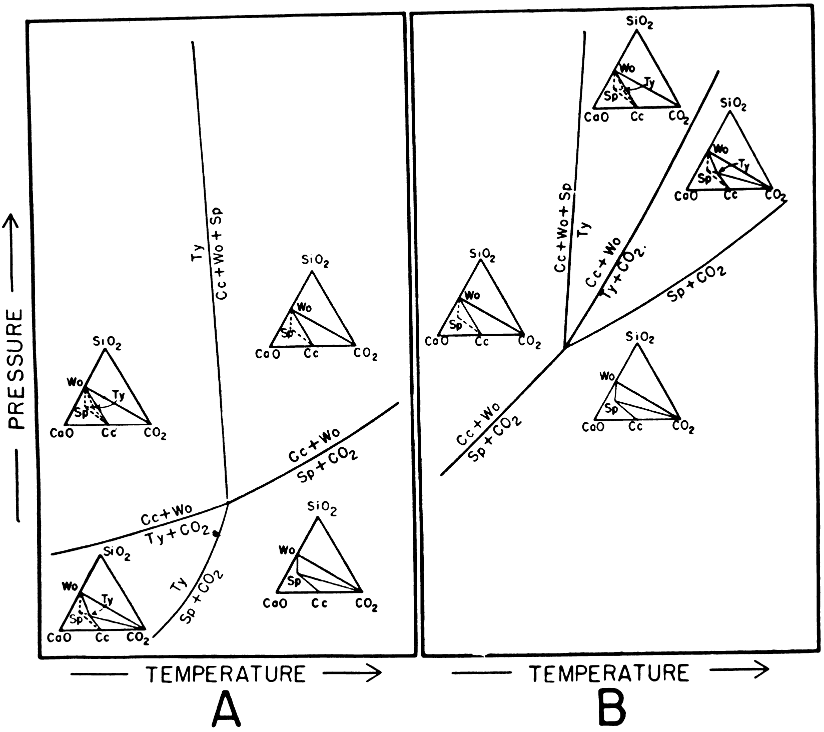

Fig. 4. Hypothetical P-T diagrams illustrating the two possible arrangements of P-T curves about a quintuple point. In the presence of excess CO_2 tilleyite can only be stable at pressures below the quintuple point in 4A, and above the quintuple point in 4B. Wo = Wollastonite; Ty = Tilleyite; Cc = Calcite, and Sp = Spurrite.

velop from calcite + wollastonite in the presence of excess CO_2 would be limited by the quintuple point.

If the first of the above quintuple points (fig. 4A) represents the true relations, the pressure at the invariant point must be very low indeed, perhaps less than 500 pounds per square inch. Only those contacts formed at very shallow depths would be expected to carry tilleyite under such circumstances.

When additional data are gathered on the breakdown of natural tilleyite, and when our work is extended to a wider range of pressures, perhaps some of the uncertainties introduced by this study will be resolved.

Bowen (1940, p. 273) pointed out that reactions of the type studied here give rise to PT curves with considerable slope whereas PT curves for reactions involving only solid phases, where the volume change is more nearly constant with increasing pressure, will usually be nearly vertical and the two classes of curves give rise to a "petrogenetic grid". The reaction studied here represents one additional fixed curve on this petrogenetic grid.

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